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Research Article

POTENTIAL USE OF HAZELNUT PROCESSING PLANT WASTES AS A SORBENT FOR THE SIMULTANEOUS REMOVAL OF MULTI-ELEMENTS FROM WATER

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Keywords

Adsorption/biosorption,
Agricultural waste,
Natural adsorbent,
Water treatment.

Abstract

In this paper, the effects of pH (1.5-8.0), initial element concentration (0.5 to 20 mg L^{-1}.) and sorbent dosage (1 - 20 g L^{-1}) were investigated on the potential use of hazelnut processing plant wastes, hazelnut shell (SH) and hazelnut skin (SK), for the simultaneous removal of Al, Cr, Cu, Cd, Pb, As and Fe from water. The surface morphology of the sorbents, elemental analysis, FTIR, SEM-EDS and BET analysis were performed and specific surface areas of the sorbents were found as 0.676 m^2 g^{-1} (for SH) and 0.768 m^2 g^{-1} (for SK). The results showed that surfaces of both sorbents are rough, contains pores that allow to entrap heavy metals and functional groups such as carboxylic acid, phenolic compounds, etc. to which the heavy metal ions can attach. While the optimum pH was determined as 5.0 for all elements in both sorbent systems, the percent removal of heavy metal increased with increase in initial heavy metal concentration up to 8 mg L^{-1} (except cadmium for SH and copper and cadmium for SK). While optimum sorbent dosage was obtained 10 g L^{-1} for SH sorbent, increase of sorbent amount led to a decrease of the percentage of removal for SK. Adsorption models were used for the mathematical description of adsorption equilibrium and isotherm constants were evaluated at room temperature (22 ± 2 ◦C). The adsorption equilibrium data were fitted well to Langmuir and Langmuir-Freundlich models in most cases and showed favorable adsorption behavior

SULARDAN ÇOKLU-ELEMENT GİDERİMİNDE FINDIK İŞLEME TESİSLERİ ATIKLARININ SORBENT OLARAK KULLANIMI

Anahtar Kelimeler

Adsorpsiyon/biyosorpsiyon,
Tarımsal atık,
Doğal adsorbent,
Su arıtımı.

Öz

Bu çalışmada; Al, Cr, Cu, Cd, Pb, As ve Fe'in sudan eş zamanlı olarak uzaklaştırılmasında fındık işleme tesisi atıklarından, fındık kabuğu (SH) ve fındık zarının (SK) potansiyel kullanımına, ortam pH'ı (1.5 - 8.0), başlangıç element derişimi (0.5-20 mg L^{-1}) ve sorbent dozunun (1 - 20 g L^{-1}) etkileri araştırılmıştır. Sorbentlerin yüzey morfolojisi, elementel analizi, FTIR, SEM-EDS ve BET analizleri yapılmış ve özgül yüzey alanları 0.676 m^2 g^{-1} (SH için) ve 0.768 m^2 g^{-1} (SK için) olarak bulunmuştur. Sonuçlar, her iki sorbent yüzeyinin pürüzlü, ağır metalleri tutabileceği gözenekler ve karboksilik asit, fenol bileşikleri gibi fonksiyonel gruplar içerdiğini göstermiştir. Her iki sorbent sisteminde tüm elementler için optimum pH, 5.0 olarak belirlenirken, başlangıç metal derişiminin 8 mg L^{-1}'e kadar artması ile birlikte element giderim yüzdesinin (SH için kadmiyum, SK için ise bakır ve kadmiyum hariç) arttığı bulunmuştur. Optimum sorbent dozu, SH için 10 g L^{-1} olarak bulunurken, SK için sorbent miktarının artması ile giderim yüzdesi azalmıştır. Adsorpsiyon dengesinin matematiksel modellemesi için adsorpsiyon modelleri kullanılmış ve izoterm sabitleri oda sıcaklığında (22 ± 2 ◦C) hesaplanmıştır. Çoğu durumda adsorpsiyon denge verileri, Langmuir ve Langmuir-Freundlich modellerine uyum sağlamış ve istemli-adsorpsiyon davranışları göstermiştir.

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1. Introduction

Many sources like municipal&industrial wastes, chemical fertilizers in agriculture, pesticide and air pollution are causing water pollution with growing population and emerging technologies. In recent years, especially heavy metal contamination became one of the main environmental problems. Human exposure to toxic elements is dramatically risen due to increase of the use of them in various areas (Gautam et al., 2014; Kadirvelu et al., 2001; Karadag, 2008; Sencan et al., 2015; Tchounwou et al., 2012; Wolfová et al., 2013; Zhang et al., 2016). Besides waste waters, the sources of drinking water (e.g., surface water, groundwater, and seawater) are likely to be polluted by toxic elements due to uncontrolled discharging of heavy metal containing waste waters through environment, the leaching of metals from water distribution system, deposition of heavy metals occurring in the atmosphere because of traffic pollution and industrial activities in soils, etc. (Ahmedna et al., 2004; Chowdhury et al., 2016; Tchounwou et al., 2012). The heavy metal pollution in drinking water sources was reported as micro levels in a study conducted by Chowdury et al. (2016). The most common metal contamination found in the waters are iron (Fe), copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb), zinc (Zn), mercury (Hg), cobalt (Co), manganese (Mn), nickel (Ni) and beryllium (Be). Arsenic (As) and selenium (Se) are other most common elements besides these heavy metals (Gautam et al,. 2014; Karadag, 2008; Wan Ngah and Hanafiah, 2008). It is important to note that arsenic (As) is a metalloid and selenium (Se) is a non-metal, however, the term "heavy metal" will be used for the description of the elements studied in this paper. Although trace concentration of some of these elements (Fe, Cu, Cr, Zn, Se, Mn, Ni) are vital for some biochemical processes and physiological functions, they can persist in the environment and can cause serious health problems even at low concentrations (Ali et al., 2016; Amuda et al., 2007; Aremu et al., 2002; Chowdhury et al., 2016; Gautam et al., 2014; Karadag, 2008; Koubaissy et al., 2014; Li et al., 2017; Sencan et al., 2015; Wan Ngah and Hanafiah, 2008; Wang and Chen, 2006).

The removal of Al, Cr, Fe, Cu, As, Cd and Pb elements was investigated in this study. Among these elements, chromium is one of the naturally occurring heavy metal in Earth's crust with oxidation states ranging from chromium (II) to chromium (VI) and can enter to the environment through natural and anthropogenic sources. Exposure to Cr compounds (especially high levels of chromium (VI)) can cause renal damage, allergy, asthma and cancer in human (Tchounwou et al., 2012). Fe belongs to the most abundant element in Earth's crust and it is essential for human existence. High concentration of Fe in water may cause color problem. Although there is not any proposed health-based guideline value for Fe by World Health Organization (WHO), it was reported that it can cause carcinogenic effects on animals (WHO, 1996; WHO, 2011).

Copper in drinking water arises due to leaching from water distribution pipes. In some cases, high amounts of dissolved oxygen accelerate the copper corrosion. The main source of copper exposure in developed countries is food and water. High levels of copper cause bitter taste of water and color problem. Copper contaminated water can cause gastrointestinal effects (WHO, 2011).

Arsenic is mostly found as its sulfides and metal arsenide or arsenates in Earth's crust. High concentrations of As can cause a number of health effects such as dermal lesions, skin cancer, bladder and lung cancers and peripheral vascular disease in humans. Volcanic eruptions, soil erosion and anthropogenic activities can cause the elevation of arsenic amount in the environment (Tchounwou et al., 2012; WHO, 2011).

