REPUBLIC OF TÜRKİYE
ADANA ALPARSLAN TÜRKEŞ SCIENCE AND TECHNOLOGY UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
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REMOVAL OF SOME HEAVY METALS FROM WASTE WATER WITH NATURAL MATERIALS AS ADSORBENT

Esin ATEŞÇİ
MASTER OF SCIENCE

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Submitted by **Esin ATEŞÇİ** in partial fulfillment of the requirements for the degree of **Master of Science in Department of Nanotechnology and Engineering Science, Adana Alparslan Türkeş Science and Technology University** by,

Assoc. Prof. Dr. Ahmet BEYCİOĞLU
Graduate School Director

Asst. Prof. Dr. H. İmge OKTAY BAŞEĞMEZ
Department Chair

Prof. Dr. Osman SİVRİKAYA
Supervisor

Thesis Committee

Prof. Dr. Osman SİVRİKAYA
Adana Alparslan Türkeş Science and Technology University

Assoc. Prof. Dr. Mahmut ALTINER
Çukurova University

Assoc. Prof. Dr. Başak DOĞRU MERT
Adana Alparslan Türkeş Science and Technology University

Thesis Defense Date
02/02/2022

I hereby declare that all information in this thesis has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all information that is not original to this work.

[Signature]

Esin ATEŞÇİ

ABSTRACT

REMOVAL OF SOME HEAVY METALS FROM WASTE WATER WITH NATURAL MATERIALS AS ADSORBENT

Esin ATEŞÇİ
Department of Nanotechnology and Engineering Sciences
Supervisor: Prof. Dr. Osman SİVRİKAYA
February 2022, 95 pages

One of the most important environmental problems is the pollution caused by heavy metals in wastewaters. In this study, the removal of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions from synthetically prepared solution was investigated with using coconut shell, olive stone, walnut shell, and their carbonized products as adsorbent. For this purpose, the effect of adsorbent type, contact time, adsorbent dose, and initial metal ion concentration were selected as independent variables while the heavy metal removal percentages, namely Zn^{+2}, Cd^{+2}, and Pb^{+2} removals, were selected as dependent variables in the heavy metal adsorption experiments. The microstructure properties of the tested adsorbents were examined using a Scanning Electron Microscope (SEM). It was found that carbonized products had more porous structure than their untreated forms. In adsorption experiments, temperature was kept constant 25 ±2 °C and pH was kept between 5.0 and 6.0. Adsorption experiments were carried out applying the batch system. Concentrations of heavy metals in synthetically prepared solution were determined by using Atomic Absorption Spectrometer analyzing technic. As a result of the experimental studies, the maximum contact time was determined as 180 min, the maximum adsorbent dose was determined as 2% adsorbent amount (g)/solution volume (mL), and the maximum metal removal was provided at lower initial ion concentration (50 ppm). It was observed that the removal percentage of heavy metal performances of carbonized products was found to be better than their untreated forms. Among the tested adsorbents, it was determined that the best adsorbent was the olive stone carbonized product for the adsorption of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions because it had the more porous structure.

Keywords: **heavy metal, wastewater, adsorption, adsorbent, coconut shell, olive stone, walnut shell**

ÖZET

ATIK SULARDAN ADSORBAN OLARAK DOĞAL MATERYALLER İLE BAZI AĞIR METALLERİN GİDERİLMESİ

Esin ATEŞÇİ
Nanoteknoloji ve Mühendislik Bilimleri Anabilim Dalı
Danışman: Prof. Dr. Osman SİVRİKAYA
Şubat 2022, 95 sayfa

En önemli çevre sorunlarından biri atık sulardaki ağır metallerin neden olduğu kirliliktir. Bu çalışmada, adsorban olarak hindistan cevizi kabuğu, zeytin çekirdeği, ceviz kabuğu ve bunların karbonize ürünleri kullanılarak sentetik olarak hazırlanmış çözeltiden Zn^{+2}, Cd^{+2} ve Pb^{+2} iyonlarının giderimi araştırılmıştır. Bu amaçla adsorban tipi, temas süresi, adsorban dozu ve başlangıç metal iyon konsantrasyonunun etkisi bağımsız değişkenler, ağır metal giderim yüzdeleri, yani Zn^{+2}, Cd^{+2} ve Pb^{+2} giderimleri bağımlı değişkenler olarak seçilmiştir. Test edilen adsorbanların mikro yapı özellikleri, bir Taramalı Elektron Mikroskobu (SEM) kullanılarak değerlendirilmiştir. Karbonize ürünlerin işlem görmemiş hallerine göre daha gözenekli yapıya sahip oldukları tespit edilmiştir. Ağır metal adsorpsiyon deneyleri sıcaklık 25±2 °C'de sabit ve pH 5.0 ve 6.0 arasında tutularak kesikli sistem uygulanarak gerçekleştirilmiştir. Sentetik olarak hazırlanan çözeltideki ağır metal konsantrasyonları Atomik Absorpsiyon Spektrometre analiz tekniği ile ölçülmüştür. Deneysel çalışmalar sonucunda maksimum temas süresi 180 dakika, maksimum adsorban dozu %2 adsorban miktarı (g)/çözelti hacmi (mL) olarak belirlenmiş ve daha düşük başlangıç iyon konsantrasyonunda (50 ppm) maksimum metal giderimi sağlanmıştır. Karbonize ürünlerin ağır metal giderim yüzde performanslarının işlenmemiş hallerine göre daha iyi olduğu görülmüştür. Test edilen adsorbanlar arasında Zn^{+2}, Cd^{+2} ve Pb^{+2} iyonlarının adsorpsiyonu için en iyi performans gösteren adsorban daha gözenekli yapıya sahip olması nedeniyle zeytin çekirdeği karbonize ürünü olduğu belirlenmiştir.

Anahtar Kelimeler: ağır metal, atık su, adsorpsiyon, adsorban, hindistan cevizi kabuğu, zeytin çekirdeği, ceviz kabuğu

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

AAS	**:** Atomic Absorption Spectrometer
g	**:** Grams
MCL	**:** The Maximum Contaminated Level
mg	**:** Milligram
mg/L	**:** Milligrams per Liter
min	**:** Minute
mL	**:** Milliliter
mm	**:** Millimeter
nm	**:** Nanometer
ppm	**:** Parts Per Million
USEPA	**:** United State Environmental Protection Agency
µg	**:** Microgram
µm	**:** Micrometer
%	**:** Percent
°C	**:** Degree Celsius

1. INTRODUCTION

The extraction of valuable minerals or other geological materials from the earth's crust is defined as 'Mining'. Mining operation provides essential raw materials for other industries such as mechanical, civil, material, plastic industry to produce goods, devices, equipment for an industrialized society. However, these procedures may cause some pollution to the surrounding area such as air, soil, flora, fauna, and specifically water at the ground or underground level during mineral extraction and processing due to some potential heavy metals. As well as mining operations, some other application like metal production, tannery industry, chloral-alkali fabrication and radiator production, iron-steel smelting and alloying industries, battery manufacturing and storage of some wastes and by products may generate heavy metal pollution (Kadirvelu et al., 2001).

The heavy metal term is used the any metallic element with fairly higher density and at even its low concentrations may be dangerous because of toxic and sometimes poisonous characteristic (Pugazhenthiran et al., 2016). Mercury (Hg), arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), and zinc (Zn) can be given as examples for heavy metals. Those heavy metals are found in the environment; however their concentration is too low. Therefore, they are not dangerous for living organisms. The concentration of these metals is important for a healthy environment, living microorganisms and humans. These elements cannot be decomposed when they enter the bodies of living creature through foods or underground or ground water, air, and accumulate in the body (Raval et al., 2016). The accumulation of any kind of the heavy metal in living creature over time is dangerous and may potentially cause health risk. Besides the increasing concentration of heavy metals in the environment may be dangerous for the organisms living around (Ali et al., 2019). Hence, the level of heavy metal must be under the permissible limits according to the environmental regulations by the government. The maximum contaminated level (MCL) standards, founded by United State Environmental Protection Agency (USEPA), include the limit of heavy metal concentration in potable water. For instance, according to those standards some of the heavy metal MCL's are 0.01 mg/L for As, 0.005 mg/L for Cd, 5 mg/L for Zn, and 0.015 mg/L for Pb (Ahmaruzzaman, 2011).

Water is very important for all living creature that is flora and fauna in terms of their survival activities and is used in all areas (*Water*, n.d.). Natural underground and ground waters are not including much heavy metal naturally in many part of the world. Some ground water sources, such as lakes, may contain heavy metals contaminated water, however this is uncommon. Human activities such as mining may a potential effect to contaminate the underground and ground waters in terms of heavy metals. Contaminated form of water with heavy metals is also called "wastewater". Wastewaters may contain not only heavy metals but also dissolved substances, dyes, nutrients and microorganisms (Warwick et al., 2013). The contaminated waters should not be allowed to pass to ground and underground waters.

When the quantity of heavy metals in water exceeds a certain level, it can be hazardous to living organisms and life. For this reason, the heavy metal in the water must be determined and if their concentration is higher than the permissible limits they have to be removed. The process in which the wastewater is tried to be purified in terms of pollutant or heavy metals is called "wastewater treatment".

There are various processes for eliminating heavy metal from wastewater such as chemical precipitation, coagulation, solvent extraction, ultrafiltration, biological systems, membrane filtration, ion exchange, reverse osmosis and adsorption (Osmanlioglu, 2018; Wanyonyi et al., 2019; J. Zhang et al., 2020; Kabuba & Banza, 2020; Lopes et al., 2020; Reyes-Serrano et al., 2020; Alalam et al., 2021; Badawi & Zaher, 2021; H. Zhang et al., 2021; Sayegh et al., 2021; Qi et al., 2021; Zhai et al., 2021). Adsorption is the most effective and applied method among all these techniques since its easy and low cost in operation, simple design, fast-reactive in nature and effective at even lower concentrations (Jain et al., 2016). In wastewater treatment, the adsorption method has a wide range of applications not only for the purification of heavy metals but also for the purification of different types of pollutants (Pathak et al., 2015). For this purpose, the activated carbon and carbon based materials are used.

Activated carbon is a processed form of carbon mainly produced from woody substances, with a random or amorphous highly porous structure with a variety of pore sizes. The pores

can be visible cracks which are macro cracks and invisible cracks which are micro cracks in molecular dimensions (Raval et al., 2016). They are used as adsorbent materials in many applications because of their permeable and porous structure and large specific surface area.

Figure 1 shows one of the dramatization of activated carbon that can be applied as an adsorbent in wastewater treatment.

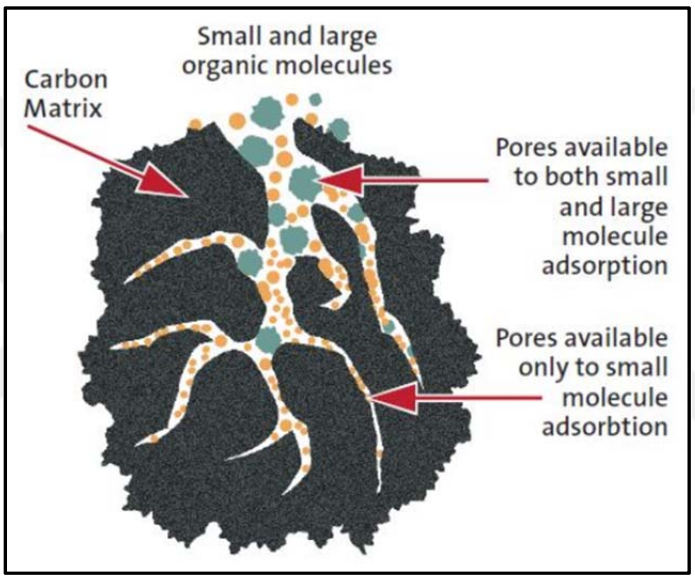

Figure 1. An activated carbon used for the wastewater treatment application as adsorbent.

The mostly used activated carbon as adsorbent in industrial applications is produced from coconut shell; however, the increasing demand for coconut shell activated carbon cause to increase the price and sometimes the supply cannot be enough for industry. Therefore, several researches have been studied in the literature to consider alternative activated carbons made from abundant and less expensive sources. For instance, some natural organic-origin material such as plant and vegetable shells (potatoes, orange, hazelnut shell), fruit seeds/stones (olive, peach, apricot) can be used as an alternative to coconut shell activated carbon because of their porous structure (Babel & Kurniawan, 2004; Kobya et al., 2005; Al-Qahtani, 2015). However, their porous structures can be enhanced by a thermal treatment that is activation process or carbonization. Furthermore, the activation operation can be done using some chemical liquids, for example, acids. Hence, those

materials can be either used directly after particle sizing or after an activation process for heavy metal adsorption from wastewater. Some of the photos for alternative sources can be used as an alternative adsorbent to coconut shell is given in Figure 2.

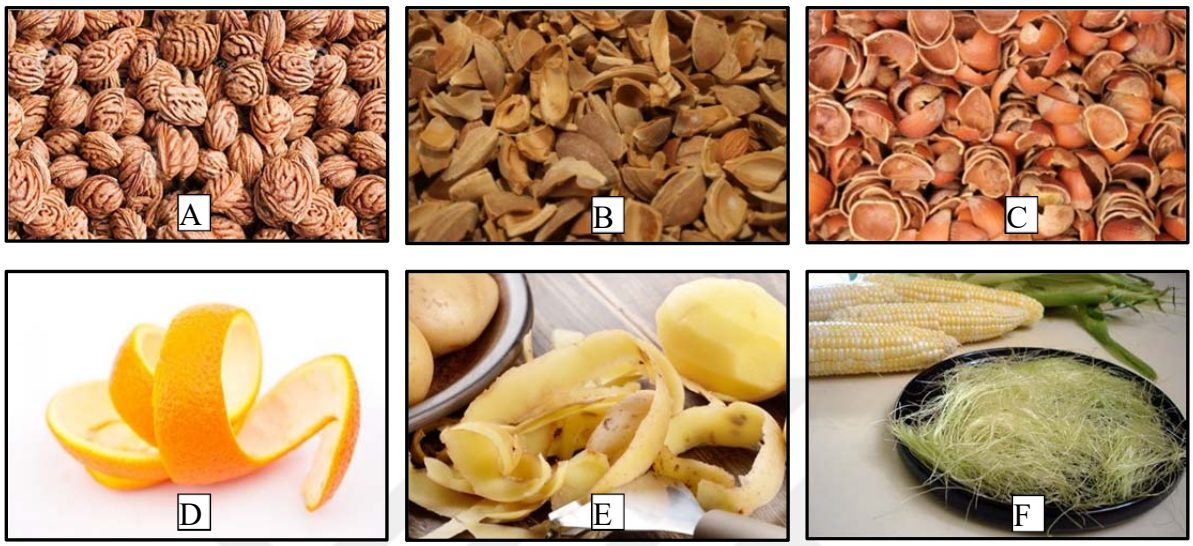

Figure 2. Some of the photos for alternative organic-origin material sources can be used as alternative adsorbent to coconut shell. A) Peach stone B) Apricot stone C) Hazelnut shell D) Orange peel E) Potatoes shell F) Corn silk

The adsorption process is affected by a few factors in the applications, such as medium pH, ambiance temperature, application contact time, applied adsorbent dose, and heavy metal abundance. The mentioned factors are responsible for binding and adsorption of metal ions in liquid solutions or mediums (Ahmaruzzaman, 2011; Jain et al., 2016).

