Assessment of Harran Plain Groundwater in Terms of Arsenic Contamination

Abstract: Arsenic (As) contamination in water, especially in groundwater, has led to major health problems. Due to the recognition that As at low concentrations in potable water causes crucial health effects, As removal methods have gained significant importance in recent years. In this study, As concentration was monitored in October and March in ten observation wells located in Harran Plain, which has the largest groundwater reserves in the Middle East. The main aim of this study is to select the proper treatment method for remediation of a groundwater resource polluted with As. According to the analyses, there was no well that exceeded the limit for As concentration (10 ppb). The results revealed that As concentrations in October were lower than in March. In March, the highest As concentration was observed in Yaygılı well with the value of 4.12 ppb. Ozanlar well had the lowest As concentration with the value of <0.5 ppb. In October, the highest As concentration was 2.39 ppb in Çamlıdere well. For Çamlıdere and Yaygılı wells, As removal methods (coagulation and flocculation, adsorption, membrane processes, advanced oxidation processes, electrocoagulation, biochar) were investigated and discussed. As a result of the assessment, it was estimated that the best available As removal method could be biochar application considering its advantages.

Keywords: Arsenic, biochar, groundwater, Harran Plain, removal methods.

Öz: Suda özellikle yeraltı suyunda arsenik (As) kirliliği, majör sağlık sorunlarına yol açmaktadır. Arsenik konsantrasyonu içme suyunda düşük konsantrasyonda bulunsa bile ciddi sağlık etkilerine seheb olabilir ve bunun sonucunda son zamanlarda As giderim metotları önem kazanmıştır. Bu çalışmada, Ortadoğu’nun en büyük yeraltı suyunun sahadır olan Harran Ovası nda yer alan on kuyuda Ekim ve Mart aylarında As konsantrasyonu izlenmiştir. Bu çalışmanın temel amacı, As ile kirlenmiş bir yeraltı suyunun doyru artımı metotlarıyla iyileştirilmesi için uygun artımı metodunu seçmektir. Analizlere göre, As konsantrasyonunu sınır değeri (10 ppb) aşan hiçbir kuyu yoktur. Sonuçlar göstermektedir ki, Ekim ayında As konsantrasyonu Mart ayında 4.12 ppb olarak tespit edilmiştir. Ozanlar kuyusuna Ekim ve Mart aylarında <0.5 ppb değerleriyle en düşük As konsantrasyonuna sahiptir. Ekim ayında en yüksek As konsantrasyonu 2,39 ppb olup Çamlıdere kuyusundadır. Çamlıdere ve Yaygılı kuyuları için As giderim metotları araştırılmış ve giderim metotları (koagülasyon ve flokülasyon, adsorpsiyon, membran prosesleri, ileri oksidasyon prosesleri, elektrokoagülasyon, biyoçar) tartışılmıştır. Değerlendirmenin sonunda, en iyi As giderim metodunun avantajları düşünüldüğünde biyoçar uygulaması olabileceğini öngörülmektedir.

Anahtar Kelimeler: Arsenik, biyoçar, yeraltı suyu, Harran Ovası, giderim metotları.

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INTRODUCTION

Arsenic (As) is a heavy metal that occurs in the environment in different oxidation states and various forms that include As(V), As(III), As(0) and As(-III) (Choonga et al., 2007). Arsenic cannot be easily degraded and can only be converted into different forms or transformed into insoluble compounds. Inorganic As generally occurs in two major oxidation states of arsenite and arsenate, both of which are toxic to flora and fauna. The presence of As in fresh water is due to leaching from source rocks and sediments containing As (Robertson, 1989; Hering and Elimelech, 1995; Choonga et al., 2007; Derin, 2019).

Arsenic contamination in natural water especially in groundwater is a worldwide problem and has become a significant issue and environmental challenge (Choonga et al. 2007). The World Health Organization recommended that As concentration should be lower than 10 ppb for the potable water resources standard (WHO, 2011). The toxicology of As is a complex phenomenon and is generally categorized in acute and chronic types. Acute As poisoning requiring prompt medical attention usually occurs through ingestion of contaminated food or drinking water. The major early manifestation of acute As poisoning involves burning and dryness of the mouth and throat, dysphasia, colicky abnormal pain, projectile vomiting, profuse diarrhea, and hematuria. Also, As has carcinogenic effect (Choonga et al., 2007; Jain and Ali, 2000). Arsenic formation at low concentrations in potable water leads to severe health problems so the technologies for As removal from water have become increasingly important. From this point of view, As contamination should be removed from groundwater using proper and adequate treatment methods. There are several methods for As removal from water. These methods include coagulation and flocculation, precipitation, adsorption and ion exchange, membrane filtration, etc. Alternative methods like ozone oxidation, advanced oxidation process, bioremediation and electrochemical treatments are also used for the removal of As (Choonga et al., 2007). Innovative treatment methods such as biochar applications can be used for removal of As from groundwater.