Cadmium can be found in sedimentary rocks at high concentrations and is generally used in industrial activities such as steel industry, plastics, batteries and production of pigments. Cd accumulates primarily in the kidneys and Cd exposure is associated with prostate, kidney and lung cancer (Colak et al., 2015; Tchounwou et al., 2012; WHO, 2011).

Lead like copper can enter water by corrosion and some anthropogenic activities such as fossil fuels burning, mining, and manufacturing (e.g. glass and electronic industries) contribute to the release of lead to the environment. Exposure to lead can cause neurodevelopmental effects, mortality, hypertension, impaired fertility and adverse pregnancy outcomes (Tchounwou et al., 2012; WHO, 2011).

Aluminum can be present in the drinking water naturally or due to aluminum salts used for coagulation purposes. Excess amount of aluminum can cause lung and bladder cancer (Colak et al., 2015). Although aluminum is not considered as a major environmental pollutant, the sorbent uptake capacity of aluminum was investigated together with other elements (Fe, Cu, Cr, As, Cd, Pb) in this study in view of the omnipresence of aluminum (Lee et al., 2004).

The discharge limits for heavy metal containing effluents of different industries were regulated in Turkish Water Pollution Control Regulation (Turkish Regulation 2004) and the values are given in Table 1.

Table 1. The discharge limits for heavy metal containing effluents of different industries

	LIMIT VALUES (mg L^{-1})				
	Mining industry	Oil industry	Dye industry	Automotive industry	Waste water discharged to sewage system
Al	3	-	-	3	-
Fe	3	10	30	3	-
Cu	5	1	-	0.3	2
Cr	2	0.5	2	0.5	5
As	-	-	-	-	-
Cd	0.5	-	-	0.05	2
Pb	2	1	2	0.3	3

The removal of heavy metals from water is vital for human life and also for aqueous organism due to their adverse health effects. Several processes such as coagulation/flocculation, oxidation/precipitation, adsorption/biosorption, electrochemical processes, ion-exchange, bioremediation, floatation, evaporation, photocatalysis and membrane technology can be used for the removal of heavy metals (Barakat, 2011; Bestawy et al., 2012; Blöcher et al., 2003; Gunatilake, 2015; Wahyuni et al., 2015). Among these methods, adsorption/biosorption is one of the preferred methods due to its easy application, cost effectiveness, high efficiency, regeneration capacity, easy recovery and sludge-free operation (Amuda et al., 2007; Aremu et al., 2002; Gautam et al., 2014; Kadirvelu et al., 2001; Karadag, 2008; Koubaissy et al., 2014; Vaghetti et al., 2009; Zhang et al., 2016).

The most commonly used adsorbent in adsorption process is activated carbon which has a very porous structure and high adsorption capacity. However, because of its high cost, researchers tended to find alternative, cheaper and naturally occurring adsorbents in recent years. Agricultural wastes such as peanut, hazelnut, walnut, rice husk, cotton stalk, etc., which have lignocellulosic structures can be considered as most appropriate adsorbents for the removal of pollutants (Ali et al., 2016; Koubaissy et al., 2014; Wan Ngah and Hanafiah, 2008; Wolfová et al., 2013).

Turkey has the biggest market share in the hazelnut production in the world. Approximately 80% of the total hazelnut production in the world is supplied from north coasts of Turkey. Hazelnut shell and hazelnut skin are the wastes of hazelnut processing plants. While hazelnut shell is utilized in plywood, linoleum and paint industry in USA, Italy and Germany, which have advanced technologies, it is mostly used for heating purposes in Turkey. Hazelnut skin occurs during the production of nutmeat and is generally used as animal feed. However, these wastes can also be utilized as a natural biosorbent for the removal of pollutants like heavy metals, non-metals, etc. (Demirbas et al., 2008; Karadeniz et al., 2008). Nutshell and nut skin have functional groups such as carboxylic and hydroxyl groups in their structures and have high affinity for ions (Amuda et al., 2007).

The biosorption of metal and non-metal ions strongly depends on the pH, ionic strength, suspended solids and also existing ions in the treated water. Contaminated waters usually contain more than one metal and non-metal species, and there would be competition between ions for the binding sites on biosorbents. In the literature, removal of heavy metals was studied by using different natural sorbents for systems containing only one or two elements (Afkhami et al., 2010; Ahmedna et al., 2004; Amuda et al., 2007; Bulut and Tez, 2007; Demirbas et al., 2008; Kadirvelu et al., 2001; Karadag, 2008; Kazemipour et al., 2008; Köysüren and Dursun, 2013; Lee et al., 2004; Pehlivan and Altun, 2008; Sencan et al., 2015; Vaghetti et al., 2009; Vazquez et al., 2009; Wan Ngah and Hanafiah, 2008; Wolfová et al., 2013; Zhang et al., 2016). However, the studies about multi-metal containing systems are very restricted. Thus, evaluation of the metal and/or non-metal adsorption studies should be done for multi-element containing systems to approach very similar situation (Gautam et al., 2014; Volesky and Holant, 1995). The objective of this study is to investigate the potential use of hazelnut processing plant wastes in raw forms, hazelnut shell (SH) and skin (SK), as sorbent for the simultaneous removal of health effecting elements (Al, Fe, Cu, Cr, As, Cd, Pb) from water as a function of initial pH, initial concentration and adsorbent dosage in a batch system.

2. Materials and Methods

2.1. Sorbents

This study includes the use of hazelnut processing plant wastes, hazelnut shell (SH) and skin (SK), as adsorbents for the simultaneous removal of metal and non-metal elements (Al, Cr, Fe, Cu, As, Cd and Pb) from water. The raw hazelnut wastes were supplied from Fiskobirlik Integrated Hazelnut Processing Plant located in Giresun, Turkey. Prior to use, hazelnut shell wastes were extensively washed with tap water to remove the soil and dust, sprayed with distilled water and then dried in an oven at 60 °C to a constant weight. Then, they were ground into small fine particles by a laboratory type grinder and particles having a size of 0.125 mm< d ≤ 1 mm were obtained and stored in glass bottles for further use. The other sorbent, hazelnut skin wastes, originates from processing of raw hazelnut and includes both nutmeat and nutmeat skin. Hence, hazelnut skin wastes were just screened and the sorbent having the same size of hazelnut shell were stored in glass bottles after drying for comparative adsorption studies. Both sorbents were used without any pre-treatment during adsorption experiments.

2.2. Batch Experiments

Batch experiments were carried out in duplicate at room temperature (22 ± 2 °C). 250 mL stoppered Pyrex glass Erlenmeyer flasks containing a definite volume (100 ml in each case) of sample solution were placed in a thermostatic shaking assembly. The required concentrations of Al, Cr, Fe, Cu, As, Cd and Pb were prepared by diluting 1000 mg L^{-1} of commercial stock solutions of heavy metals (SCP Science, Canada). Ultra-pure water obtained from Sartorius Ultrapure Water System (Sartorius, NY, USA) with a resistivity of 18.2 M⍰.cm was used for all dilution purposes. Nitric acid (5% (v/v) (HNO3, Merck, Germany) washed laboratory glassware was used for the experiments.
For the adsorption studies with both sorbents, 0.1 g of sorbent was treated with 100 mL of elements containing solution at a defined pH and temperature. All the final solutions contained 1.0 g L^{-1} of sorbent. The pH of each solution was carefully adjusted to the required value by using diluted or concentrated HNO_3 (Merck, Germany) and NaOH (Merck, Germany) solutions and final volume of 100 mL was obtained before mixing the sorbent. The concentration range of prepared heavy metal solutions was varied between 0.5 to 20 mg L^{-1}. Discharge limit values given in Table 1 were considered for the selection of concentration range. Before running the experiments, the aqueous medium and the sorbents were mixed by gently shaking the flasks and the pH was re-measured and re-adjusted if required. pH of the solutions was not re-adjusted during the adsorption period. However, pH values were checked during and at the end of the adsorption period and it was noted that initial pH value did not change significantly. The effect of adsorbent dosage was also studied by varying amount of 0.1 g to 2 g of sorbents treated with 100 mL of heavy metal containing solution.