1.1 Pollution

Environment refers to the biological, physical, economic, social, and cultural environment in which living creature maintain their relationships and interact with each other (Stratejik Çevresel Değerlendirme Yönetmeliği, 2017). Human activities such as industrial productions, and natural conditions may change the natural structure of the environment and the negative effects of living creature to environment can be called environmental pollution (Fırat, 2007; *Çevre Kirliliği*, n.d.).

1.2 Water Pollution

Water is a tasteless and odourless substance required for all known life forms. However, with the increase in industrialization, urbanization, population growth, unconscious use of pesticides and chemical fertilizers and the discharge of substances or energy directly or

indirectly to the water environment, the water we need is polluted (*Çevre Kirliliği*, n.d.). In other words, water pollution can also be defined as adversely affecting of the water source in terms of physical and chemical properties. Furthermore, bacteriological, radioactive, and ecological characteristics of water may be changed when water pollution happen in any water source (Su Kirliliği Yönetmeliği, 2004).

1.3 Heavy Metals

Heavy metal definition is used for elements with higher atomic weights. That is elements with greater than 63.5 and with lower than 200.6 g per mol are called as heavy metal. In addition, their densities are characterized greater than 5.0 g / cm^3 in terms of physical properties. This group includes more than sixty elements, including Pb, Cr, Zn, Cd, As, Cu, Ni, and Hg (Fu & Wang, 2011; İnce & Kaplan İnce, 2017; Seven et al., 2018). These elements are generally present in the form of carbonate, oxide, silicate and sulphur, or trapped in silicates on the earth (Bakar & Baba, 2009).

Erosion, volcanic activities at the seabed, terrestrial volcanic activities, forest fires, burning of fossil fuels such as coal and petroleum, including industry-wastes or by-products may cause the heavy metal pollution. On the other hand, the use of fertilizer and pesticides; minerals and chemicals production, smelting and metal coating processes; accumulator production; personal or industrial engine exhaust gases; fly ash from coal combustion in thermal power plants, and the rapid population increase brought about environmental and water pollution. The industrial sources of some heavy metal ions are listed in Table 1. (Salman et al., 2014). The fact that water is used in every field and indispensable for life has shown the importance of the protection of water resources (Peters & Shem, n.d.; Murathan & Koçyiğit, 2014).

Table 1. Industrial source of heavy metals (Salman et al., 2014)

Heavy Metals	Major Source
Lead	Mining, paint, pigments, electroplating, manufacturing of batteries, burning of coal
Copper	Plating, copper polishing, paint, printing operations
Cadmium	Plastic, welding, pesticide, fertilizer, mining, refining
Zinc	Mining, refineries, brass manufacturing, plumping
Mercury	Batteries, paper industry, paint industries, mining
Nickel	Porcelain enamelling, non-ferrous metal, paint formulation, electroplating
Arsenic	Smelting, mining, rock sedimentation, pesticides
Chromium	Textile, dyeing, paints and pigments, steel fabrication

Heavy metals are found as natural compounds in the earth's crust. They are not bio-degradable unlike organic components. Most of these heavy metals given in the table are toxic at high concentrations since they have accumulation ability in the bodies of organisms (Salman et al., 2014).

The metals which damage the body of living creature when they enter it are called "toxic metals". Toxicity varies in terms of metal types, living creature types, and the concentration value (Fırat, 2007), and the toxicity effects of some heavy metal ions are listed in Table 2 (Salman et al., 2014).

Table 2. Toxicity effects of heavy metals (Salman et al., 2014)

Heavy Metals	Toxicity Effects
Lead	Anaemia, brain damage, anorexia, malaise, loss of appetite, liver, kidney, gastrointestinal damage, mental retardation in children
Copper	Neurotoxicity, and acute toxicity, dizziness, diarrhoea
Cadmium	Kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer, lung insufficiency, hypertension, Itai–Itai disease, weight loss
Zinc	Causes short term 'metal-fume fever', gastrointestinal distress
Mercury	Damage to nervous system, protoplasm poisoning, corrosive to skin, eyes, muscles, dermatitis, kidney damage
Nickel	Chronic bronchitis, reduced lung function, lung cancer
Arsenic	Bronchitis, dermatitis, bone marrow depression, hemolysis, hepatomegaly
Chromium	Carcinogenic, mutagenic, teratogenicity, epigastria pain nausea, vomiting, severe diarrhoea, producing lung tumors

1.3.1 Conventional Treatment Processes for Heavy Metals

As it is known, the mining industry is responsible for an important part of the heavy metal pollution in water when the necessary precautions are not taken. The presence of metals in the structure of rocks, ore, and minerals in the earth crust and the wastes generated by the processes during the recovery of metals from ores becomes a source of pollution. At the same time, these heavy metals cannot be disintegrated and heavy metals bio-accumulate in living creature, thus they must be removed from the wastewater.

There are various processes for eliminating heavy metals from wastewater such as chemical precipitation, coagulation, solvent extraction, ultrafiltration, biological systems, membrane filtration, ion exchange, reverse osmosis, and adsorption (Ahluwalia & Goyal, 2007; Das et al., 2008; Lin et al., 2008; Ahmaruzzaman, 2011; Dhir, 2014; Gunatilake, 2015).

1.3.2 Chemical Precipitation

This process enhances the removal of heavy metal in specific system conditions. Insoluble precipitation includes heavy metal hydroxide, phosphate, carbonate, or sulphide, and then filtration or sedimentation processes are applied to precipitate the solids and therefore they can be separated from the water (Fu & Wang, 2011; Gunatilake, 2015). Figure 3 shows that how chemical precipitation applying in a laboratory and specifically Pb^{+2} ion in the solution is precipitated with the addition of sulphate $(SO_4)^{2-}$ ions as solid lead sulphate ($PbSO_4$). The formed $PbSO_4$ can be filtered from the system.

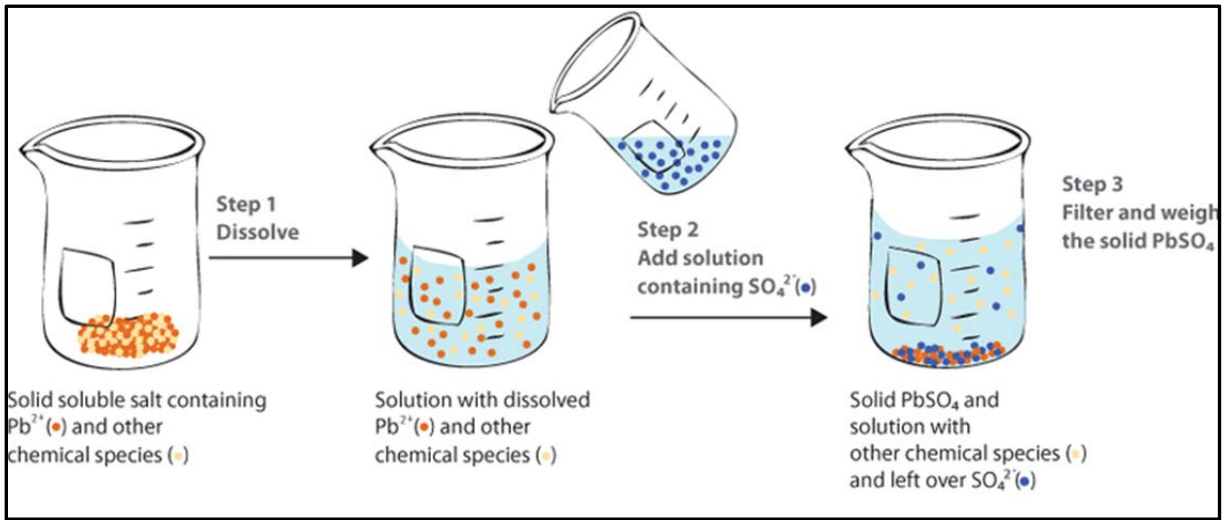

Figure 3. Chemical precipitation process (*Chemical Precipitation*, n.d.)

1.3.3 Coagulation and Flocculation

Colloidal solution including particle size ranging from 2 to 500 nm is a heterogeneous mixture. Figure 4 shows particle size of different colloidal solutions.

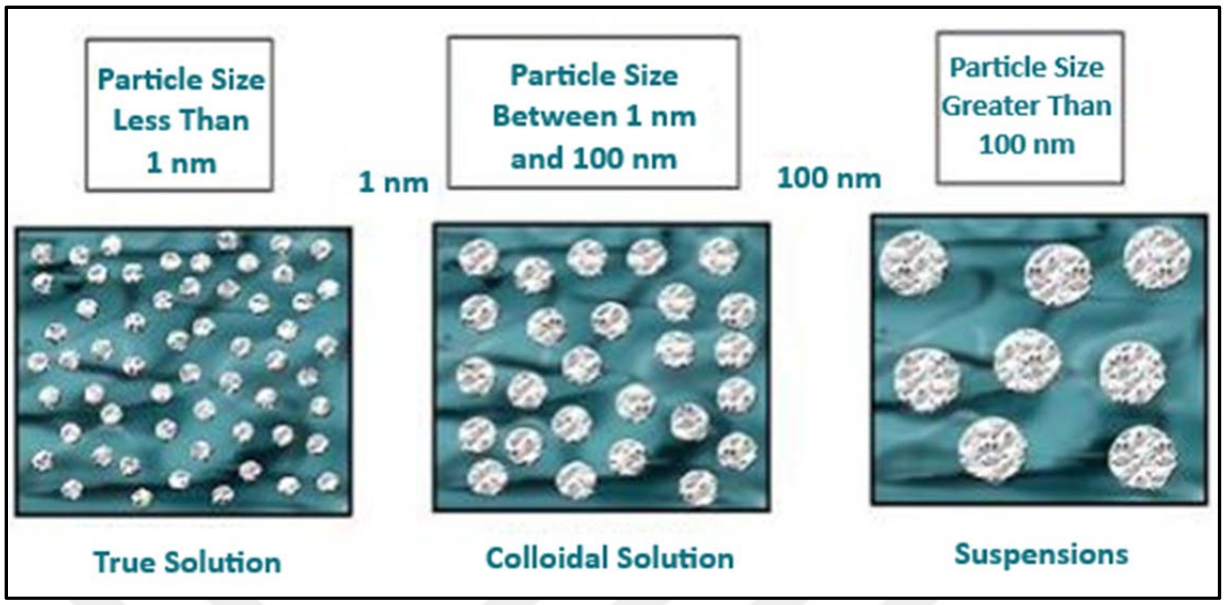

Figure 4. Particle size of colloidal solution (*Particle Size of Colloidal Solution*, n.d.)

Coagulation and flocculation can be applied based on physical and electrostatic interaction between colloidal particles. Coagulants-flocculants are used to achieve the produce large size agglomerates in the impurity including wastewaters. The coagulants contribute to the ultra-fine materials in solution to agglomerate together into large particles called flocs or agglomerates, as shown Figure 5.

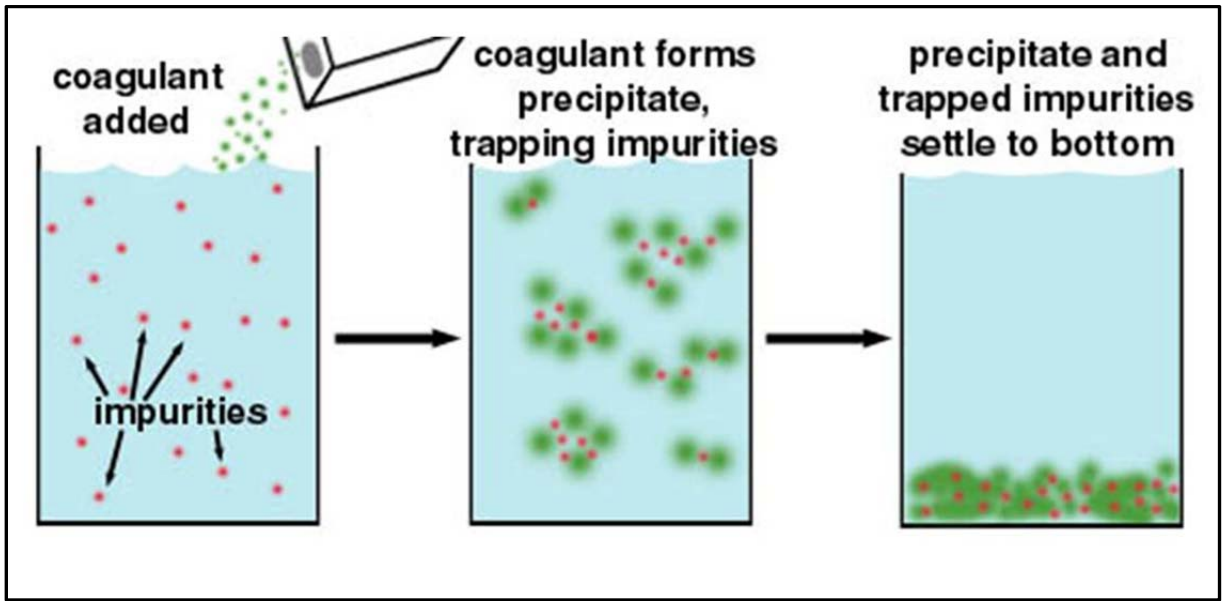

Figure 5. Coagulation stage of colloidal materials/impurities in wastewater (Casiday et al., 1999)

Flocculation is a process of increasing the size of particles by slow mixing and addition of flocculants mostly synthetic large molecular weight polymers. Figure 6 shows coagulation and flocculation processes. The most commonly used coagulants are aluminium and iron salts. These are aluminium sulphate, sodium aluminate, iron(3)chloride, iron(3)sulphate, and iron(2)sulphate.

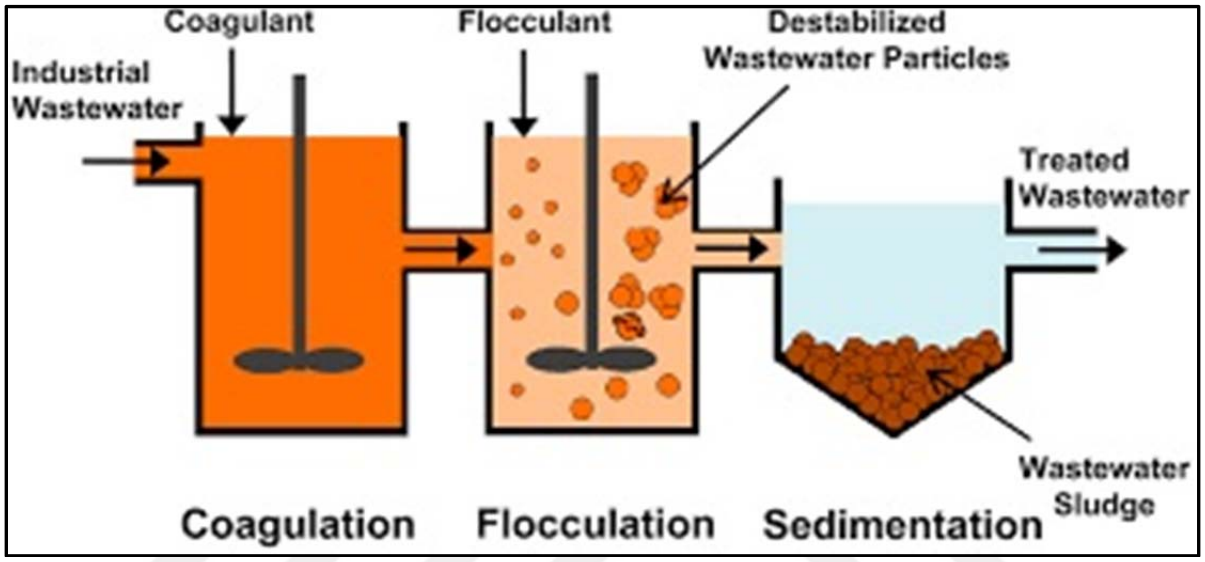

Figure 6. Coagulation and flocculation process (*Coagulation and Flocculation Process*, n.d.)