Harran Plain has the largest groundwater reserves in the Middle East. In this study, As concentrations in ten observation wells located in Harran Plain were monitored in October (post irrigation) and in March (before irrigation). Then, treatment methods were investigated and discussed to remove As from groundwater. This paper aims to select the proper treatment method for remediation of a groundwater resource polluted with As.

MATERIALS AND METHODS

Study Area

Harran Plain has the largest irrigation area in southeastern Turkey and the largest groundwater reserves in the Middle East. Harran Plain is located in the southeast of Şanlıurfa province. The drainage area is 3,700 km², the lowland area is 1,500 km² and the irrigation area is 141,500 ha in Harran Plain. Ten wells called Çamlıdere, Yardımıç, Kısat, Uğurlu, Ozanlar, Kızıldoruc, Olgunlar, Yaygılı, Bolatlar and Uğraklı are observation wells for As concentration in Harran Plain. Figure 1 shows the location map of the study area. The main reasons to select these wells are that they are vulnerable and located in the superficial aquifer and nearby agricultural fields. The other reasons are accessibility and many previous studies were performed in this superficial aquifer.
Harran Plain is composed of Eocene limestone, occurring in a graben structure bordered by large N–S striking faults. Geological units in the study area and their main geological and hydrogeological properties are described below. From bottom to top, the area is composed of Paleocene, Eocene, Miocene, Pliocene and Pleistocene aged units. There are two types of aquifer in the study area. The first is a deep aquifer also called the confined aquifer, lower aquifer or Eocene aquifer. The second is an upper aquifer, also called the unconfined aquifer, shallow aquifer or Pleistocene aquifer (DSI, 1972; 2003; Yeşilnacar and Güllüoğlu, 2008). Geological formations in the region consist of sedimentary and volcanic rocks. Only basalts are found as igneous rocks. Basalts are seen locally on some hills surrounding the plain. These basalts are the result of eruptions of Karacadağ volcanism (DSI, 1972; 2003). It can be considered that As in the water wells may originate from basalt composition. It can be said that it is a geogenic formation. Figure 2 shows the geologic structure of the sampling points. The wells are fed from the limestone aquifer with basalt intrusions.

**Figure 1.** Location map of the study area.

**Şekil 1. Çalışma alanının konumu.**

**Figure 2.** Geological map of the study area and sampling points (DSI, 2003; Yeşilnacar and Güllüoğlu, 2008).

**Şekil 2. Çalışma alanının jeoloji haritası ve örneklemeye noktalarının konumu (DSİ, 2003; Yeşilnacar and Güllüoğlu, 2008).**
Experimental Planning

In this study, As analyses were performed according to the Standard Methods (APHA, 1995) using inductively coupled plasma mass spectrometry (ICP-MS) technique by an outsourcing service for the sampling points Çamlıdere (1), Yardımcı (2), Kısas (3), Uğurlu (4), Ozanlar (5), Kızıldoruç (6), Olgunlar (7), Yaygılı (8), Bolatlar (9) and Uğraklı (10) wells. Arsenic analyses were performed in March (before irrigation) and in October (post irrigation).

Removal Methods

Coagulation and flocculation, adsorption, membrane processes, advanced oxidation processes (AOPs), electrocoagulation, and biochar application were investigated and discussed in this study. Among As treatment processes, coagulation and flocculation are among the most common methods applied. Ferric salts are common for use as a coagulant for this purpose (Choonga et al., 2007). Yuan et al. (2003) studied a combination system of a ferric sulfate coagulation system for As removal from potable water. This method is economic and effective. Zouboulis and Katsoyiannis (2002) studied As removal by implementing modifications to a conventional coagulation/flocculation process. In adsorption processes, contaminated water is passed through a medium in which As is adsorbed and removed from the water (Choonga et al., 2007). Eguez and Cho (1987) applied this process to remove As from water. Membrane processes can be used for As removal from potable water (Choonga et al., 2007). Especially, nanofiltration (NF) and reverse osmosis (RO) are the major membrane processes for As removal from water. Saltu et al. (2005) studied the impacts of operating conditions on the removal of As from water by nanofiltration. Kang et al. (2000) studied the impact of pH on removal of As using reverse osmosis. Advanced oxidation processes (AOPs) are the main advanced removal techniques for contaminants in potable water. Especially oxidant materials such as ozone, UV, and hydrogen peroxide are used for As removal. Frank and Clifford (1986) implemented this process for As removal from water.