The flasks were agitated on the shaker at 200 rpm and adsorption experiments were conducted for 48 h to ensure equilibrium was reached. Samples (3 mL) were taken before mixing the adsorbent and heavy metal containing solution. The analysis of 9 samples which were taken from each flask at pre-determined time intervals were done for the residual nonadsorbed heavy metal concentrations in the solution. Before analysis, the samples were filtrated through coarse filter paper and the supernatant liquid was analyzed for the remaining heavy metals.

The percentage of removed heavy metals was calculated by using equation (1) (Aksu et al., 2008; Tunç Dede, 2018.):

$$\mathbf{R}(\%) = \frac{(\mathbf{C_0} - \mathbf{C_{Res}})}{\mathbf{C_0}} * \mathbf{100} \qquad (1)$$

where
C_0: the initial heavy metal concentration (mg L^{-1}),
C_{Res}: the residual (nonadsorbed) heavy metal concentration at any time (mg L^{-1}),
R: the removal efficiency of heavy metals

2.3. Analysis

An infrared spectrum was obtained using Fourier Transform Infrared Spectrophotometer (Shimadzu, FTIR 8000, Japan) to identify the functional groups and chemical bonding of the hazelnut waste sorbents. Elemental analysis of both sorbents was done by using an elemental analyzer (Costech ECS 4010 Elemental Analyzer, USA) and BBOT standard (C: 72.53% H: 6.09%, N: 6.51%, S: 7.44%, O: 7.43%) as a certified reference material (CRM). Scanning electron microscopy (Jeol JSM 6610 SEM-EDS, Japan) was performed to characterize the shape of the sorbents. Specific surface areas of the sorbents were measured by using multi point-N2-BET method (instrument: Autosorb iQ, Quantachrome, USA) and pH adjustments were carried out by Hanna HI 9812-5 (Hanna, USA) pH-Meter. In order to define some functional groups on the structure of hazelnut wastes, GC-MS (Agilent GC-MS Model: 5975C inert MSD, USA) analysis were also done.

The concentration of nonadsorbed heavy metals in the medium was analyzed by using inductively coupled plasma - mass spectrometry (Bruker 820-MS ICP-MS) (CA, USA) for all elements with ten replicates. ICP-MS analyses were done at Central Research Laboratory in Giresun University, Turkey. The isotopes analyzed and their limit of detection values (LOD) were given in Table 2. For control purposes of the results obtained by ICP-MS, a quality control solution (Certipur, Merck, Germany) with 100 mg/L concentration was analyzed prior to sample analysis with less than 15% relative standard deviation (RSD).

Table 2. The limit of detection values

ISOTOPES	LOD (ng L^{-1})
^{27}Al	2
^{52}Cr	8
^{57}Fe	300
^{63}Cu	0.3
^{75}As	20
^{111}Cd	0.2
^{208}Pb	0.3

2.4. Isotherm models

The use of appropriate adsorption isotherm models and analyzing the equilibrium data is important to the design and optimization of the adsorption processes. Adsorption data provide information about the relationship between the pollutant and the adsorbent, the capacity of the adsorbent and the amount required for the removal of pollutant based on a unit mass. The most frequently used models for the investigation of the adsorption isotherm are Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich models (Ali et al., 2016; Gautam et al., 2014).

The uptake of heavy metals by unit mass of sorbent at any time (q) was determined from equation 2 (Ali et al., 2016; Gautam et al., 2014).

$$q=\frac{C_0\text{-}C_{Res}}{X}, \qquad (2)$$

where

C_0: the initial heavy metal concentration (mg L^{-1}),

C_{Res}: the residual (nonadsorbed) heavy metal concentration at any time (mg L^{-1}),

X: the sorbent concentration (g L^{-1}).

C_{Res} is equal to C_{eq} and q is equal to q_{eq} at equilibrium.

Among the adsorption isotherm models, the Langmuir model is valid for monolayer adsorption on a homogenous surface with a finite number of binding sites. It assumes that there is negligible interaction between adsorbed ions. It can be expressed by the following equation (3):

$$\mathbf{q_{eq}}=\frac{Q^0 bC_{eq}}{1+bC_{eq}}, \qquad (3)$$

where C_{eq} and q_{eq} are nonadsorbed metal ion solution and adsorbed metal ion on the sorbent at equilibrium, respectively. Q_0 and b are the Langmuir constants represents maximum adsorption capacity and affinity of the binding sites. These parameters can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq}.
The Freundlich isotherm model is the earliest known empirical equation which describes the adsorption on a heterogeneous surface. The mathematical description of this model is (Ali et al., 2016; Gautam et al., 2014).:

$$\mathbf{q_{eq}=K_F C_{eq}^{1/n}}, \qquad (4)$$

where KF and n are the Freundlich constants indicate the adsorption capacity and adsorption intensity. Logarithmic linearization of this equation can be used for the determination of the constants.

The Redlich–Peterson model is a three-parameter equation and has a linear relationship with concentration in the numerator but an exponential one in the denominator. This equation is given by (Ali et al., 2016; Gautam et al., 2014).:

$$\mathbf{q_{eq}}=\frac{K_{RP}C_{eq}}{1+a_{RP}C_{eq}^{\beta}}, \qquad (5)$$

Langmuir–Freundlich model is also a three-parameter model and it is a combination of the Langmuir and Freundlich adsorption isotherm models. The formula is given by (Ali et al., 2016; Gautam et al., 2014).:

$$\mathbf{q_{eq}}=\frac{AC_{eq}^{m}}{1+BC_{eq}^{m}}, \qquad (6)$$

where A, B and m are the Langmuir–Freundlich parameters. When m≥1, it indicates heterogeneous adsorbents. If m is closer or equal to 1, the equation reduced to Langmuir model and indicates homogenous adsorbents (Afkhami et al., 2010; Aksu et al., 2008; Ali et al., 2016; Amuda et al., 2007; Demirbas et al., 2008; Gautam et al., 2014; Karadag, 2008; Sencan et al., 2015; Vaghetti et al., 2009; Vazquez et al., 2009; Wang and Chen, 2006; Zhang et al., 2016).

The average percentage error between the experimental and estimated equilibrium data are calculated by using following equation (Aksu et al., 2008).:

$$\boldsymbol{\varepsilon\%}=\frac{\sum_{i=1}^{N}\left|(q_{eq,i,exp.}-q_{eq,i,calc.})/q_{eq,i,exp.}\right|}{N}*\mathbf{100} \qquad (7)$$

where $q_{eq,i,exp.}$ and $q_{eq,i,calc.}$ are experimental and calculated uptake values and N the number of measurements.

3. Results

3.1. Characterization of Sorbents

The elementary content of sorbents and surface areas were presented in Table 3.