1.3.4 Ultrafiltration

Ultrafiltration is a separation process that includes using of membranes for eliminating suspended solids, impurities, heavy metals and macromolecules. The primary removal mechanism is the size separation; It is shown in Figure 7 that the pore size of ultrafiltration membranes is between 100 nm and 10 nm. Although the pore size of the membranes is prominent, the surface chemistry and electrical properties of particles or characteristic of the membrane may affect the clarification/removal performance (Fu & Wang, 2011; Gunatilake, 2015).

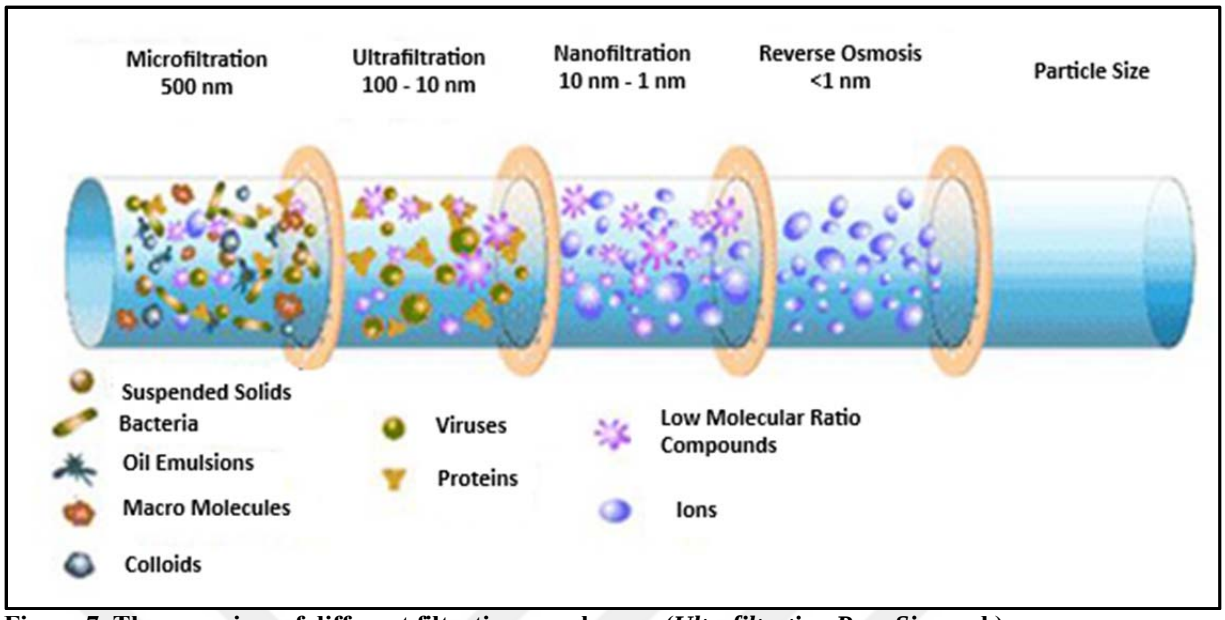

Figure 7. The pore sizes of different filtration membranes (*Ultrafiltration Pore Size*, n.d.)

1.3.5 Reverse Osmosis

Reverse osmosis is a separation process using pressure to force a solution through a membrane that retains the solute on one side and allows the pure solvent to pass to the other side, as shown in Figure 8. The membrane here is semipermeable, meaning it allows the passage of solvent but not for the metals (Fu & Wang, 2011; Gunatilake, 2015).

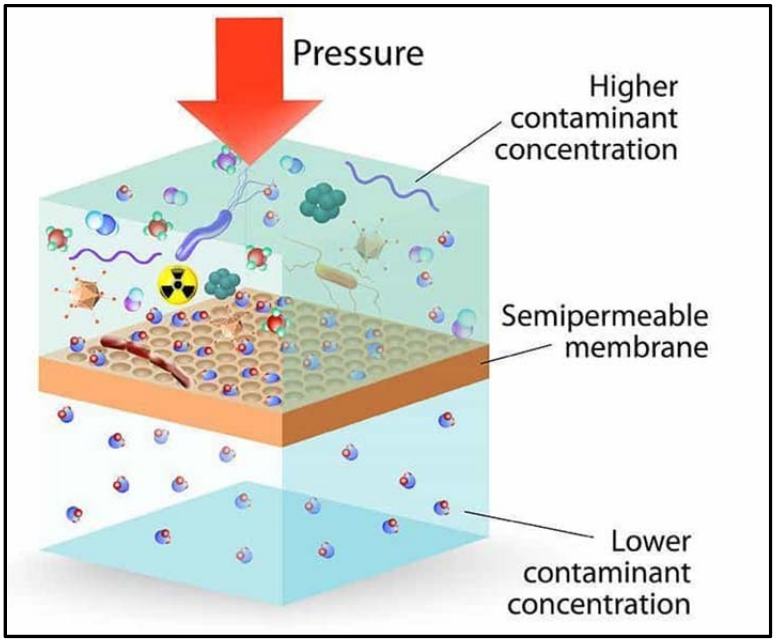

Figure 8. Reverse osmosis process (*Reverse Osmosis*, n.d.)

1.3.6 Ion-Exchange

Schematic diagram of the process given in Figure 9 is the most common applied method for water treatment industry. For removal of metal ions in the solution, cation or anion ion exchangers; commonly synthetic organic ion exchange resin is used. Ion exchange resins are water-insoluble solid substances which can absorb positively or negatively charged ions from an electrolyte solution and release other ions with the same charges into the solution in an equivalent amount (Fu & Wang, 2011; Gunatilake, 2015).

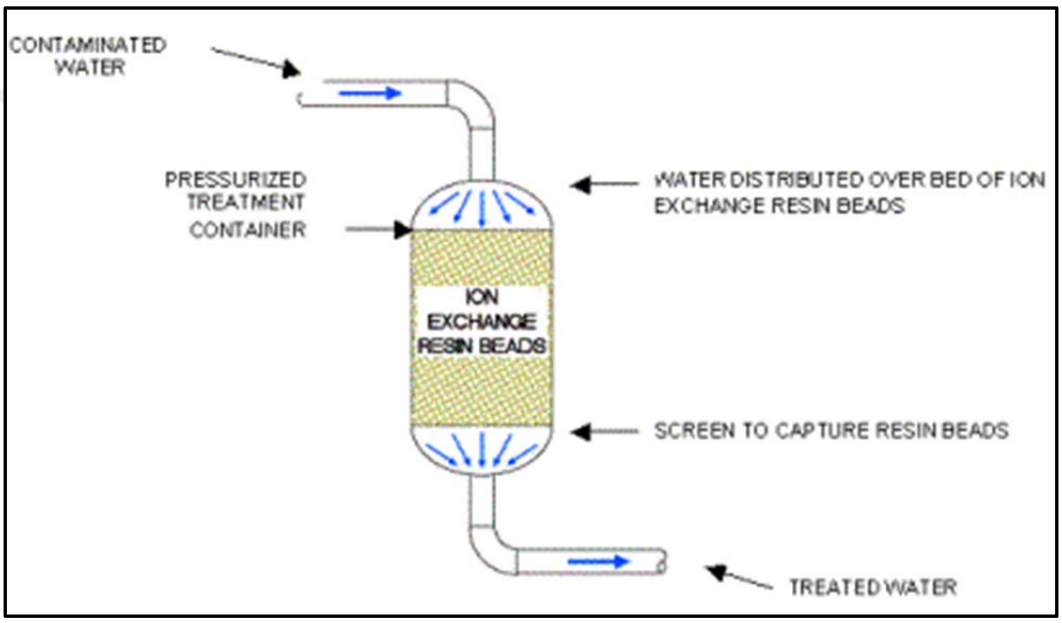

Figure 9. Ion-exchange process (*Ion-Exchange Process*, n.d.)

1.3.7 Electro-dialysis

Electro-dialysis (Figure 10) is an electro-chemical, membrane separation process in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics (Fu & Wang, 2011; Gunatilake, 2015).

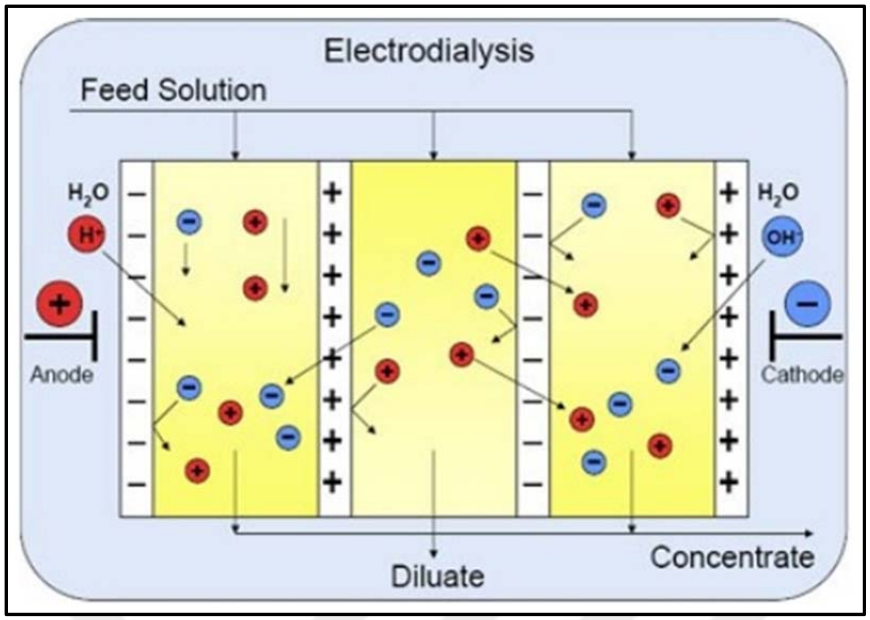

Figure 10. Electro-dialysis process (*Electro-Dialysis Process*, n.d.)

These methods are not sufficiently effective at low concentrations and can be very expensive due to the high chemical reagent and energy requirements as well as the disposal problem of toxic secondary sludge (Abdolali et al., 2016). As a result, certain alternative low-cost, simple, and efficient methods are being researched and implemented in industry. Adsorption is one of these strategies. The following sections provide more information on adsorption.

1.4 Adsorption

The adhesion of dissolved substance to a solid surface in any medium by physical, chemical or ionic forces is called 'adsorption' (İpek, 2014). Adsorption may be defined, is a mass transfer process involving the accumulation of substances at the interface of two phases, such as the liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent (De Gisi et al., 2016). In Figure 11, an adsorption phenomenon of heavy metal (in the form of liquid solution) by clay particle (in the form of solid) is shown (González et al., 2017; Mo et al., 2018).

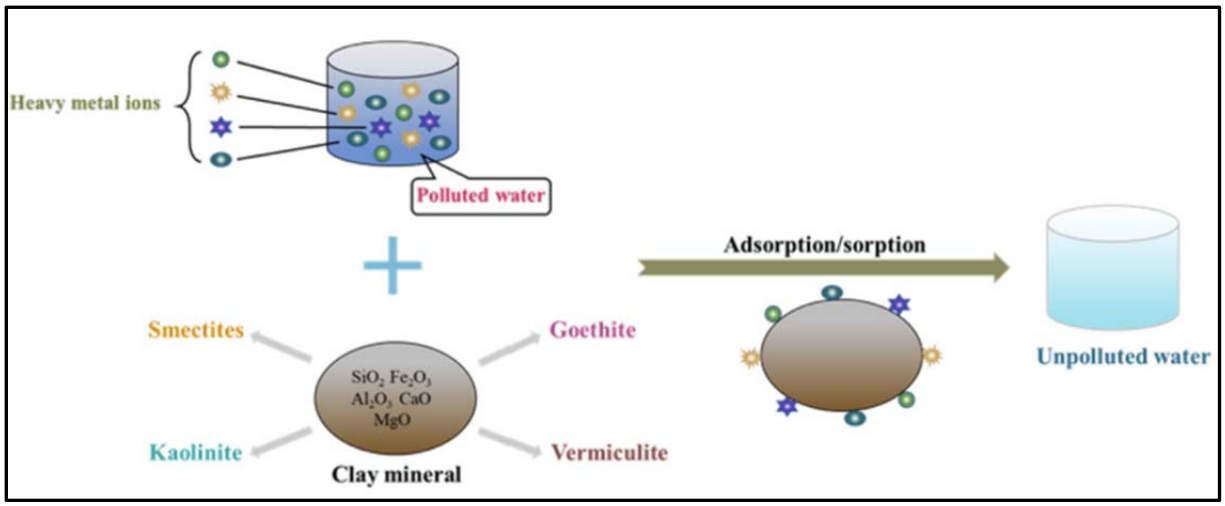

Figure 11. Adsorption process of heavy metals by clay (Mo et al., 2018)

Adsorption is the most preferred over other methods because of its easiness to operation, low-cost and simple design working flexibility, effectiveness, efficiency reuse of adsorbents after process and high quality purified product (Raval et al., 2016; İnce & Kaplan İnce, 2017; Kaur & Sharma, 2017; Mo et al., 2018). Adsorption occurs in a variety of ways, based on the attractive forces between the adsorbent and the adsorbate substance.

1.4.1 Adsorption Types

1.4.1.1 Physical Adsorption

It is the weak Van der Waals forces that provide surface adhesion in physical adsorption. This type of adsorption is affected by the attraction forces between the solid surface and the adsorbent molecules. It does not enter the crystal lattice of the adsorbent layer and is insoluble but completely covers the surface. The layer adsorbed on a smooth surface is no more than a few molecular thicknesses. However, since the capillary condensation event occurs in addition to this surface adsorption in the capillaries of a porous solid, the total amount adsorbed increases significantly compared to flat surfaces. It is a multi-layered and easy to regenerate adsorption type that can occur in the low temperature range. Desorption is achieved by increasing the temperature or lowering the pressure. Due to its reversible character, the adsorbents used in any application can be used again applying the de-sorption process (Fırat, 2007). This property of the technique makes it economic.