The electrocoagulation (EC) process is a separation process that involves several chemical and physical mechanisms for contaminant removal from water (Mollah et al., 2004, Nidheesh and Singh, 2017). The EC process is regarded as a very efficient method for removing various water contaminants (Nidheesh and Singh, 2017). The removal of As from water by the EC process was reported by several authors (Ucar et al., 2013; Vasudevan et al., 2010). Biochar can be applied for carbon sequestration, soil amendment, waste management, wastewater treatment, groundwater remediation, and greenhouse gas emission minimization (Qambrani et al., 2017). Biochar can be produced from many types of biomass such as plants, sewage sludge, animal manures, and agro-industrial biomass by various generation methods that include slow pyrolysis, fast pyrolysis, gasification or combustion (Yuan et al., 2016). The production method is a type of renewable energy because biomass is a renewable energy resource. Biochar applications have become very popular for water treatment in recent years. Niazi et al. (2018) and Bakshi et al. (2018) tried to remove As from water with biochar applications.

RESULTS AND DISCUSSION

According to the assessment results, As concentrations in March (before irrigation) were higher than in October (post irrigation). It is estimated that irrigation decreases the As concentrations in groundwater. Precipitation may increase the dilution of As concentrations. There was no well that exceeded the As concentration of the WHO (2011) drinking water standard limit value (10 ppb) in Harran Plain. However, it can be said that there is As contamination in Harran Plain. Table 1 shows the results of As analyses.
Table 1. Arsenic concentrations in observation wells in March and October.

| Sample name | Observation well | As concentration (ppb) |
|-------------|------------------|------------------------|
|             |                  | March | October |
| 1           | Çamlıkdere       | 2.5   | 2.39    |
| 2           | Yardımıci        | 1.06  | 0.85    |
| 3           | Kırası           | 0.6   | 0.63    |
| 4           | Uğurlu           | 0.9   | 0.82    |
| 5           | Ozanlar          | 0.49  | 0.47    |
| 6           | Kızıldoruç       | 1.3   | 1.05    |
| 7           | Olgunlar         | 1.32  | 1.24    |
| 8           | Yaygılı          | 4.12  | 1.2     |
| 9           | Bolatlar         | 1.07  | 0.81    |
| 10          | Uğraklı          | 0.79  | 0.58    |

The highest As concentration was monitored in Yaygılı well with the value of 4.12 ppb in March. The lowest average As concentration corresponds to Ozanlar well with the value of <0.5 ppb in March. Figure 3 shows the variation of As concentration in March. The highest As concentration was observed in Çamlıkdere well with the value of 2.39 ppb in October. The lowest As concentration corresponds to Ozanlar well in October, similar to March, with the value of <0.5 ppb. The variation of As concentration in October is given in Figure 4. Figure 5 shows the comparison of As concentration variations of the sampling points. Baba et al. (2019) found that As concentrations of geothermal fluid near Harran Plain ranged from 13.4 to 3000 ppb, with the increased As in geothermal fluid originating from water-rock interaction associated with As-containing formations.

The results revealed that As contamination which is under the limit (10 ppb) was observed in Harran Plain. So, As removal should be applied for some wells such as Yaygılı well and Çamlıkdere well. Coagulation and flocculation, adsorption, membrane processes, advanced oxidation processes (AOPs), electrocoagulation, and biochar applications were investigated and discussed in this study. Table 2 shows the assessment of As removal methods.
Table 2. Assessment of As removal methods.

| Removal Method           | Assessment                                                                 | Reference                  |
|-------------------------|-----------------------------------------------------------------------------|----------------------------|
| Coagulation and flocculation | Coagulation with disinfection is one of the commonly used treatment methods. Disinfection can have an adverse impact on other water quality parameters such as the formation of by-products and the release of taste and odor compounds. | McNeill and Edwards, 1995  |
| Adsorption              | Regeneration and backwashing process has many challenges for adsorption process. Also, the adsorbent is considered hazardous waste. | Eguez and Cho, 1987       |
| Membrane processes      | To operate this system is very difficult; for membrane backwashing and cleaning processes large amounts of fresh water are required. | Kang et al., 2000          |
| AOPs                    | An expensive and efficient treatment method.                               | Frank and Clifford, 1986   |
| Electro-couglulation    | An expensive and efficient treatment method.                               | Nidheesh and Singh, 2017   |
| Biochar                 | A cheaper, more environmentally-friendly and efficient method.              | Bakshi et al., 2018; Niazi et al., 2018 |

Among treatment methods, biochar appears to be the feasible method to remove As from groundwater because of its advantages. It is cheaper than the other techniques, and biochar can adsorb As immediately. Biochar has gained significant attention recently due to its role in many environmental management issues and environmental challenges (Qambrani et al., 2017). It can also minimize greenhouse gases released into the atmosphere from groundwater. For this region, biochar can be generated from Urfa red peppers with the pyrolysis method. The recommended remediation method is described in Figure 6. Firstly, aeration should be applied to treat the groundwater from Yaygılı well and Çamlıdere well. Then biochar applications can be implemented to remove As from the groundwater before the disinfection process. Arsenic removal should be provided by biochar application for both wells.