Table 3. The characterization of the sorbents

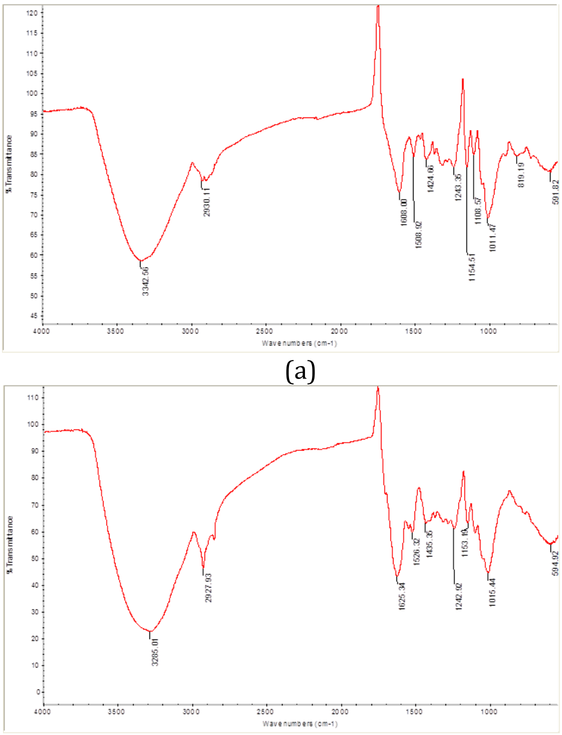
	CRM (BBOT)	**Hazelnut Shell (SH)**	**Hazelnut Skin (SK)**
Specific surface area, BET ($m^{2\cdot}g^{-1}$)	-	0.676	0.768
Elemental analysis			
C (w%)	71.95	46.82	39.96
H (w%)	6.35	5.26	5.84
N (w%)	6.24	1.06	4.09
S (w%)	7.85	n.d.	n.d.
*O (w%)	n.d.	46.86	50.11
Ash content (w%)	-	2.86	3.31

* Oxygen amount could not be analyzed from elemental analyzer. It was calculated from the difference; n.d.: not detected.

In order to explore the qualitative adsorption characteristics of surface functional groups of the hazel nut shell and skin, the FTIR spectra in the range of 4000-500 cm^{-1} were recorded and shown in Figure 1. There is an apparent wide band at around 3342 cm^{-1} for SH and 3285 cm^{-1} for SK. When it is compared to literature data, these bonds belong to O-H phenolic and alcoholic groups which are present in cellulose and lignin in the hazelnut. While bands at 2927 and 2930 cm^{-1} are assigned to methyl and methylene C–H vibrations in the literature, bands at 1625 and 1608 cm^{-1} are due to C=C vibrations. Bands at about 1,100 cm^{-1} can be assigned to C–O bonds of alcohols and ethers. The peaks at 591 and 594 cm^{-1} are due to the vibrational bending in the aromatic compounds (Koubaissy et al., 2014; Sencan et al., 2015; Vazquez et al., 2009; Wolfová et al., 2013).

GC-MS analysis showed that both sorbents have benzene carboxylic acid, 2-pentadecanone, 6,10,14-trimethyl, hexadecanoic acid, methyl ester, decane and dodecane groups in their structures and thus corroborates the FTIR results.

The surface morphology and structural features of the sorbents can be characterized by scanning electron microscopy (SEM). The surface morphologies of raw hazelnut sorbents were characterized by SEM and EDS analysis before and after adsorption of heavy metal ions. Figure 2 shows the SEM image of the raw hazelnut shell and hazelnut skin surfaces before heavy metal adsorption. It indicates that the hazelnut shell and skin are mostly irregular in shape and have rough uneven surfaces (Ali et al., 2016).



(a)

(b)

Figure 1. FTIR spectra of the two sorbents (a) hazelnut shell (b) hazelnut skin

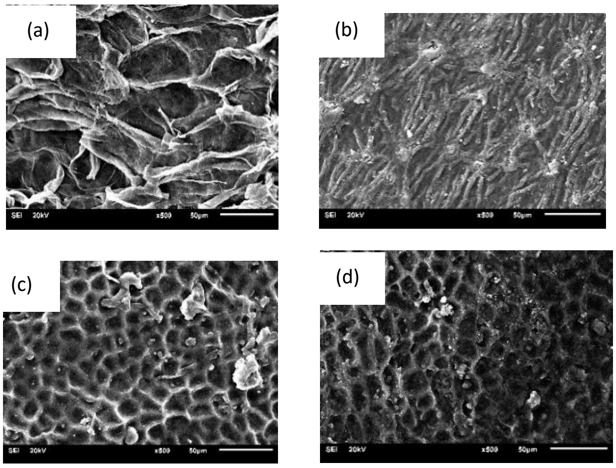
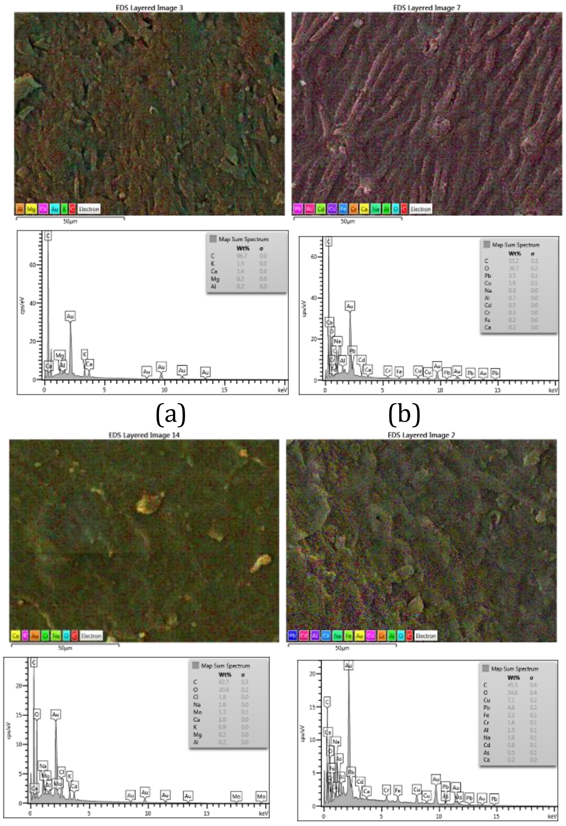


Figure 2. SEM images of hazel nut shell (a) before adsorption (b) after adsorption and hazel nut skin (c) before adsorption (d) after adsorption

EDS analysis confirmed the adsorption of heavy metal ions for both sorbents (Figure 3). The elemental distribution images from EDS analysis revealed that the whole hazelnut shell and skin surfaces are covered by heavy metal ions.