1.4.1.2 Chemical Adsorption

Chemical adsorption is the adsorption type which is formed by the chemical affinity of the adsorbed ions and the adsorbent materials. In this type adsorption, functional groups of both materials are responsible in adsorption. The particles bound to the surface generally form a covalent bond. Chemical adsorption is irreversible, monolayer and usually occurs in the high temperature range, and regeneration is also very difficult. The heat released during the adsorption is greater than the reaction temperature and the activation energy is also high (Fırat, 2007; Dönmez, 2006).

1.4.1.3 Ionic Adsorption

The electrical attraction between the adsorbent surface and the adsorbed material can be defined as ionic adsorption. Here, the adsorbent having opposite electric charges and the adsorbent surface are attracted to each other. Ions with high electrical charge and ions with small diameters are better adsorbed.

No definitive distinction can be made between physical, chemical and ionic adsorption, these three adsorption types can be seen simultaneously or consecutively (Fırat, 2007).

1.4.1.4 Biological Adsorption

The ability of some kinds of inactivated or dead biomasses for binding and accumulation that is concentration of heavy metals in the aqueous medium can be defined as bio-sorption. In addition bio-sorption can be carried out even at low concentration. Biomass demonstrates this property by acting as an ion exchanger of biological origin. It has been found that the main structure responsible for this process is the cell wall of some algae, fungi, bacteria and other biomasses (Fırat, 2007).

1.4.2 Factors Affecting Adsorption

Adsorption process is influenced with application variables like surface properties; physical and chemical, of the adsorbent and adsorbate materials.

Adsorption is affected by the physicochemical and surface properties of the adsorbent, like elemental composition, porosity, particle density, bulk density, surface and medium pH, specific surface area, functional groups present on the surface, and thermal properties.

Factors like electrical charges on adsorbate, size of moiety, functional groups, solubility, hydrophobicity/hydrophilicity, reactivity, relative affinity between the solution and the adsorbent, thermodynamics of the solution, and in case of organic pollutants, dissociation constant also affects the adsorption (Pathak et al., 2015).

1.4.2.1 Effect of Solution pH

pH is assessed to be the most important parameter in the adsorption process. It affects the solution chemistry, functional group activity on the adsorbent surface, and the composition of the adsorbate. As the pH varies from acidic to basic, it enhances adsorptive removal of cationic metals (Pathak et al., 2015).

1.4.2.2 Effect of Contact Time

Contact time of any adsorption process is the necessary time to reach the equilibrium of the system. This solid/liquid heterogeneous system is often subjected to different mass transfer steps. Therefore, it is necessary to determine the contact time to ensure equilibrium is (Pathak et al., 2015).

1.4.2.3 Effect of Temperature

It is well known that the temperature affects the reactions. In adsorption studies, when the temperature increases the mobility of the ions increases as well and as a result adsorption rate increased. On the other hand, viscosity of liquid medium is reduced. In researches, the thermodynamic parameters; enthalpy, entropy and free energy, are studied to evaluate the effects of the temperature on the efficiency of the adsorption experiments (Pathak et al., 2015).

1.4.2.4 Effect of Initial Ion Concentration

Another factor is the initial ion concentration of adsorbate which is an important factor necessary to achieve the mass transfer resistance between the adsorbate and the adsorbent materials. Higher initial concentrations provide higher loading (Pathak et al., 2015).

1.4.2.5 Effect of Adsorbent Dose

The dose of adsorbent determines the extent of surface binding sites available for adsorption. Therefore, the percentage removal of adsorbate increases with adsorbent dosage. Once the equilibrium is reached, no further change in the percentage of adsorbate removal occurs. This shows at a given concentration that when the optimum solid/liquid

ratio is used, the amount of adsorbent is sufficient for the maximum removal of adsorbate ions from the solution. Even if more adsorbent is used, it does not affect removal (Pathak et al., 2015).

1.4.2.6 Effect of Adsorbent Specific Surface Area

Specific surface area is a significant property of solid materials, and it always increases when particle size of adsorbent material becomes finer. Also porous and permeable-porous structure adsorbent materials have higher specific surface area. If specific surface area is great then it provides greater binding possibility between adsorbent and adsorbate. Small particle size lowers the mass transfer driving force per unit area of adsorbent particles, which increases the uptake/saturation capacity per unit mass of adsorbent (Pathak et al., 2015).

1.5 Adsorbents Types for Heavy Metal Adsorption

Activated carbon is the raw form of carbon-based organic materials with a random or amorphous structure. It has highly porous structure. The pores can be micro or macro cracks depending on the activated carbon source. Activated carbons are mainly used as adsorbents in different industrial applications. It can be used in water or air filtration system. One of the application areas is the elimination of heavy metal pollutants from water sources. Because of its expanded specific surface area is reasonable for great adsorption capacity. It is mostly used since production easiness from organic substances and renewable sources, reuse capacity, micro porous form and good surface reactivity (Raval et al., 2016).

One of the most widely used adsorbents in wastewater treatment containing heavy metal ions is commercially active carbon. But it is expensive; the fact that they are exhausted after their use. Consequently, the cost of reusing the procedure is an additional expense (Raval et al., 2016).

In recent years, natural or synthetic, living or non-living, cheaper, more effective, reusable new adsorbent materials have been investigated and tried to be used as adsorbent to eliminate these causes.

1.5.1 Natural Materials

1.5.1.1 Chitosan

Chitin is a natural inorganic raw material in production of chitosan which is a bio-sorbents. Chitin is the source of chitosan and chitosan is used mostly after than cellulose in application of adsorption. Molecular structure of chitosan is more important than chitin and takes role in the adsorption mechanism. Chitin is mainly found in the body shellfish exoskeleton and chitosan is obtained through alkali N-deacetylation processing of chitin.

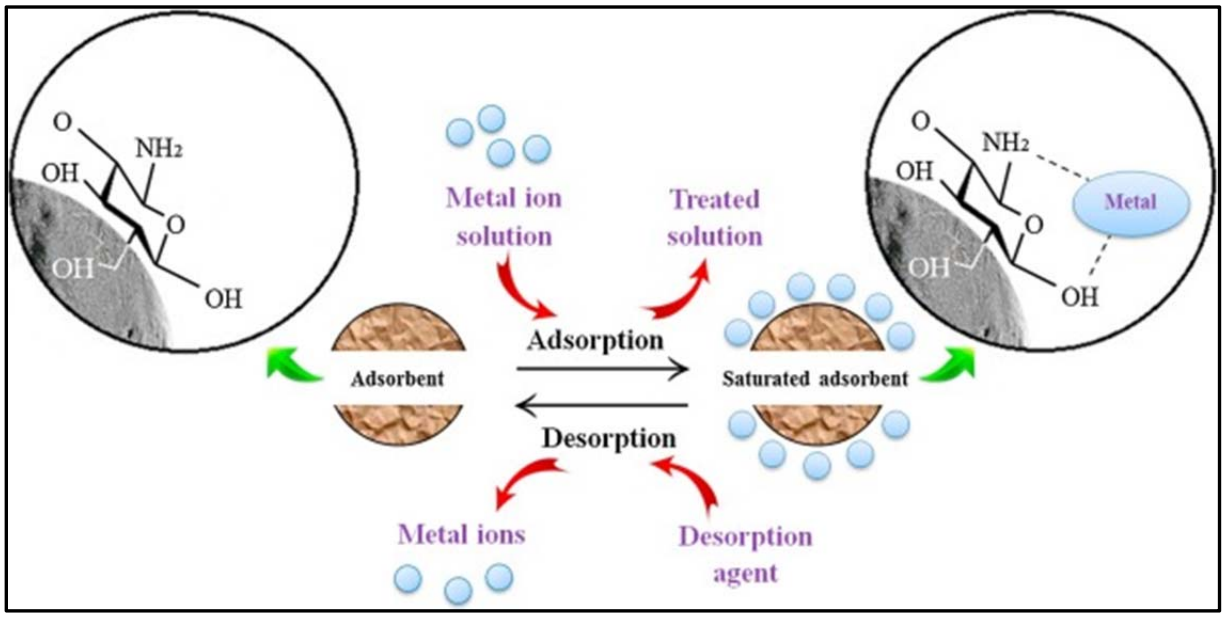

Figure 12. Adsorption mechanism of chitosan (Vakili et al., 2019)

As it is an effective collector and adsorbent for heavy metals due to its low price and abundance, antibacterial property, non-toxicity, biocompatibility, biodegradability, macromolecular structure, hydrophilicity, cationicity, active sites, and high adsorption capacity (Vakili et al., 2019). The increasing need for new low-cost adsorbent sources, the increasing waste disposal problems, the increased cost of synthetic resins make chitosan one of the most attractive materials for wastewater treatment (Babel & Kurniawan, 2003). Figure 12 shows the schematic diagram of chitosan adsorption.

1.5.1.2 Zeolites

Zeolites are natural materials formed in the earth crust in a definite crystalline structure consisting of alumina-silicate by the association of tetrahedral molecules bonded together by common oxygen atoms.

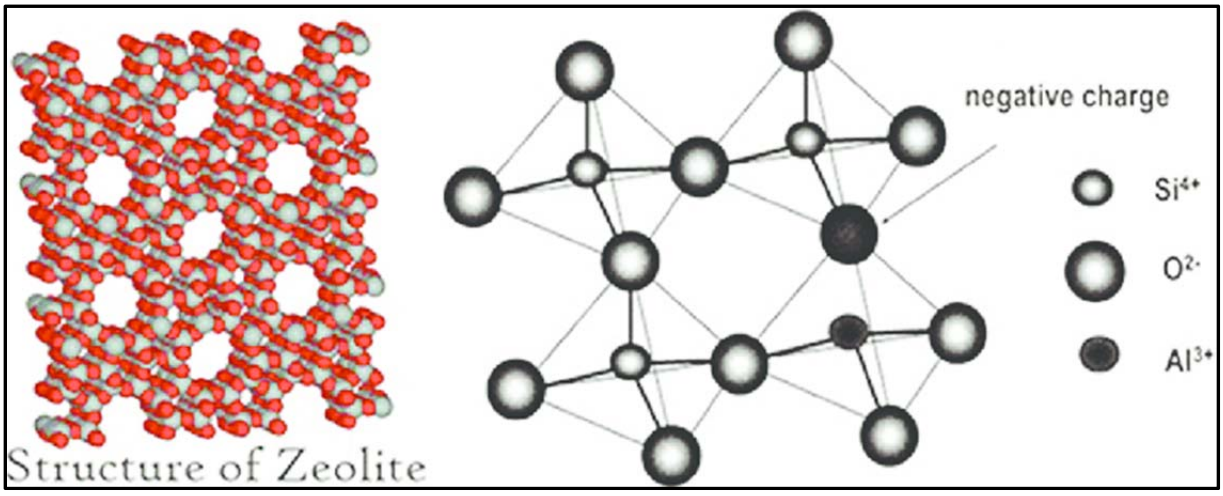

Figure 13. Structure of zeolite (Golomeova & Zendelska, 2016)

Shown in Figure 13 the micro porous structure provides a high specific surface area of the zeolite in which reactions can occur. Therefore, it acts 'molecular sieve'. This feature is used to capture or separate gases in agriculture (e.g. ammonia) and to treat wastewater containing radioactive pollutants or other heavy metals (Golomeova & Zendelska, 2016).

Zeolites consist of a wide variety of species such as clinoptilolite and chabazite. Clinoptilolite is the most abundant in nature and is readily available from more than forty natural zeolite species. Among the most commonly used natural zeolites, clinoptilolite is known with high affinity to some heavy metal ions; Pb^{+2}, Cd^{+2}, Zn^{+2}, and Cu^{+2} (Babel & Kurniawan, 2003).

1.5.1.3 Clay

Due to certain characteristics such as high cation exchange capacity, large specific surface area, chemical and mechanical stability and layered structure, clays have high adsorption capacity for heavy metals. Because of these advantages, and easily accessible and cheap compared to other adsorbents (Kaur & Sharma, 2017) it is used to adsorb various pollutants, particularly heavy metal ions from the aqueous solutions. Montmorillonite behaves as a potential ionic exchanger for heavy metals because of its easy manipulation, high abundance, friendly and safe to the environment between natural clays (İnce & Kaplan İnce, 2017; Babel & Kurniawan, 2003). For this reason, some researches have been carried out montmorillonite type clay and others, to demonstrate the efficiency of the

removal of heavy metal ions such as Hg^{+2}, Cd^{+2}, As^{+3}, Zn^{+2}, Pb^{+2} and Al^{+3} from liquid solutions (Babel & Kurniawan, 2003).

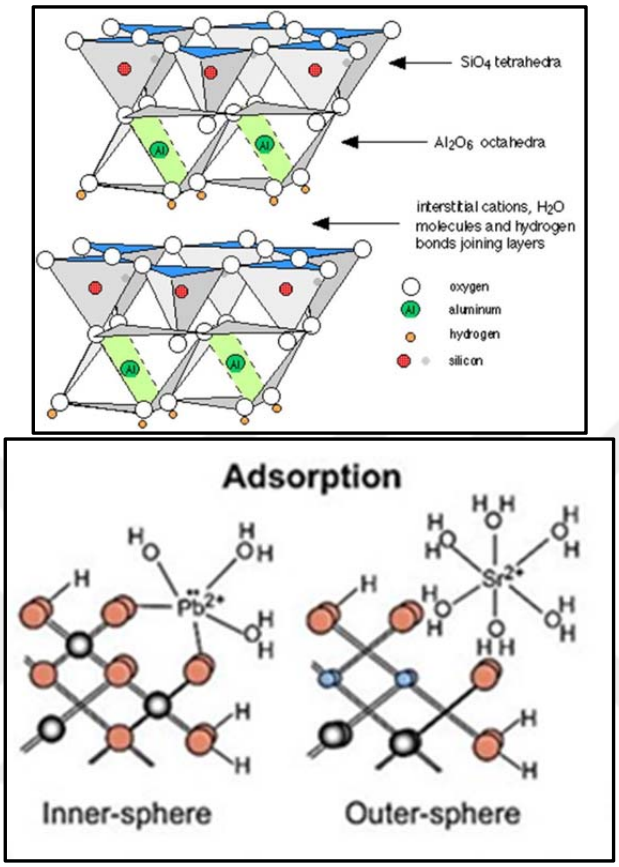

Figure 14. Structure of clay minerals and adsorption of clay minerals (Aboudi Mana et al., 2017)

1.5.1.4 Peat Moss

Peat moss is a complex soil material consisting of lignin and cellulose as main components. It is one of the highly porous natural adsorbents that can be used to adsorb some heavy metals to its structure. Peat moss is abundant and widely available and has a large specific surface area (> $200 m^2/g$). Its low cost, abundant and widespread nature, increases the usability of this natural adsorbent (Kaur & Sharma, 2017; Babel & Kurniawan, 2003).