![Figure 6. Recommended As treatment flow scheme.](image)

Şekil 6. Önerilen As arıtımı akım şeması.
GENİŞLETİLMİŞ ÖZET

Arsenik (As), farklı oksidasyon durumlarında ve As (V), As (III), As (0) ve As (-III) içeren çeşitli formlarda oluşan bir ağır metaldir (Choonga vd., 2007). Arsenik kolayca suda parçalanmaz ve sadece farklı formlara dönüştürülerek sudan uzaklaştırılır. İnorganik As türlerinden olan arsenit ve arsenat, flora ve fauna için toksiktir ve oksidasyon sonucu meydana gelirler. Arseniğin içme suyundaki varlığı, As içeren kayaç ve sedimentlerden olsa bile ciddi sağlıksız sorunlara sebep olmaktadır. Bu nedenle, son zamanlarda dünyada geniş çapta arıtılmaya çalışılmaktadır.

Harran Ovası, güneydoğu Türkiye’nin en büyük sulama alanı ve Orta Doğu’nun en büyük yeraltı suyu rezervlerine sahiptir. Harran Ovası Şanlıurfa il merkezinin güneydoğusunda yer almaktadır. Harran Ovası’nda drenaj alanı 3700 km², ova alanı 1500 km² ve sulama alanı 141 500 hektardır. Bu çalışmada, Ortadoğu’nun en büyük yeraltı suyu rezervlerine sahip olan Harran Ovası’nda yer alan on kuyuda Ekim ve Mart aylarında As konsantrasyonu izlenmiştir. Bu kuyuların seçilmesinin sebebi ana akıfere ve tarımsal alanlara yakın olmasıdır. Ayrıca kuyulara ulaşım kolaylığı ve şehir merkezine yakın olması tercih sebebidir.

Bu çalışmının temel amacı, As ile kirlenmiş bir yeraltı suyunun doğru arıtma metoduyla iyileştirilmesi için uygun arıtma metodunu seçmektir. Mart ayında (sulama öncesi) ve Ekim ayında (sulama sonrası) numuneler almıp As konsantrasyonu ICP-MS yöntemi kullanılarak belirlenmiştir. Analizlere göre, yeralı suyunun As konsantrasyonu WHO (2011) içme suyu sınır değerini (10 ppb) aşmadığı tespit edilmiştir. Ekim ayında yeraltı suyunun As konsantrasyonu Mart ayından daha düşüktür. Bunun nedeni, olaya sonucu seyrelmenin etkisiyle yeraltı suyunda As konsantrasyonundaki derişimin azalması olabileceğini öngörülmektedir. Mart ayında, en yüksek As konsantrasyonu Yaygılı kuyusunda 4,12 ppb olarak gözlemlenmiştir. Olanlar kuyusu, Ekim ve Mart aylarında <0,5 ppb değerlerle en düşük As konsantrasyonuna sahiptir. Ekim ayında en yüksek As konsantrasyonu 2,39 ppb olup Çamlıdere kuyusundadır.

Çamlıdere ve Yaygılı kuyuları için, As giderim metotları araştırılmıştır ve giderim metotları arasında koagülayış ve flokülasyon, adsorpsiyon, membran prosesleri, ileri oksidasyon prosesleri, elektrokoagülayış ve biyoçar uygulaması tartışmıştır. Biyoçar (biyokömür), çöçümlü biyomaslardan (hayanı gibi, atık bitki, orman atıkları, artırmı çamur) terma yöntemlerle yüksектir, sıcaklık altında üretilebilir. Biyoçar, su arıtımı, atık yönetimi, atık su arıtımı, toprak remediyaşyonu, yeraltılı suyun arıtımı gibi birçok alanda uygulanabilmektedir. Biyoçar aynı zamanda iyi bir adsorbtör ve suyun, atık ve kirletici (NO₃⁻, As vb.) adsorplama kapasitesi çok yüksektir. Biyoçar aynı zamanda termodoksik gazı depolama özelliği vardır. Bu sebeple gazzı emisyonu azaltıcı etkisi de bulunmaktadır. Değerlendirmelerin sonucunda, en iyi As giderim metodunun, avantajları dijital olduğundan biyoçar uygulaması olabileceğini öngörülmektedir. Bunun sebebi, biyoçar uygulamasının daha ucuz ve çevre dostu teknoloji olması gösterebilir. Bununla beraber biyoçar Şanlıurfa da attık atıkları piroliz yöntemiyle ekonomik bir şekilde üretilebilir. Arseniği bu alanda kolayca adsorplayabileceği için ideal bir uygulamadır.

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