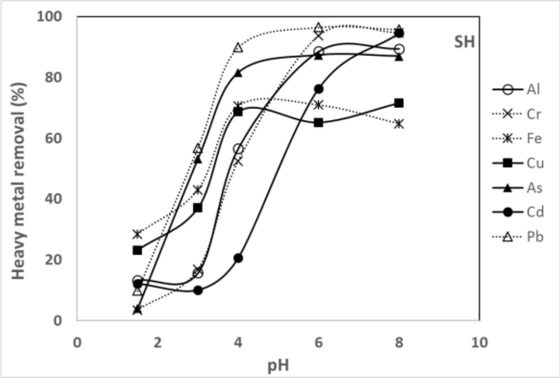
(a) (b)

(c) (d)

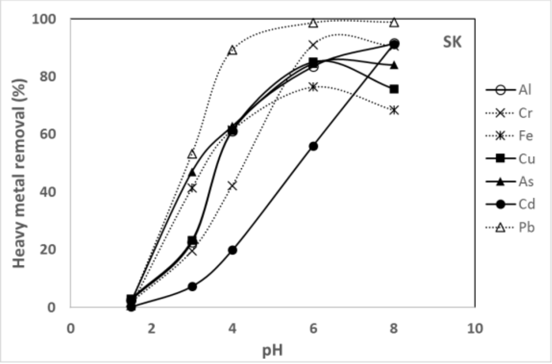
Figure 3. EDS images for hazelnut shell (a) before adsorption (b) after adsorption and hazelnut skin (c) before adsorption (d) after adsorption

3.2. Effect of Initial pH

Heavy metal adsorption experiments were performed over a pH range of 1.5-8.0 to find a suitable pH value for the effective simultaneous adsorption of all heavy metals by hazelnut waste sorbents. Percentage of heavy metal removal change with pH is given in Figure 4 for all heavy metals and sorbents at about 10 mg L^{-1} initial heavy metal concentration for each element. Both sorbents indicated similar binding properties for all heavy metals. As seen from Figure 4, increasing pH from 1.5 to 6.0 caused increase in the removal of almost all elements. Fe, Cu, As and Pb removal were reached maximum values at pH 4 for hazelnut shell sorbent and did not change with increasing pH. However, Cd adsorption was increased with increasing pH and maximum removal were found at pH 8.0 for both sorbents. For the remaining elements, maximum values obtained at around pH 6.0. During the adsorption process, metal hydrolysis and precipitation can begin above pH 6.0 [Chowdhury et al. 2016; Koubaissy et al. 2014]. In our studies, precipitation was observed above pH 6.0. As seen from Figure 4, while some elements (Fe, Cu for SH) has optimum pH as 4.0, some of them are 6.0 (Al, As, Pb for SH and Cr, Fe, Cu, As for SK) and the rest are 8.0. Because of the precipitation problem, pH 6.0 and above was considered as risky and the optimum pH value was chosen as pH 5.0 both sorbents. The other adsorption experiments were performed at pH 5.0. (a)



(a)



(b)

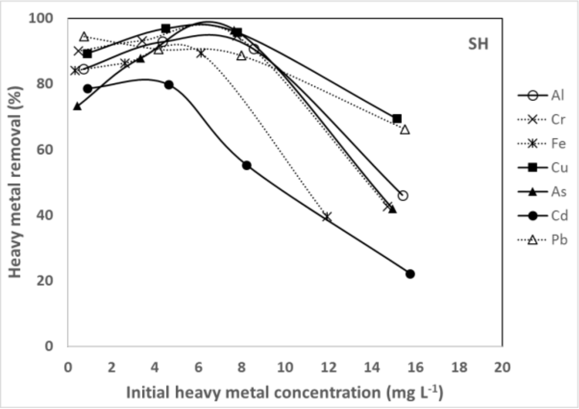
Figure 4. Effect of initial pH on heavy metal removal capacity of hazelnut shell (SH) (a) and skin (SK) (b) sorbents (C_0: 10 mg L^{-1}, T: 22 ± 2 °C, X: 1.0 g L^{-1}, agitation rate: 200 rpm, number of samples (n)=9 for each sorbent system)

3.3. Effect of Initial Heavy Metal Concentration

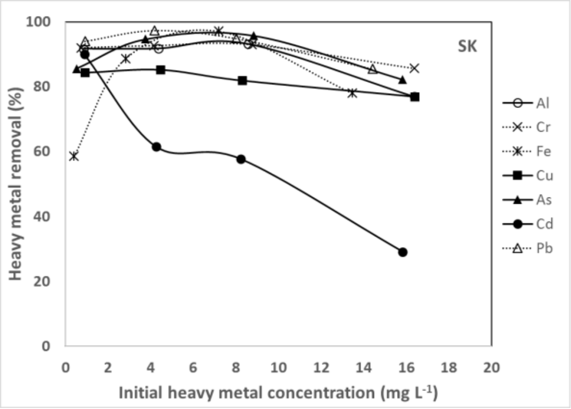
The effect of initial heavy metal concentration was evaluated for four different concentration values varying between 0.5 - 20 mg L^{-1} at an initial pH value of 5.0 at the temperature of 22 ± 2 °C. The results are illustrated in Figure 5 for both sorbents. For SH sorbent, the percent removal of heavy metal increased with increasing initial heavy metal concentration for all metal ions except cadmium up to 8 mg L^{-1}. Further increase in heavy metal concentration decreased the removal percent. For SK sorbent, the percent removal of heavy metal increased with increase in initial heavy metal concentration for all metal ions except copper and cadmium to 8 mg L^{-1} as in the case of SH sorbent. Further increase of initial heavy metal concentration led to a decrease of removal percentage.

3.4. Effect of The Amount of Adsorbent

The effect of adsorbent dosage was studied at an initial pH value of 5.0 and at the temperature of 22 ± 2 °C by varying the adsorbent amount from 1 to 20 g L^{-1}. The results are shown in Figure 6 for both sorbents.



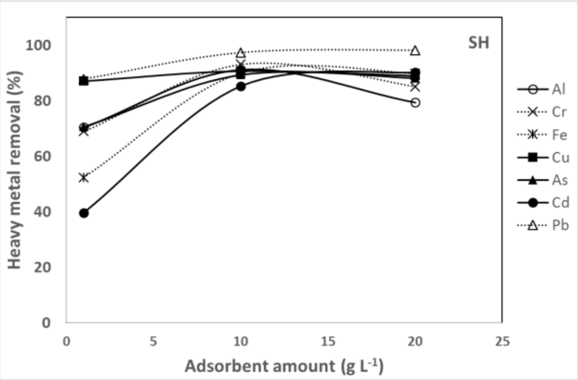
(a)



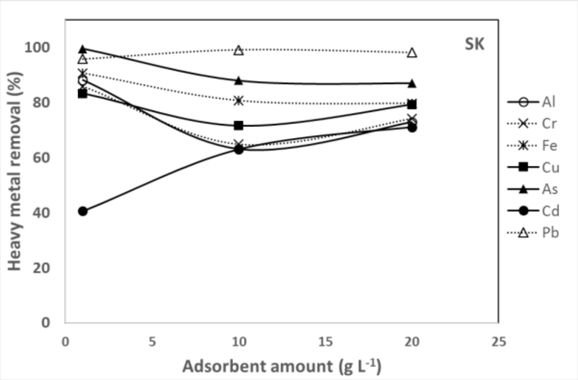
(b)

Figure 5. Effect of initial heavy metal concentration on heavy metal removal capacity of hazelnut shell (SH) (a) and skin (SK) (b) sorbents (pH: 5.0, T: 22 ± 2 °C, X: 1.0 g L^{-1}, agitation rate: 200 rpm, n=9 for each sorbent system).

For SH sorbent, the percent removal of heavy metal increased with increasing amount of adsorbent up to 10 g L^{-1}. More than 90% removal of heavy metal was attained due to the greater availability of the adsorbent. Further increase did not change the percentage of removal significantly. However, for SK sorbent, increase in the amount of adsorbent led to a decrease of the percentage of removal except for lead and cadmium. This might be due to the contents of hazel nut skin sorbent. The hazelnut skin wastes, originates from processing of raw hazelnut and includes both nutmeat and nutmeat skin. When heavy metal containing solution are treated with SK sorbent, it was observed that the solution turbidity was increased after starting the adsorption experiments and an oily solution was obtained. The level of turbidity increased with increasing amount of adsorbent. This might be due to the fat content of nutmeat. When the fat content of the nutmeat was transferred to the heavy metal solution, the adsorption of heavy metal could be precluded.