1.5.1.5 Agricultural Wastes

Agricultural wastes are mainly agricultural and forest biomass, such as straw, bark (Hansen et al., 2010), shells (Babel & Kurniawan, 2004; Hansen et al., 2010; Pino et al., 2006), burrs and crumbs, fruit stones (Bohli et al., 2015; Fiol et al., 2006; Hansen et al., 2010;

Kobya et al., 2005; Milojković et al., 2016; Yakout & Sharaf El-Deen, 2016; Calero et al., 2018) and peels (Pathak et al., 2015), plant wastes. Plant wastes have many advantages including large availability, chemical stability, cheapness, fast renewable cycle, short and easy regeneration cycle, environment friendly and green energy. In addition, their structures have high porosity and large specific surface area, which makes them easier to physically adsorb heavy metal ions such as Ni^{+2}, Cu^{+2}, Hg^{+2}, Cd^{+2}, As^{+3}, Zn^{+2}, Pb^{+2} and Al^{+3}. Agricultural wastes mainly contain cellulose, lignin, and hemi-cellulose in their structures (Mo et al., 2018; Tripathi & Rawat Ranjan, 2015).

1.5.2 Industrial Wastes

1.5.2.1 Fly Ash

Fly ash is a disposal product of coal-burning thermal power plants. Fly ash is considered as an economical alternative to other conventional adsorbent materials such as carbon and resins-based adsorbents because it is easily accessible and inexpensive (S. Wang et al., 2007).

The chemical composition and surface appearance of the fly ash depends on the initial source (coal type), the combustion process and the combustion equipment (furnace type).The main components of fly ash are alumina, silica, ferric oxide and calcium oxide (Ayala et al., 1998). Fly ash is used in wastewater applications due to its suitable chemical composition, low price and good adsorbent capacity (porous structure, sufficient specific surface area and proper particle size distribution) (Visa et al., 2012).

1.5.2.2 Sludge and Slag

Electroplating industry produces a waste material called as sludge which is a dried form of the waste material. It is also obtained from integrated iron and steel industries (De Gisi et al., 2016). It is formed via precipitation process of metal ions in wastewater with calcium hydroxide chemicals. Sludge contains both insoluble metal hydroxides and other salts (Ahmaruzzaman, 2011).

Blast and electric arc furnace slags, which are discarded after metal production in integrated iron and steel plants, are another low-cost waste material that can be employed

as an adsorbent. This product can be used for wastewater treatment in terms of its capacity to adsorb heavy metals (Ahmaruzzaman, 2011).

1.5.2.3 Saw Dust

Sawdust is a by-product from the wood industry. It contains cellulose, lignin and hemicelluloses together with polyphenolic groups. These organic structures in sawdust bind heavy metals to itself and therefore sawdust is used to eliminate the heavy metals from wastewaters (Kaur & Sharma, 2017).

1.5.3 Bio-sorption

Bio-sorption term can be defined as the ability of biological materials, to accumulate heavy metals from wastewater via metabolically mediated or physico-chemical uptake routes (Salman et al., 2014).

Bio-sorbents can be obtained from following sources such as;

1. Non-living biomass like lignin, shrimp, krill, squid, and crab shell.
2. Algae biomass.
3. Microbial biomass like bacteria, fungi, and yeasts (Kaur & Sharma, 2017).

Bio-sorption has been used as an alternative technology for removing heavy metals from wastewaters (Begum et al., 2015).

1.6 Heavy Metal Found in Wastewater and Their Properties

1.6.1 Cadmium

Cadmium is one of the elements in the periodic table with the symbol Cd and atomic number 48. Cd is a shiny, silvery-white, ductile, malleable metal and is soft enough to be cut with a knife. Cadmium and its compounds are highly toxic; Table 2 shows the toxic effects of cadmium.

Cadmium is mostly used in electrolytic coating since it is more resistant to atmospheric, alkali and salt water corrosion than zinc. In addition, various cadmium compounds are used in the production of other cadmium compounds, in photography, galvanoplasty, batteries, cotton dyeing, lithography, to give reddish yellow colour to glass, in porcelain works, in luminescence powders, as antiseptic and pigment (İpek, 2014).

Cadmium can be released from cadmium-using industries; therefore cadmium including industrial processing wastes in both solid and liquid media should be cleaned before storage in stock areas.

1.6.2 Lead

Lead is one of the elements in the periodic table with the symbol Pb and atomic number 82. It is a soft, heavy, toxic and easily malleable metal. It is the one with the highest atomic number among the stable elements. Electrical conductivity is low. Due to its corrosion resistance, it is used for the storage of corrosive liquids (e.g. sulphuric acid).

The main uses of lead are; automotive and machinery manufacturing industry (accumulator and automobile, various machinery and equipment production), construction (coating, lead pipe, installation material, lead wool making), defence industry (as an alloy for the production of bullets and various weapons and equipment), packaging industry (in the production of package seal lead, various packaging materials), printing (in the production of printing letters and mold making), chemical industry (lead oxide, lead chromate, basic chromate, superstructure, powder lead grease, lead borosilicate production), other (acid-resistant in-house coatings, anti-vibration blocks, X-ray protection devices, as solder, as anode, for hunting scattering).

Lead is a highly toxic metal that enters biological systems by mixing air, water and soil, breathing and nutrients and shows the toxic effects given in Table 2. Undesirable concentrations of lead pollution are also found in lead mines and metal industries, battery and battery factories, oil refineries, paint industry and explosive industry wastewater. 5.66 mg/L in battery factory waste water, 0.02-2.5 mg/L in acidic mine drainage, 125-150 mg/L organic and 66-85 mg/L inorganic lead pollution in factory wastewater producing tetraethyl lead (Fırat, 2007).

1.6.3 Zinc

Zinc is a hard and brittle metal in blue-white appearance. Zinc is a metal with an atomic number 30, symbol Zn, which is fragile at room temperature but can be forged and drawn at 100-150 °C.

The main uses of zinc are galvanizing of pipes and conveying lines (55-60%), production of brass (15-20%), zinc plate production (3%), zinc oxide production and tire industry (8-10%), battery manufacturing (3%), zinc alloy, die casting industry (6-7%), textile, ceramic industry, and chemical industry.

Zinc also; as a fundamental element for the human-body, zinc is used in the preparation of vitamins, as a key component of many enzymes, in the structure of insulin hormone and in the reproductive system.

Zinc is a basic metal in terms of nutrition. Inadequate health problems occur as a result. Poisoning due to excessive zinc intake is not common, but the toxic effects that may occur in case of excessive intake are given in Table 2 (Ayten, 2006; Bolatkhan, 2009).

1.6.4 Arsenic

Arsenic is an element with symbol As, and atomic number 33. In the earth crust it usually combines with sulphur and metals, and also it can be found as a single element.

Common usage areas of arsenic; mining activities, fossil fuel combustion, pesticide production, ceramics, cement, cosmetics, paint, leather, paper industries and animal feed additives. Also, arsenic and its compounds are used in wood preservatives, glass manufacturing, electronics, catalysts, alloys, feed additives and it is also widely used in veterinary chemicals (Rahman, 2017).
Humans may be exposed to arsenic element via inhalation, feeding and drinking water.

The most dangerous form of arsenic to human health is its inorganic forms which are arsenite and arsenate. In addition to the toxic effects given in Table 2, long-term exposure can cause skin lesions, internal cancers, neurological problems, lung disease, peripheral vascular disease, hypertension and cardiovascular disease, and diabetes mellitus (Jaishankar et al., 2014).

1.6.5 Copper

Copper is the best electrical conductor after silver, its symbol is Cu and its atomic number is 29. It is mostly found in nature as oxide, carbonate and sulphur minerals. Copper is a

metal that can be shaped by hammering, is resistant to shrinkage, has no magnetic susceptibility, and has high electrical and thermal conductivity.

Besides the use of copper as a conductor; in the coating of ship hulls, in the production of printing plates in printing, water pipe, hot water serpentine pipes, thermo siphon, L.P.G. It is widely used in making gas pipes, household items and ornaments.

Copper is an essential element for biological systems. In case of insufficiency; (anemia), malnutrition, and Menke syndrome occur. In case of excess, it causes health problems such as Wilson's cirrhosis, concentration disorder, loss of appetite, other than those mentioned in Table 2 (Ayten, 2006).

1.6.6 Mercury

With an atomic number of 80, mercury is another heavy metal element with the symbol of Hg. Mercury can be found in the earth crust in three different combinations with other elements mainly sulphur. Mercury can be found as elemental, inorganic and organic forms in nature. The elemental form of mercury is liquid at room temperature.

Mercury metal has toxic characteristic for both humans and the environment. It can accumulate in the body of humans and other living things. The toxic effects of mercury are given in Table 2 (Öngül Bülbül, 2019).

1.6.7 Chromium

Chromium is an element with symbol Cr and atomic number 24. Chromium is found in nature in oxidation stages ranging from +2 to +6 and in the form of Cr^{+3} oxides, hydroxides and sulphates. The most common forms are Cr^{+3} and Cr^{+6}. Although hexavalent chromium is soluble in water; trivalent chromium is insoluble in water both forms are toxic to living things and the toxic effects of Cr are given in Table 2 (Jaishankar et al., 2014).

Chromium is used in industries such as metallurgy, paper and cellulose, organic chemical, petro-chemistry, chemical fertilizers, iron and steel foundry, metal, textile, leather tanning, and electroplating (Doğu, 2019).

1.6.8 Nickel

Nickel with atomic number 28, and symbol 'Ni' is one of the heavy metals that cause pollution in water. Nickel, which is found in nature as sulphur, silicate and arsenide minerals, is hard and silvery heavy metal.

Nickel is mostly used as an alloy. Widely used in plating, Ni is used in the electrolytic coating of alloys made of steel, copper and aluminium, especially in automobile machinery and components, in the construction of marine tools. Among the alloys, the most widely used in industry is stainless steel. Stainless steel, which contains an alloy of iron and chromium, contains 35% nickel. It is also used as a cathode in nickel-cadmium batteries, to give green colour to glass, in magnets and coins.

It is known that nickel, which has a permissible limit value of 20 μg/L in drinking and potable water, causes health problems indicated in Table 2 when it is taken into the body through the skin, inhalation and food above this value (İpek, 2014).

1.7 Objective of the Thesis

Recently, researchers have been investigating to obtain cheaper, more abundant, and more effective alternative adsorbents for waste water treatment due to the high price of activated carbon used in the industry (Babel & Kurniawan, 2003; Babel & Kurniawan, 2004; Hegazi, 2013; De Gisi et al., 2016; Raval et al.,2016).

This study aims to investigate the removal of Zn^{+2}, Cd^{+2}, and Pb^{+2} heavy metal ions from a synthetically prepared wastewaters using coconut shell, olive stone, walnut shell, and their carbons after a carbonization process as adsorbent.

The effects of adsorbent type, contact time, adsorbent dose, and initial ion concentration on the % adsorption of adsorbents (% removal of metals) have been examined comparatively. This study searched the answers to the following questions;

- How did the contact time affect the adsorption of adsorbents?
- How did the adsorbent dose affect the adsorption of the adsorbents?
- How did the initial ion concentration affect the adsorption of the adsorbents?
- Which heavy metal had the highest percentage of removal efficiency?
- Which adsorbent had the best percentage of removal efficiency?

2. LITERATURE SURVEY

The removal of Hg^{+2}, Pb^{+2}, Cd^{+2}, Ni^{+2}, and Cu^{+2} ions from industrial wastewater by the coir pith carbon as an adsorbent by activating chemical method has been studied by Kadirvelu, Thamaraiselvi, and Namasivayam (2001).The removal of heavy metals from industrial wastewater has shown that the success of experiments varies depending on the composition and pH of the solution. As a result of this study, it was demonstrated that the coal obtained from coir pith was economical for heavy metal adsorption (Kadirvelu et al., 2001).

In 2002, Al-Rub, Kandah, and Al-Dabaybeh in their study using sheep manure waste as the adsorbent for removing of Ni^{+2} ions from aqueous solution, contact time, initial pH, the amount of adsorbent, adsorbent particle size, initial concentration of Ni^{+2} ions, salt and chelate agent on the effects of Ni^{+2} ions elimination had been studied. This study showed that sheep manure waste had a high affinity for Ni^{+2} binding (Al-Rub et al., 2002).

In the study of Igwe, Ogunewe, and Abia (2005), the competitive adsorption of Zn^{+2}, Cd^{+2}, Pb^{+2} metal ions from aqueous and non-aqueous solutions was investigated using modified and unmodified maize cobs and husks. According to this; the highest adsorption with unmodified adsorbents Zn^{+2} ions at the concentration of 495.9 mg/g was obtained. As a result of Igwe, Ogunewe, and Abia 2005 study, it was showed that the presence of other heavy metals and chemicals as a design parameter in the treatment and management of heavy metal pollutants using cellulosic materials affects adsorption (Igwe et al., 2005).

In 2005, Kobya et al. in their study after the carbonization of apricot stone and activated with sulphuric acid as adsorbents, they investigated the removal of Ni^{+2}, Co^{+2}, Cd^{+2}, Cu^{+2}, Pb^{+2}, Cr^{+3} and Cr^{+6} ions by adsorption method from aqueous solutions with these adsorbents. According to the study, the highest adsorption was observed around pH 1.0-2.0 for Cr^{+6} and pH 3.0-6.0 for the remaining metal ions. As a result of this study, Kobya et al. showed that adsorption of ions was related to solution pH value (Kobya et al., 2005).

The bio-sorption capacity of cadmium was studied with using green coconut shell powder as adsorbent by Pino et al. in 2006. In this study, the effects of pH and metal ion concentration on adsorption capacity were investigated and the results were evaluated for Freundlich and Langmuir adsorption isotherm models. Also the kinetic of Cd^{+2} bio-sorption was investigated. Pino et al. (2006) applied to data the pseudo first-order and pseudo second-order kinetic models and observed that the most suitable model is pseudo second-order kinetic model (Pino et al., 2006).

Fiol et al. (2006) studied the adsorption of Pb^{+2}, Ni^{+2}, Cu^{+2} and Cd^{+2} ions from aqueous solutions using olive stone waste as an adsorbent. The effects of contact time, solution pH, ionic medium and initial metal concentration on metal adsorption were studied and the highest metal adsorption was found to be around 5.5-6.0 pH and increasing ionic strength concentration caused a decrease in metal removal. Their kinetic studies showed that initial uptake was rapid and that all metals examined were equilibrated in 1 hour and the data followed the pseudo-second order reaction. Also for single metal systems in the study, Freundlich model has been found to provide the best correlation. According to the results of this study, it was concluded that olive stone waste, which is a low-cost adsorbent, is suitable for heavy metal adsorption (Fiol et al., 2006).

In 2007, Amarasinghe and Williams examined the adsorption of Cu^{+2} and Pb^{+2} ions from aqueous solutions using tea wastes as adsorbent, using variable parameters such as adsorbent dose, initial metal ion concentration, solution pH, adsorbent particle size. In this study, to determine the factor affecting adsorption and kinetics and to investigate practical applicability, they performed batch and fixed bed column experiments. They observed the higher adsorption rate and capacity for smaller particle sizes and the highest metal adsorption was around at pH 5.0-6.0. The results of this study showed that tea waste is a better adsorbent for metal removal compared to other low-cost absorbents (Amarasinghe & Williams, 2007).

The adsorption of Cd^{+2} with different parameters from aqueous solutions by using sugarcane bagasse, maize corncob and jatropha oil cake was investigated by Garg et al. (2008). The initial metal ion concentration, pH and adsorbent dose were used as experiment parameters. They found that the highest adsorption capacity belongs to JOC

with 99.5% and the maximum metal removal was observed at pH 6.0. Additionally they investigated number and position of the functional groups of adsorbents with FT-IR spectrum (Garg et al., 2008).

The removal of Cu^{+2} ions from aqueous solutions with using potato shell charcoal as an adsorbent have been examined by Aman et al. in 2008. In this study, they investigated the effects of various parameters such as temperature, pH and solid-liquid ratios. They carried out kinetic and isotherm studies by studying the effects of those mentioned parameters. They observed that for Cu^{+2} adsorption, the optimum pH value was 6.0 (Aman et al., 2008).

Hansen et al. (2010) investigated Cu^{+2} adsorption capacity, kinetics and isotherms of different low-cost residual agricultural materials in their study. They used seven different materials: peanut shells, nut shells, plum seeds, eucalyptus barks, olive pips, peach stones and pine sawdust as adsorbents. The best adsorption results were obtained at acidic pH for olive pips, peach stones and pine sawdust (Hansen et al., 2010).

In 2010, the removal of Cd^{+2} ions from aqueous solutions using bamboo charcoal as adsorbent according to interaction time, pH value, initial metal concentration, and adsorbent dose parameters have been investigated by Wang et al.. This study showed that the adsorption of Cd^{+2} ions was rapid at first but reached equilibrium within 6 hours and high pH ($\geq$8.0) was suitable for adsorption and removal of Cd^{+2} ions. Consequently, this study demonstrated that bamboo charcoal could be used to remove Cd^{+2} ions from wastewater (F. Y. Wang et al., 2010).

The removal of Cr^{+6} from aqueous solutions by producing activated carbon from peach stone and acrylonitriledivinylbenzene copolymer as an adsorbent have been investigated by Durano et al. (2010). As a result of the study, the highest adsorption capacity was reached at pH 2.0 and the adsorption performance of the produced peach coals was found to be close to the commonly used coal performance, and the acceptability of the use of peach stones coal as an adsorbent for the removal of Cr^{+6} from aqueous solutions was demonstrated (Duranoğlu et al., 2010).

Moodley et al., in their study in 2011, studied the adsorption capacity of Ni^{+2} element according to pH, adsorbent dose and heavy metal initial concentration using pine sawdust, which are low-cost adsorbent from nickel and other heavy metal-containing wastewaters. As a result of the study showed that the use of pine sawdust is capable of separating Ni ion from multi-component aqueous solutions (Moodley et al., 2011).

Hegazi (2013) examined the removal of heavy metal from galvanic industry wastewater by using rice husk and fly ash as adsorbent depending on the adsorbent dose, contact time and pH. According to this study; fly ash was effective for Cd^{+2} and Cu^{+2} adsorption, the contact time required for the highest adsorption was 2 hours and the pH range for the highest heavy metal adsorption was between 6.0, and 7.0 (Hegazi, 2013).

In 2014, Murathan et al. examined the removal of Cd^{+2} pollution in water with adsorption on packed adsorption columns using oak valonia and horse chestnut as adsorbents. As a result of the study, oak valonia was found to have adsorption capacity of 26.32 mg Cd^{+2} / g adsorbent and horse chestnut 14.59 mg Cd^{+2} / g adsorbent. It has shown that the highest adsorption capacity belongs to oak valonia with 40.24 mg Cd^{+2} / g adsorbent (Murathan & Koçyiğit, 2014).

The removal of Cd^{+2}, Cr^{+3} and Zn^{+2} ions from aqueous solutions using different fruit cortexes (banana, kiwi, tangerine) as adsorbents has been investigated by Al-Qahtani (2015). By examining the effects of initial concentration, pH, adsorbent dose and contact time on adsorption capacity, experiments showed that natural adsorbent can effectively remove impurities from wastewater (Al-Qahtani, 2015).

3. MATERIALS AND METHODS

3.1 Preparation of Adsorbents

In this study, three natural organic agricultural waste materials, namely, coconut shells, olive stones, walnut shells, and their carbonized products are selected as adsorbent materials for removal of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions from synthetically prepared wastewater to determine their suitability for using them as adsorbent materials for the mentioned heavy metals. Coconut shell was intentionally selected in this study since it is mostly used in researches in the literature (Chandana et al., 2018; Abdul Rahim et al., 2020; Packialakshmi et al., 2021; James & Yadav, 2021), and in industry with the purpose of activated carbon adsorption in gold cyanidation, water treatment, air and gas treatment, chemical and food industry. Therefore performances of the other selected two adsorbent's can be compared with its performance.

Those three adsorbents were obtained from an operating industrial plant in which commercial charcoal and hookah charcoal are produced for the local market. And also the carbonized products of those three adsorbent materials were also obtained from the above-mentioned plant. In plant, the raw materials are converted to their carbonized products by burning under suitable conditions; close atmosphere and pressure, in an industrial furnace.

After carbonization process the structures of organic materials are affected and their porosity can be changed. Therefore, the carbonized products of the tested adsorbent materials were also used in the heavy metal adsorption experiments in the present study.

The photos of the adsorbent materials used in the experiments are shown in Figure 15.

Figure 15. Raw materials used as adsorbent in the experiments; A) Coconut shell, B) Olive stone C) Walnut shell D) Coconut shell carbonized product E) Olive stone carbonized product F) Walnut shell carbonized product

Since the raw materials are not suitable to directly use in the adsorption experiments because of their particle sizes, they were crushed and ground to get suitable particle sizes. The crushing was carried out using a laboratory scale jaw crusher (Figure 16), and the grinding was carried out using a laboratory scale Retsch ZM 200 brand centrifugal grinder/mill (Figure 17).

Ground raw materials were sieved with Retsch brand laboratory scale sieves 200 mm in diameter and Retsch brand laboratory scale sieve shaker (Figure 18). At the end of the sieving, the particle size in the range of -1000 μm + 850 μm was chosen to be used in the adsorption experiments.

After screening, the photos of the adsorbent materials used in the experiments are shown in Figure 19.

Figure 16. Jaw crusher used for crushing the adsorbent materials

Figure 17. Centrifugal grinder used for grinding the adsorbent materials

Figure 18. Retch brand sieves (left) and sieve shaker (right) used to screen the ground adsorbent materials

Figure 19. Desired particle size of adsorbent materials used in the experiments; A) Coconut shell, B) Olive stone C) Walnut shell D) Coconut shell carbonized product E) Olive stone carbonized product F) Walnut shell carbonized product

3.2 Examination of Micro Images of Adsorbents

Microstructures of coconut shell, olive stone, walnut shell and their carbonized product used as adsorbent were coated with gold and analysed with Scanning Electron Microscopy (SEM) technique. FEI brand Quanta 650 Field Emission model SEM device was used. These analyses were carried out in Cukurova University Central Research Laboratory.

SEM was performed at 500X, 1000X, and 2000X magnification levels to observe the porous structure of the adsorbents.

The micro images obtained for coconut shell, olive stone, walnut shell and their carbonized product used as adsorbent were given in the following section. They were comparatively examined and their differences from each other were discussed.

3.2.1 Micro Images of Coconut Shell and Coconut Shell Carbonized Product

SEM images of coconut shell and coconut shell carbonized product taken at different magnification levels were illustrated in Figure 20.

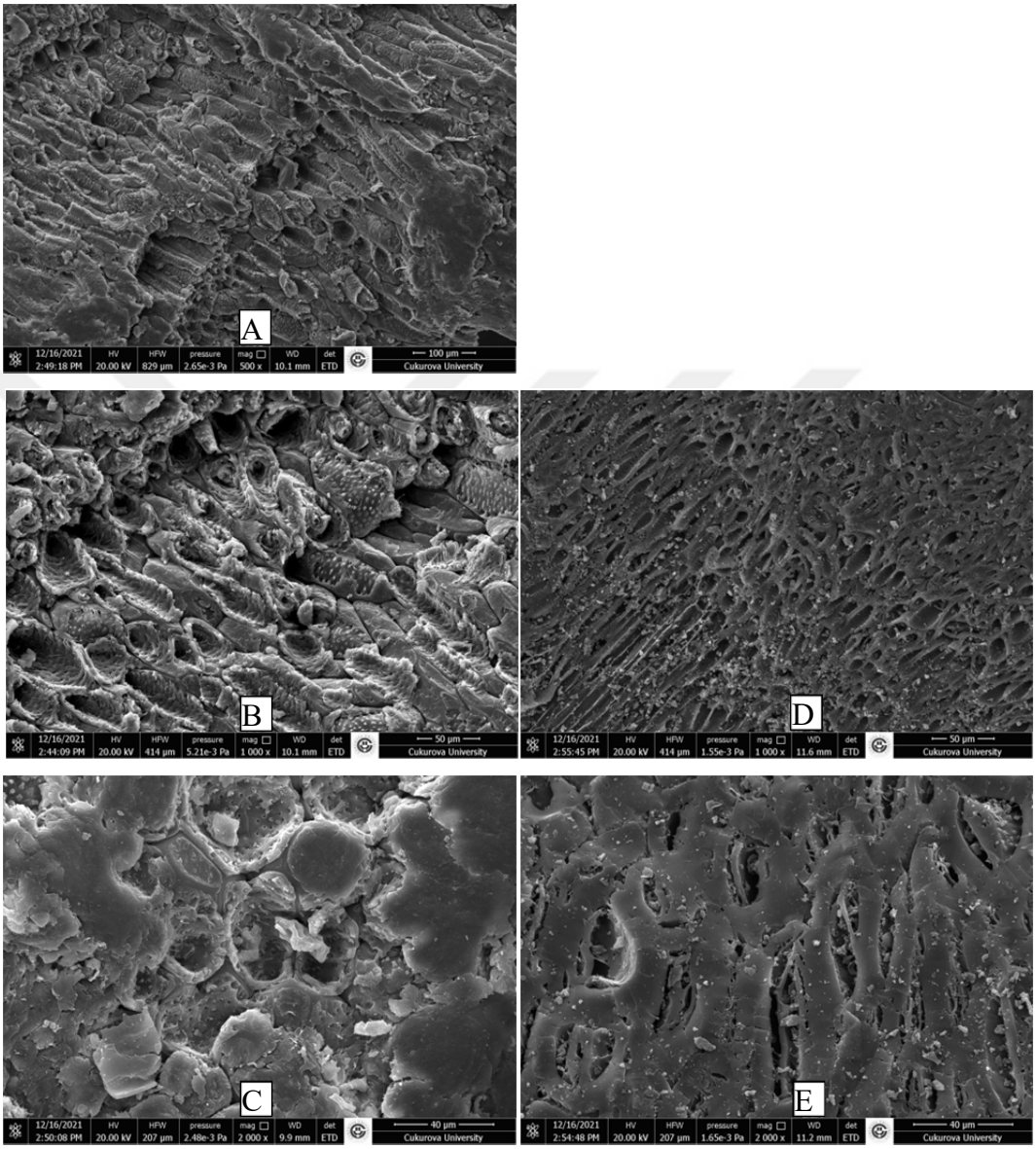

Figure 20. SEM images of coconut shell and coconut shell carbonized product; A)500X, B)1000X, C)2000X magnification levels belong to coconut shell at left column and D)1000X, E)2000X magnification levels belong to coconut shell carbonized product at right column.

When the micro images of mentioned adsorbent are examined, it can be seen obviously that the surface of coconut shell have less porous structures than its carbonized products. Obtained results in this study were also found in the literature (Claoston et al., 2014; Abdul Rahim et al., 2020). They reported that when the organic matters are carbonized they reach at a higher porous structure with the removal of volatile substances after the carbonization

process. This can be seen from Figure 20 that, the carbonized products have higher porous structures, pores are well distributed, and the numbers of the pores are also much higher.

3.2.2 Micro Images of Olive Stone and Olive Stone Carbonized Product

SEM images of olive stone and olive stone carbonized-product taken at different magnification levels were illustrated in Figure 21.

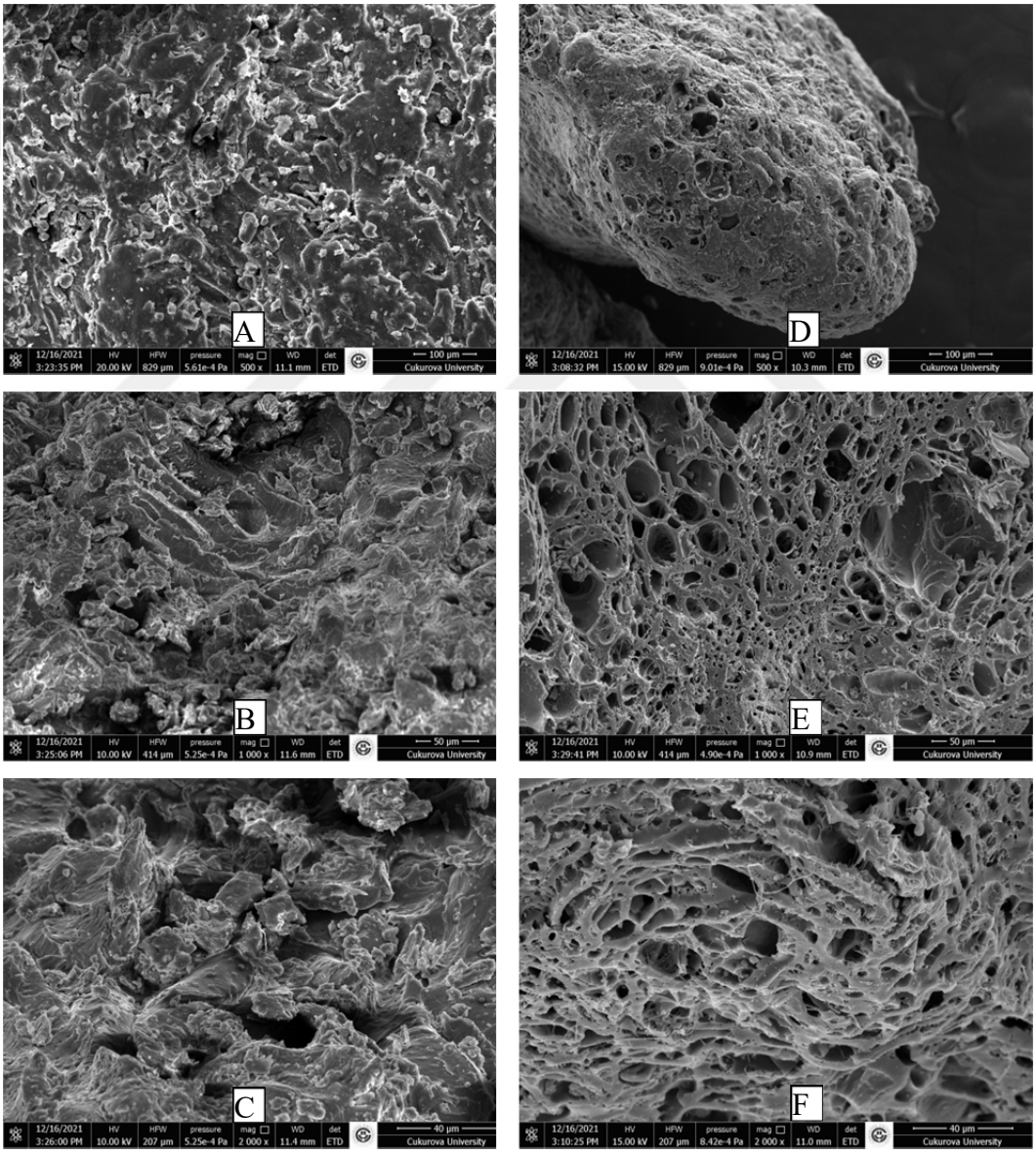

Figure 21. SEM images of olive stone and olive stone carbonized product; A)500X, B)1000X, C)2000X magnification levels belong to olive stone at left column and D)500X, E)1000X, F)2000X magnification levels belong to olive stone carbonized product at right column.