(a)



(b)

Figure 6. Effect of adsorbent amount on heavy metal removal capacity of hazelnut shell (SH) (a) and skin (SK) (b) sorbents (pH: 5.0, T: 22 ± 2 °C, agitation rate: 200 rpm, C_0:8 mg L^{-1} n=9 for each sorbent system).

3.5. Equilibrium Studies

All model parameters were calculated by non-linear regression analysis and tabulated in Tables 4&5 with the error values in percent (ε%) and R^2 values. All parameters for each equilibrium model were calculated and given in tables. The best suited model for each sorbent-element system was decided according to having less ε% and high R^2 values. The models which have R^2 values close to 1 is selected as the best suited model.

Table 4. Comparison of the Langmuir and Freundlich isotherm constants of heavy metals on hazelnut shell (SH) and skin (SK) at T: 22 ± 2 °C (n=9 for each sorbent system)

	SHELL	**LANGMUIR**			
	q_{max} (mg g^{-1})	**Q^0**	**b**	**ε%**	**R^2**
Al	7.75	8.31	0.709	31.08	0.531
Cr	7.36	6.80	1.419	28.23	0,480
Fe	5.47	5.35	1.033	24.14	0.565
Cu	10.51	14.14	0.623	35.09	0.711
As	7.39	8.40	0.339	38.95	0.212
Cd	4.55	3.73	1.214	19.78	0.699
Pb	10.26	7.14	1.094	47.46	0.986
		FREUNDLICH			
		K_F	**n**	**ε%**	**R^2**
Al	7.75	2.12	1.751	37.29	0,.359
Cr	7.36	2.08	1.933	37.83	0,283
Fe	5.47	1.50	1.728	35.47	0.342
Cu	10.51	3.78	1.504	37.85	0.660
As	7.39	1.41	1.446	41.65	0.205
Cd	4.55	1.33	2.589	29.15	0.346
Pb	10.26	3.77	1.657	28.62	0.854
	SKIN	**LANGMUIR**			
	q_{max} (mg g^{-1})	**Q^0**	**b**	**ε%**	**R^2**
Al	12.60	17.74	0.648	12.60	0.919
Cr	14.04	28.51	0.413	11.23	0.965
Fe	10.50	13.10	0.110	61.85	0.627
Cu	12.60	31.85	0.173	4.31	0.998
As	13.00	44.42	0.146	34.17	0.762
Cd	4.60	5.29	0.601	22.84	0.911
Pb	12.33	19.21	0.854	23.23	0.924
		FREUNDLICH			
		K_F	**n**	**ε%**	**R^2**
Al	12.60	4.96	1.427	24.11	0.838
Cr	14.04	6.96	1.217	18.38	0.926
Fe	10.50	2.50	0.756	43.33	0.626
Cu	12.60	4.04	1.172	10.19	0.987
As	13.00	5.05	1.100	35.55	0.747
Cd	4.60	1.93	2.779	12.14	0.806
Pb	12.33	7.18	1.369	28.71	0.867

Table 5. Comparison of the Redlich-Peterson and Langmuir-Freundlich isotherm constants of heavy metals on hazelnut shell (SH) and skin (SK) at T: 22 ± 2 °C (n=9 for each sorbent system)

	SHELL	**REDLICH-PETERSON**				
	q_{max} (mg g^{-1})	**K_{RP}**	**a_{RP}**	**β**	**ε%**	**R^2**
Al	7.75	1.91	0.484	0.441	61.38	0.300
Cr	7.36	9.65	1.419	1.000	28.23	0,480
Fe	5.47	1.83	0.601	0.557	58.00	0.302
Cu	10.51	2.71	0.110	0.390	62.19	0.620
As	7.39	1.78	0.329	0.693	53.12	0.198
Cd	4.55	1.26	0.770	0.595	54.17	0.268
Pb	10.26	2.62	0.177	0.396	58.10	0.758
		LANGMUIR-FREUNDLICH				
		A	**B**	**m**	**ε%**	**R^2**
Al	7.75	1.66	0.656	0.337	62.04	0,591
Cr	7.36	36.42	5.723	1.196	33.87	0,745
Fe	5.47	17.81	3.713	1.392	10.25	0.788
Cu	10.51	1.80	0.691	0.192	64.09	0.819
As	7.39	32.55	5.181	1.968	27.96	0.204
Cd	4.55	1.33	0.002	0.387	29.13	0.346
Pb	10.26	12.11	0.946	0.875	4.00	0.982
	SKIN	**REDLICH-PETERSON**				
	q_{max} (mg g^{-1})	**K_{RP}**	**a_{RP}**	**β**	**ε%**	**R^2**
Al	12.60	11.50	0.648	1.000	24.11	0.919
Cr	14.04	11.78	0.430	1.000	18.38	0.965
Fe	10.50	1.47	0.148	0.000	63.32	0.627
Cu	12.60	5.47	0.143	1.000	4.95	0.996
As	13.00	6.49	0.146	1.000	34.17	0.762
Cd	4.60	1.45	0.676	0.545	48.29	0.687
Pb	12.33	16.41	0.854	1.000	23.23	0.924
		LANGMUIR-FREUNDLICH				
		A	**B**	**m**	**ε%**	**R^2**
Al	12.60	18.05	1.220	1.166	6.61	0.957
Cr	14.04	23.32	1.335	1.314	7.35	0.995
Fe	10.50	46.18	4.318	2.326	69.03	0.611
Cu	12.60	5.93	0.219	1.037	2.75	0.999
As	13.00	1.43	0.864	0.316	67.38	0.940
Cd	4.60	1.96	0.013	0.365	11.95	0.809
Pb	12.33	1.78	0.717	0.101	64.00	0.991

4. Discussion

The hazelnut processing plant wastes, hazelnut shell and hazelnut skin, were used as sorbent for the removal of heavy metals in this study. For the indication of the surface morphology of the sorbents, elemental analysis, FTIR, SEM-EDS and BET analysis were performed. Specific surface areas of the sorbents were found as 0.676 $m^2\ g^{-1}$ (for SH) and 0.768 $m^2\ g^{-1}$ (for SK). All these analyses showed that the surfaces of both sorbents are rough, contains pores that allow to entrap heavy metals. In addition, the sorbents have functional groups such as carboxylic acid, phenolic compounds, etc. to which the heavy metal ions can attach. However, SEM-EDS results of both sorbents (Figure 2 and 3) before and after adsorption process indicate that heavy metal ions are attached to the sorbent surfaces rather than inside the pores.

The pH of the aqueous solution is an important influencing factor in the adsorption process. In general, the adsorption capacity for metal cations increases with increasing pH value. When pH of the solution is low (pH<3), the hydrogen ion concentration increases. This means that metal ions must compete with H+ ions for the available active sites on the sorbent which results in low adsorption efficiency of metal ions at low pH values. With increasing pH, H^+ ion concentrations will be neutralized with the existence OH^- ions in the solution and heavy metal ions do not have to compete. Thus, the adsorption efficiency of heavy metals will be high. However, too high a pH value (above pH 6) can cause metal hydrolysis and precipitation. The effect of initial pH was studied over a pH range of 1.5-8.0 for all heavy metals and sorbents at about 10 mg L^{-1} initial heavy metal concentration (for each element) and optimum pH was found as 5.0 (Figure 4).

Although isoelectric point of hazelnut sorbents could not be achieved in this study, it was found that the isoelectric point of hazelnut was tried to determine by Demirbas et al. (2008). Demirbas et al. (2008) reported that the zeta potential values were negative for pH range of 2 to 10 and the isoelectric point could not be determined. This can be concluded that hazelnut shell surface has negative charge groups. By the way, hazelnut shell and skin carry the surface functional groups containing oxygen such as carboxylic and phenolic groups which are the active ion exchange compounds. These groups can be protonated or deprotonated in acidic and/or basic solutions (Demirbas et al., 2008). Electrostatic attraction between positively charged metal ions with these functional groups may be one of the specific adsorption mechanisms. This means that heavy metal cations can be easily adsorbed on the adsorbent naturally.

This study also covers the investigation of the effect of initial heavy metal concentration on adsorption process (Figure 5). It is expected that increasing initial heavy metal concentration enhance the sorption process due to providing a significant driving force to overcome mass transfer resistance between metal ions and sorbents. In this study, the percent removal of heavy metal increased with increase in initial heavy metal concentration for all metal ions (except cadmium for SH and copper and cadmium for SK) up to 8 mg L^{-1}. At higher concentrations, while copper removal has almost remained unchanged, cadmium left unadsorbed. This might be due to competition between metal ions. At higher concentrations, more heavy metal ions are left unadsorbed in the aqueous medium due to the saturation of active binding sites. This may be because of energetically less favorable binding sites become involved with increasing heavy metal concentration in the solution (Amuda et al., 2007).

The analyzing and proper assessment of the adsorption equilibrium data is important to design and optimize the adsorption processes. It gives information about the capacity of the adsorbent and the amount required for the removal of pollutant based on a unit mass. Four most frequently used isotherm models were applied to investigate the equilibrium data. Isotherm graphics showed positive, regular and concave to the x-axis (concentration axis) which indicates an affinity for sorption. Obtained results were introduced in Tables 4&5 for all heavy metals and both sorbents.

The values of average percentage errors (ε%) and R^2 values were used for the selection of the most suitable adsorption isotherm model. The best model fitted the adsorption equilibrium data of all heavy metal elements were listed in Table 6.

Table 6. The list of the best adsorption isotherm models fitted the equilibrium data for all elements and both sorbents (SH:Shell; SK:Skin)

HEAVY METALS	ADSORBENT	BEST SUITABLE ADSORPTION ISOTHERM MODEL
Al	**SH** **SK**	Langmuir Langmuir-Freundlich
Cr	**SH** **SK**	Langmuir Langmuir-Freundlich
Fe	**SH** **SK**	Langmuir-Freundlich Freundlich
Cu	**SH** **SK**	Langmuir Langmuir-Freundlich
As	**SH** **SK**	Langmuir-Freundlich Langmuir
Cd	**SH** **SK**	Langmuir Langmuir-Freundlich
Pb	**SH** **SK**	Langmuir-Freundlich Langmuir

The values of adsorption model constants represent the surface properties, adsorption mechanisms and capacity and/or affinity of the sorbent. The Freundlich constant, K_F, is a relative measure of adsorption capacity and shows the adsorption strength. n is an indicator of the adsorption intensity and n values greater than 1 means a favorable adsorption. While the Langmuir constant, Q_0 demonstrates monolayer adsorption at equilibrium, other constant b is related to the adsorbent affinity. The higher b values mean strong bonding of heavy metals. Values of KRP from Redlich-Peterson and A from Langmuir-Freundlich models indicate also heavy metal adsorption capacity of sorbent. The other constants are related to the affinity of the sorbent. While the value of β between zero and 1 means favorable adsorption, m value close to 1 is sign of homogenous sorbent. According to Tables 4&5, the equilibrium data were fitted very well to Langmuir and Langmuir-Freundlich models in most cases. The adsorption of heavy metals with hazelnut shell and skin sorbents show a favorable adsorption behavior.

Desorption studies and real sample application should also be performed for the sorbents. Desorption studies are important for the regeneration and reusability of the hazelnut shell and hazelnut skin sorbents. Pehlivan (2008) has investigated desorption of chromium ion from hazelnut shell by using NaOH and achieved 42% desorption with no damage on shell. Real samples would contain other parameters (Ca, Mg, salt, suspended solids, etc.) besides heavy metals. These parameters can affect the uptake capacity of sorbents. Real sample application was performed by Kazemipour et al. (2008) and they achieved 94.1% and 74.4% removal of copper and zinc by hazelnut.

Table 7. Adsorption capacities for some natural adsorbents reported in the literatures (mg g^{-1})

	Al	**Cr**	**Fe**	**Cu**	**As**	**Cd**	**Pb**	**REFERENCE**
Hazelnut shell	7.75	7.36	5.47	10.51	7.39	4.55	10.26	This study
Hazelnut skin	12.60	14.04	10.50	12.60	13.00	4.60	12.33	
Walnut shell	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	8.69	(Wolfová et al. ,2013)
Hazelnut shell	n.a.	n.a.	n.a.	n.a.	n.a.	5.22	16.23	(Bulut and Tez, 2007)
Almond shell	n.a.	n.a.	n.a.	n.a.	n.a.	3.18	5.43	
Chestnut shell	n.a.	n.a.	n.a.	6.36	n.a.	n.a.	26.61	(Vazquez et al., 2009)
Apricot kernel shell	n.a.	1.84.	n.a.	n.a.	n.a.	n.a.	n.a.	(Köysüren and Dursun, 2013)
Waste crab shell	n.a.	n.a.	n.a.	n.a.	8.30	n.a.	n.a.	(Gautam et al., 2014)
Oliva pomace	n.a.	n.a.	n.a.	10.00	n.a.	5.50	n.a.	
Orange peels	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.22	
Saw dust	n.a.	n.a.	n.a.	12.70	n.a.	n.a.	n.a.	(Wan Ngah and Hanafiah, 2008)
Jute fibers	n.a.	n.a.	n.a.	4.23	n.a.	n.a.	n.a.	

n.a. not available

The hazelnut processing plant wastes can be utilized as a promising sorbent for the simultaneous removal of heavy metals due to their low cost and because they are easily available and environmentally friendly, have good adsorption capacity properties even in a large-scale process. The adsorption capacities of hazel nut shell and skin were compared with some natural adsorbents reported in the literatures (mg g^{-1}) and given in Table 7. As future research direction, however, adsorption studies with physically and/or chemically activated hazelnut waste sorbents, comparative studies between commercial activated carbon and activated carbon obtained from hazel nut waste, desorption and reuse of sorbents and real sample treatment can be highlighted.

5. Conclusion

This paper has demonstrated that potential use of hazelnut processing plant wastes, hazelnut shell (SH) and skin (SK), as a promising, cheap, easily available and environmentally friendly sorbent for the simultaneous removal of heavy metals (Al, Fe, Cu, Cr, As, Cd, Pb) from aqueous medium. The removal of heavy metal from water strongly depends on the pH of the medium and also on the element to remove. The studies about multi-metal containing systems are very restricted in the literature. Thus, this study will be one of the case studies for approaching real conditions.

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Conflict of Interest

No conflict of interest was declared by the authors.