It was again determined that the olive stone has also little porous structure as seen in Figure 21 A, B, C. However, after carbonization process, it was observed in Figure 21 D, E, F that the number of pores in the structure increased as happened in the coconut shell carbonized products. It was found that the shapes of the pores are large and small longitudinally circular.

3.2.3 Micro Images of Walnut Shell and Walnut Shell Carbonized Product

SEM images of walnut shell and walnut shell carbonized product taken at different magnification levels were illustrated in Figure 22.

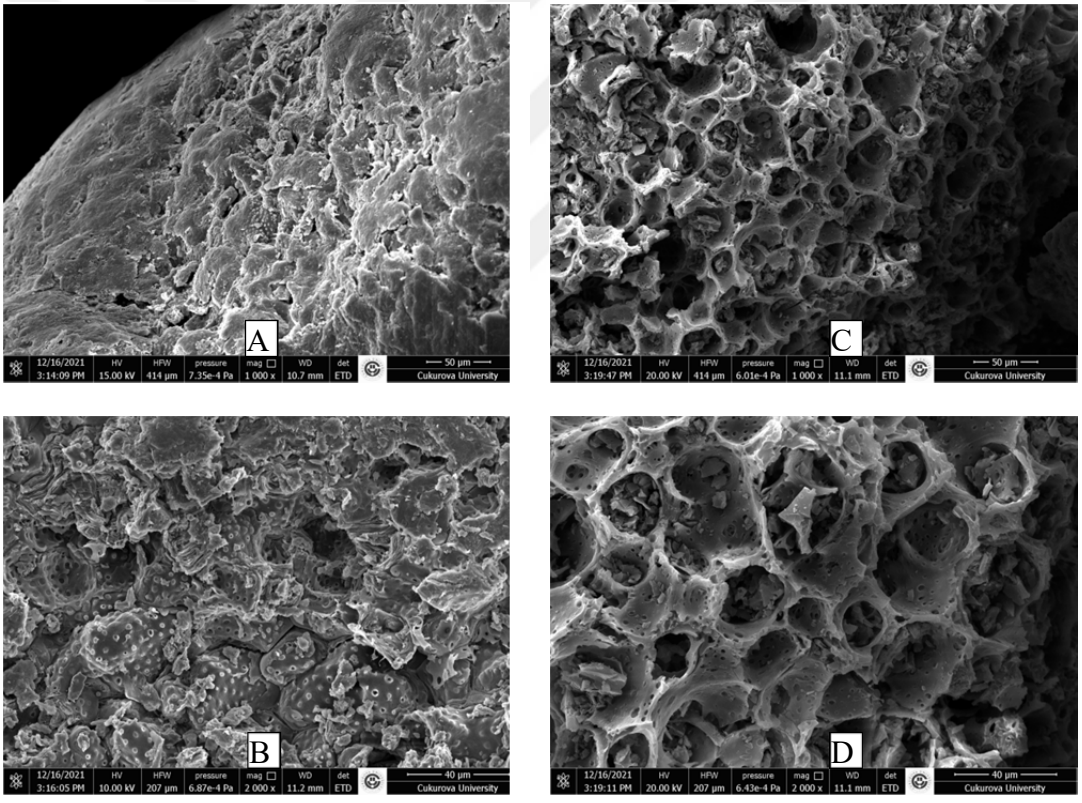

Figure 22. SEM images of walnut shell and walnut shell carbonized product; A)1000X, B)2000X, magnification levels belong to walnut shell at left column and C)1000X D)2000X magnification levels belong to walnut shell carbonized product at right column

In Figure 22, as with other previous adsorbents, it was observed that more porous structures due to carbonization process which is responsible for the removal of volatile compounds in the walnut shell structure. When these porous structures were examined, it was found that the shapes of those pores are more round or circular when compared the

previous pores found in olive stone carbonized product. And the sizes of the pores of walnut shell carbonized product are greater and the numbers of the pores are less when compared to the olive stone carbonized product.

3.3 Comparison of the Micro Images of Adsorbents

In order to compare the micro structures of all three tested adsorbent in this study, their micro photos were given side by side in Figure 23. Their micro photos taken at 2000X magnification levels were given and examined comparatively.

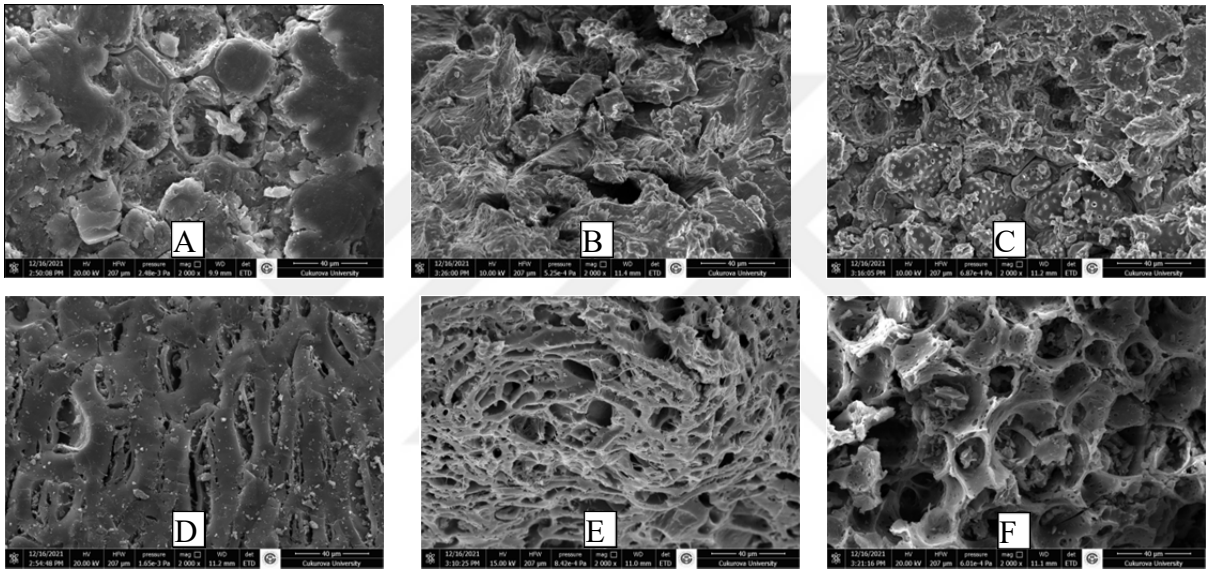

Figure 23. SEM images of adsorbents A) Coconut shell B) Olive stone C)Walnut shell D) Coconut shell carbonized product E) Olive stone carbonized product F) Walnut shell carbonized product

After the examination of the adsorbents it was found that, the structures and the surfaces of both untreated adsorbents and carbonized products adsorbents were different than each other.

When the untreated adsorbents were compared with each other, olive stone was found to have the more porous structures than others (Figure 23 A, B and C).

When the carbonized products adsorbents were compared with each other, olive stone carbonized product was found to have the most porous structure as seen Figure 23 E. The other adsorbents (Figure 23 F and D) namely walnut shell carbonized products and coconut shell carbonized products followed the olive stone carbonized products for the porous structure, respectively.

As said before here and in the literature, carbonization process removes the potential volatile components in the organic material structure, and after separation of volatile matters the material structure here adsorbents can have a more porous structure. As a result, their specific surface areas are increased and this type of materials can be used for the previous mentioned purposes. These findings were also observed in this micro photos examination and it is expected that the specific surface areas of the tested adsorbents increased (Figure 23 D, E, F).

The preparation of chemicals used to prepare heavy metal stock solution is explained below and then adsorption tests have been carried out.

3.4 Chemicals Used to Prepare Heavy Metal Stock Solution

The synthetic stock solution used in this study was prepared as a mixture using Honeywell brand analytical reagent grade of Lead (II) nitrate ($Pb(NO_3)_2$), Cadmium Nitrate Tetrahydrate ($Cd(NO_3)_2.4H_2O$), and Fisher Scientific brand analytical grade of Zinc Nitrate Hexahydrate ($Zn(NO_3)_2.6H_2O$), in distilled water.

3.5 Procedure

Adsorption experiments were carried out applying the batch system. In the experiment, to prepare the 1000 ppm Zn^{+2} stock solution, 2275.9 mg $Zn(NO_3)_2.6H_2O$ is first dissolved in distilled water in a beaker and then transferred to a 500 mL flask, to prepare the 1000 ppm Cd^{+2} stock solution, 1370.1 mg $Cd(NO_3)_2.4H2O$ is first dissolved in distilled water in a beaker and then transferred to a 500 mL flask, to prepare the 1000 ppm Pb^{+2} stock solution, 800.8 mg $Pb(NO_3)_2$ is first dissolved in distilled water in a beaker and then transferred to a 500 mL flask, and the mix solutions at the desired concentrations (50ppm, 100ppm, 200ppm) were prepared by dilution from the stock solution, respectively.

Adsorption was carried out in 100 mL erlenmeyer using IKA KS 4000 ic control shaker (Figure 24) at room temperature (25 ±2 °C).

Figure 24. IKA KS 4000 ic control shaker

At the end of the adsorption processes, the liquid phase was taken from the samples and filtered with Macherey-Nagel brand 110mm diameter pore width 7-12 µm filter paper. The ion concentrations in the solutions were determined using the Perkin Elmer PinAAcle 900H brand Atomic Absorption Spectrometer (AAS) at Mining Engineering Department, Çukurova University (Figure 25). AAS analyses were carried out repeatedly and mean values were taken. The adsorption of Zn^{+2}, Cd^{+2}, Pb^{+2} ions using coconut shell, olive stone, walnut shell, and their carbonized products were examined according to contact time, adsorbent dose and initial concentration variables. From the results, the removal percentages of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions were calculated. These values are calculated using the following equation.

$$\%\text{Removal Efficiency} = \frac{Ci - Cf}{Ci} * 100$$

C_i = Initial concentration of metal in the solution

Cf = Final concentration of metal in the solution after adsorption process

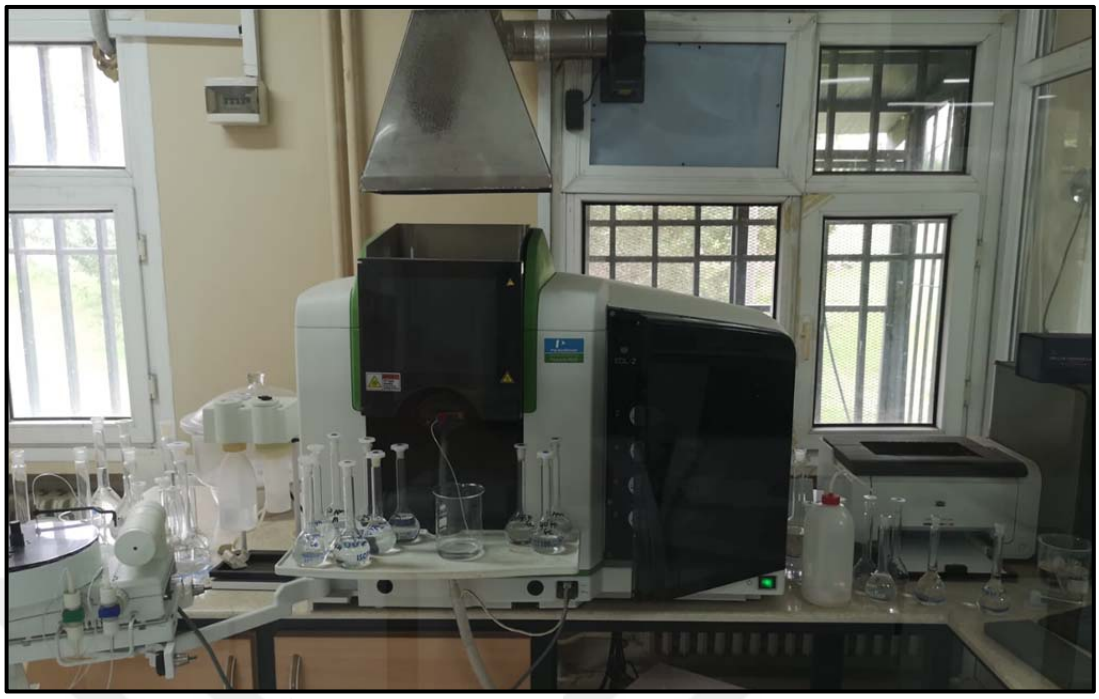

Figure 25. Perkin Elmer brand PinAAcle 900H model AAS used to determine the heavy metal ion concentrations.

3.6 Independent and dependent variables

The particle size of the different adsorbent materials was kept as constant to be -1000 µm +850 µm, the adsorption temperature was kept constant 25 ±2 °C, and the medium pH was measured with Hanna HI2211 brand pH meter and was kept between 5.0 and 6.0 for all the heavy metal adsorption experiments. Those values were selected and determined according to the results of the previous completed researches published in the related literature.

The effect of adsorbent type, contact time, adsorbent dose, and initial ion concentration were selected as independent variables in the heavy metal adsorption experiments. And the heavy metal removal percentages, namely $Zn^{+2,}$ Cd^{+2}, and Pb^{+2} removals, were selected as dependent variables.

4. RESULT AND DISCUSSION

4.1 Zn^{+2}, Cd^{+2}, and Pb^{+2} Adsorption Experiments

4.1.1 Effect of Contact Time

The effects of contact time on the adsorption of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions from waste water using coconut shell, olive stone, walnut shell and their carbonized products were investigated.

A certain amount of per adsorbents was taken and mixed with 100 mL 100 ppm Zn^{+2}, Cd^{+2}, and Pb^{+2} mixture solution at room temperature for 30, 60 and 180 min with IKA KS 4000 ic control shaker at 180 rpm (Figure 24). At the end of the adsorption experiment periods, samples were taken and filtered with a Macherey-Nagel brand with a pore opening of 7-12 μm filter paper, and the concentrations of Zn^{+2}, Cd^{+2}, and Pb^{+2} remaining in the filtrate were determined by AAS.

The results of the removal of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions were given below respectively.

In Figure 26, 27, and 28; removal percentages of Zn^{+2} ions verse the contact time were plotted.