References

Afkhami, A.; Saber-Tehrani, M.; Bagheri, H., 2010. Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2,4-dinitrophenylhydrazine. J. of Hazar. Mater. 181, 836-844.

Ahmedna, M.; Marshall, W.E.; Husseiny, A.A.; Rao, R.M.; Goktepe, I., 2008. The use of nutshell carbons in drinking water filters for removal of trace metals. Water Res. 38, 1062-1068.

Aksu, Z.; Tatli, A.I.; Tunc, O., 2008. A comparative adsorption/biosorption study of Acid Blue 161: Effect of temperature on equilibrium and kinetic parameters. Chem. Eng. J. 142, 23-39.

Ali, R.M.; Hamad, H.A.; Hussein, M.M.; Malash, G.F., 2016. Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. Ecol. Eng. 91, 317-332.

Amuda, O.S.; Giwa, A.A.; Bello, I.A., 2007. Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. Biochem. Eng. J.. 36, 174-181.

Aremu, D.A.; Olawuyi, J.F.; Meshitsuka, S.; Sridhar, M.K.; Oluwande, P.A., 2002. Heavy metal analysis of groundwater from Warri, Nigeria. Int. J. of Environ. Health Res. 12, 261-267.

Barakat, M.A., 2011. New trends in removing heavy metals from industrial wastewater. Arabian J. of Chem.. 4, 361-377.

Bestawy, E.E.; Helmy, S.; Hussien, H.; Fahmy, M.; Amer, R., 2012. Bioremediation of heavy metal-contaminated effluent using optimized activated sludge bacteria. Applied Water Sci. 3, 181-192.

Blöcher, C.; Dorda, J.; Mavrov, V.; Chmiel, H.; Lazaridis, N.K.; Matis, K.A. 2003. Hybrid flotation—membrane filtration process for the removal of heavy metal ions from wastewater. Water Res. 37, 4018-4026.

Bulut, Y.; Tez, Z., 2007. Adsorption studies on ground shells of hazelnut and almond. J. of Hazar. Mater. 149, 35-41.

Chowdhury, S.; Mazumder, M.A.; Al-Attas, O.; Husain, T., 2016. Heavy metals in drinking water: Occurrences, implications, and future needs in developing countries. The Sci. of the Total Environ. 569-57, 476-488.

Colak, E.H.; Yomralioglu, T.; Nisanci, R.; Yildirim, V.; Duran, C., 2015. Geostatistical Analysis of the Relationship Between Heavy Metals in Drinking Water and Cancer Incidence in Residential Areas in the Black Sea Region of Turkey. J. of Environ. Health. 77, 86-93.

Demirbas, O.; Karadag, A.; Alkan, M.; Dogan, M., 2008. Removal of copper ions from aqueous solutions by hazelnut shell. J. of Hazard Mater. 153, 677-684.

Gautam, R.K.; Mudhoo, A.; Lofrano, G.; Chattopadhyaya, M.C. 2014. Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. J. of Environ. Chem. Eng. 2, 239-259.

Gunatilake, S.K., 2015. Methods of Removing Heavy Metals from Industrial Wastewater. J of Multidiscip Eng Sci Studies (JMESS) 1, 12-18.

Kadirvelu, K.; Thamaraiselvi, K.; Namasivayam, C., 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresour. Technol. 76, 63-65.

Karadag, A., 2008. The removal of some metal ions from industrial wastewaters by biosorbent. Institute of Science, Departmant of Chemistry. Balikesir, Balikesir University.

Karadeniz, T.; Bostan, S.Z.; Tuncer, C.; Tarakçıoğlu, C., 2008. Fındık Yetiştiriciliği. Ordu.

Kazemipour, M.; Ansari, M.; Tajrobehkar, S.; Majdzadeh, M.; Kermani, H.R., 2008. Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. Journal of Hazard. Mater. 150, 322-327.

Koubaissy, B.; Toufaily, J.; Cheikh, S.; Hassan, M.; Hamieh, T., 2014. Valorization of agricultural waste into activated carbons and its adsorption characteristics for heavy metals. Open Eng. 4.

Köysüren, H.N.U.; Dursun, Ş., 2013. The removal of heavy metal ions from the aquatic environment by modified apricot kernel shells. J. of the Faculty of Eng. and Archit. of Gazi Univ. 28, 427-436.

Lee, H.S.; Suh, J.H.; Kim, I.B.; Yoon, T., 2004. Effect of aluminum in two-metal biosorption by an algal biosorbent. Minerals Eng. 17, 487-493.

Li, W.C.; Law, F.Y.; Chan, H.M., 2017. Biosorption studies on copper (II) and cadmium (II) using pretreated rice straw and rice husk. Environ Sci and Pollut Res 24(10), 8903–891.

Pehlivan, E.; Altun, T., 2008. Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell. Journal of Hazard. Mater. 155, 378-384.

Sencan, A.; Karaboyaci, M.; Kilic, M., 2015. Determination of lead(II) sorption capacity of hazelnut shell and activated carbon obtained from hazelnut shell activated with ZnCl2. Environ. Sci. and Pollut. Res. Int. 22, 3238-3248.

Tchounwou, P.B.; Yedjou, C.G.; Patlolla, A.K.; Sutton, D.J., 2012. Heavy metal toxicity and the environment. Exs. 101, 133-164.

Tunç Dede, Ö., 2018. Atık sulardan metallerin gideriminde fındık kabuğunun adsorbent olarak kullanılması: Adsorpsiyon mekanizması ve kinetik modelleme. Sakarya University Journal of Science, 22 (2), 232-242. DOI: 10.16984/saufenbilder.327245

Turkish Regulation, 2004. Turkish Water Pollution Control Regulation in: Urbanization M.o.E.a., ed. 25687. Official Gazette, Ankara, Official Gazette.

Vaghetti, J.C.P.; Lima, E.C.; Royer, B.; Cardoso, N.F.; Martins, B.; Calvete, T., 2009. Pecan Nutshell as Biosorbent to Remove Toxic Metals from Aqueous Solution. Sep. Sci. and Technol. 44, 615-644.

Vazquez, G.; Calvo, M.; Sonia Freire, M.; Gonzalez-Alvarez, J.; Antorrena, G., 2009. Chestnut shell as heavy metal adsorbent: optimization study of lead, copper and zinc cations removal. J. Hazard. Mater. 172, 1402-1414.

Volesky, B.; Holant, Z.R., 1995. Biosorption of Heavy Metals. Biotechnol Prog. 11, 235-250.

Wahyuni, E.; Aprilita, N.; Hatimah, H.; Wulandari, A.; Mudasir, M., 2015. Removal of Toxic Metal Ions in Water by Photocatalytic Method. Am. Chem. Sci. J. 5, 194-201.

Wan Ngah, W.S.; Hanafiah, M.A., 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresour. Technol. 99, 3935-3948.

Wang, J.; Chen, C., 2006. Biosorption of heavy metals by Saccharomyces cerevisiae: a review. Biotechnol. Adv. 24, 427-451.

WHO, 1996. Iron in drinking-water. Geneva: World Health Organization.

WHO, 2011. Guidelines for drinking-water quality Geneva: World Health Organization.

Wolfová, R.; Pertile, E.; Fečko, P., 2013. Removal of lead from aqueous solution by walnut shell. J. of Environ. Chem. and Ecotoxicol. 5, 159-167.

Zhang, L.; Zeng, Y.; Cheng, Z., 2016. Removal of heavy metal ions using chitosan and modified chitosan: A review. J. of Mol. Liq. 214, 175-191.