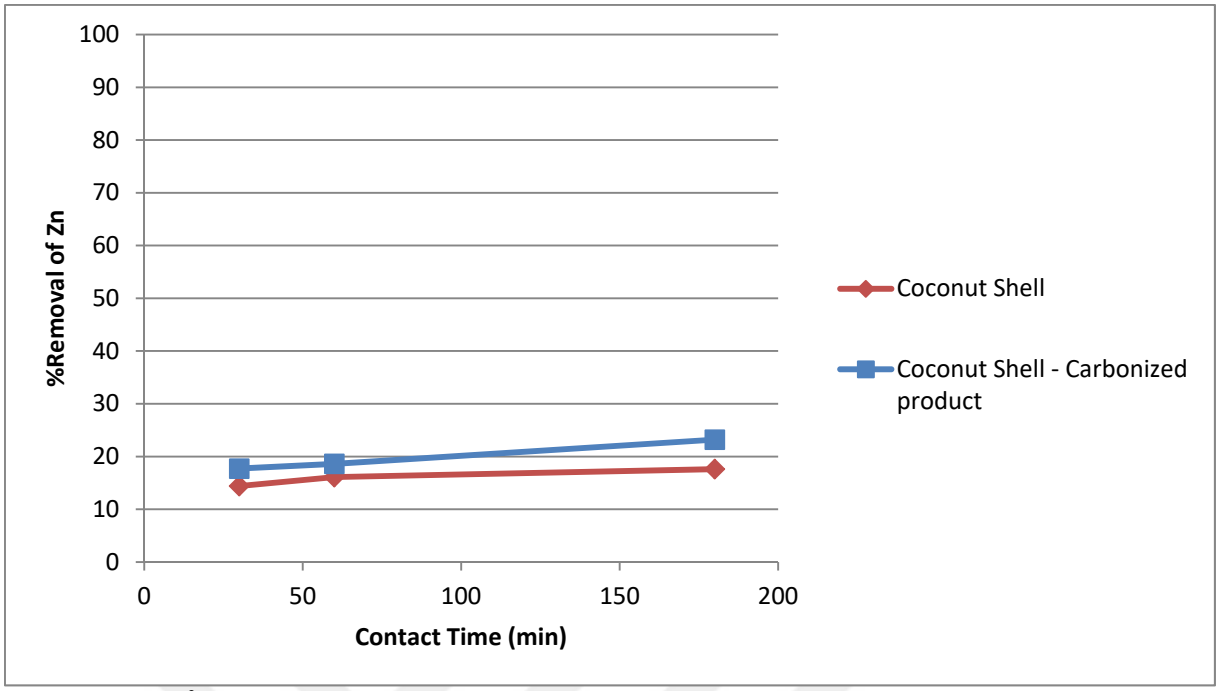

Figure 26. Zn^{+2} ion uptake by coconut shell and coconut shell carbonized product as a function of contact time

It can be seen in Figure 26, 27, and 28 that the removal of Zn^{+2} ions was increased depended on contact time for all the adsorbent types. The better performed adsorbent ones are walnut shell, coconut shell and olive stone, respectively.

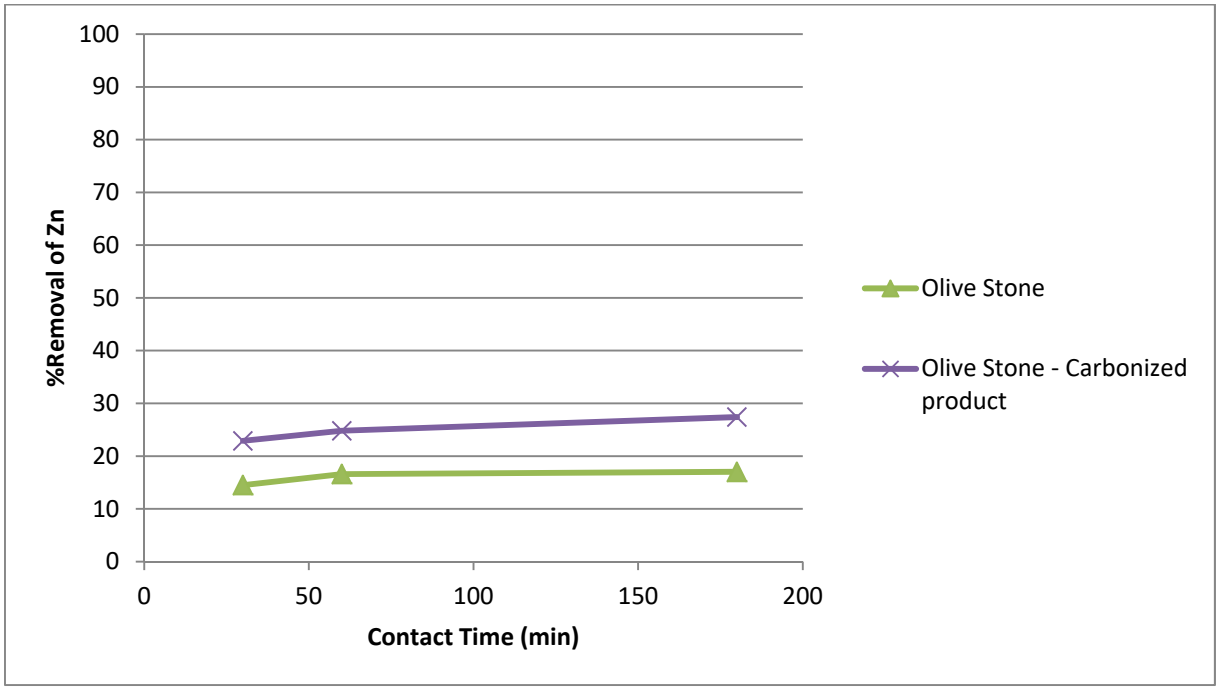

Figure 27. Zn^{+2} ion uptake by olive stone and olive stone carbonized product as a function of contact time

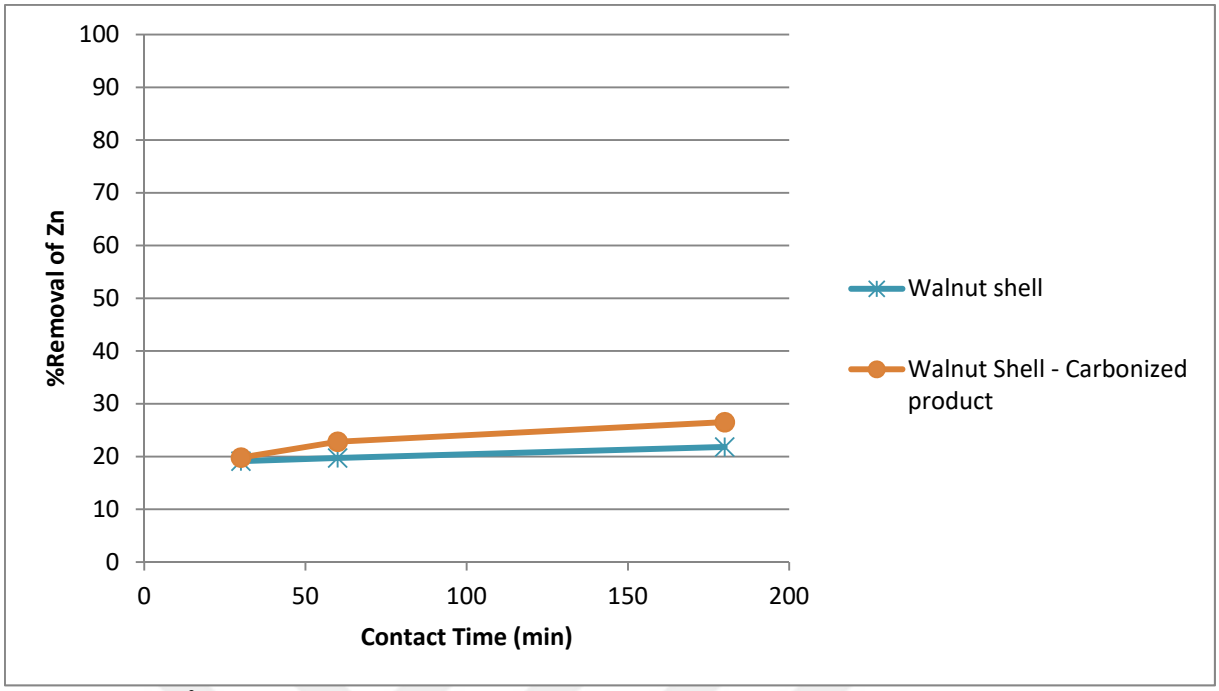

Figure 28. Zn^{+2} ion uptake by walnut shell and walnut shell carbonized product as a function of contact time

Performances of their carbonized products were found to be better for the removal of Zn^{+2} ions from solution. As seen in previous studies, the carbonization process increased the surface area of the adsorbent as it removed the volatile components (Gündoğdu, 2010; Abdul Rahim et al., 2020). Olive stone carbonized products and walnut shell carbonized products were performed almost same and they were found to be better adsorbents than coconut shell carbonized products for the removal of Zn^{+2} ions from solution. The performances of the other adsorbents namely coconut shell, olive stone and walnut shell were lower than their carbonized products. And the descending order of them was found to be walnut shell, coconut shell and olive stone, respectively. For Zn^{+2} ion, it was observed that the best adsorbent is olive stone carbonized products.

Removal percentages of Cd^{+2} ions from wastewater were presented as a function of contact time in Figure 29, 30, and 31.

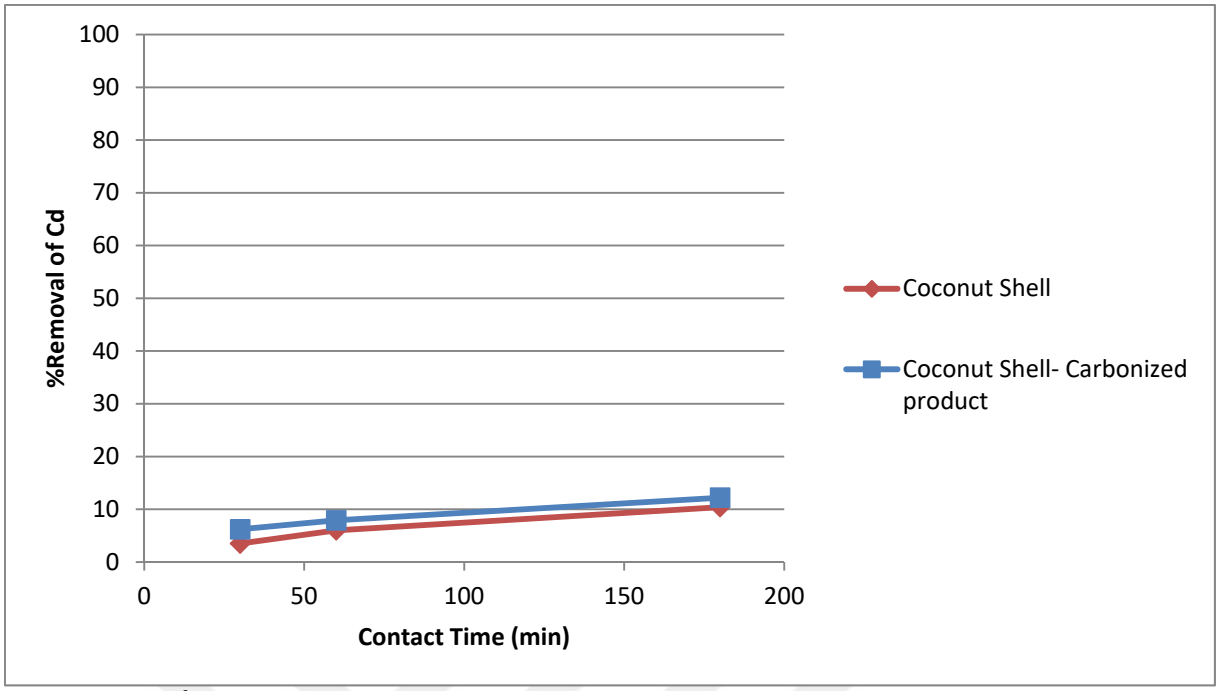

Figure 29. Cd^{+2} ion uptake by coconut shell and coconut shell carbonized product as a function of contact time

It can be seen from Figure 29, 30, and 31 the removal for Cd^{+2} ions increased regularly when the contact time increased. For the removal of Cd^{+2} ions from the solution, the better performed adsorbent ones among the untreated adsorbents are olive stone, coconut shell, and walnut shell, respectively.

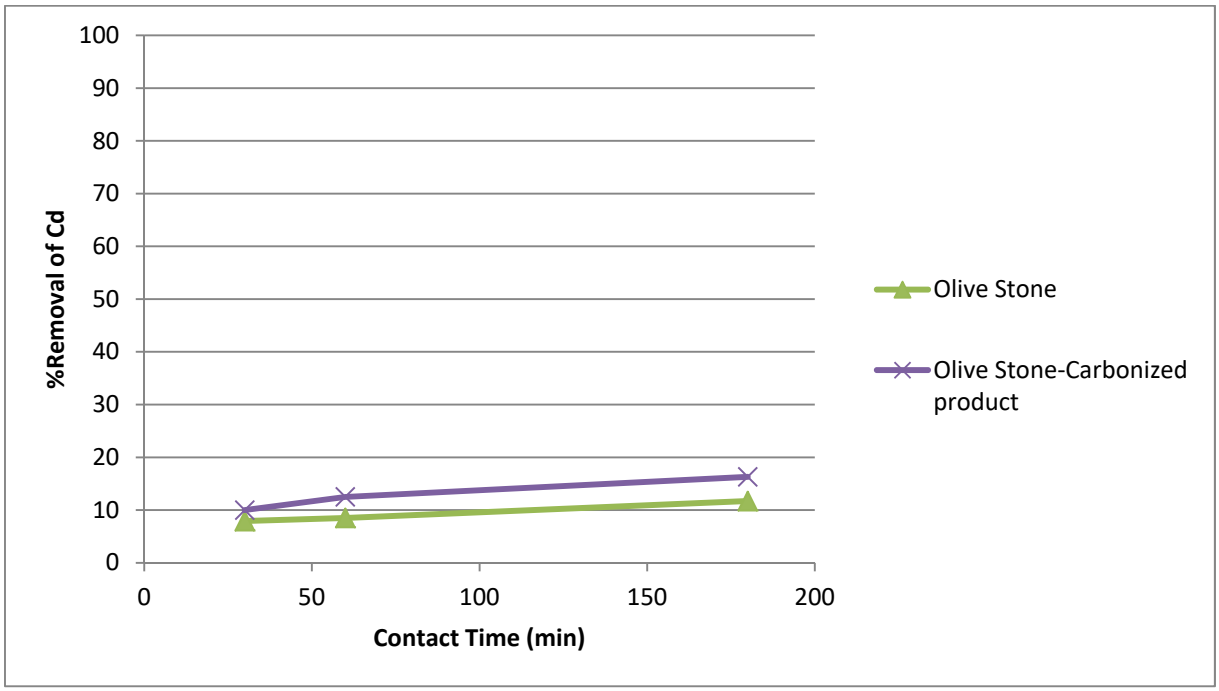

Figure 30. Cd^{+2} ion uptake by olive stone and olive stone carbonized product as a function of contact time

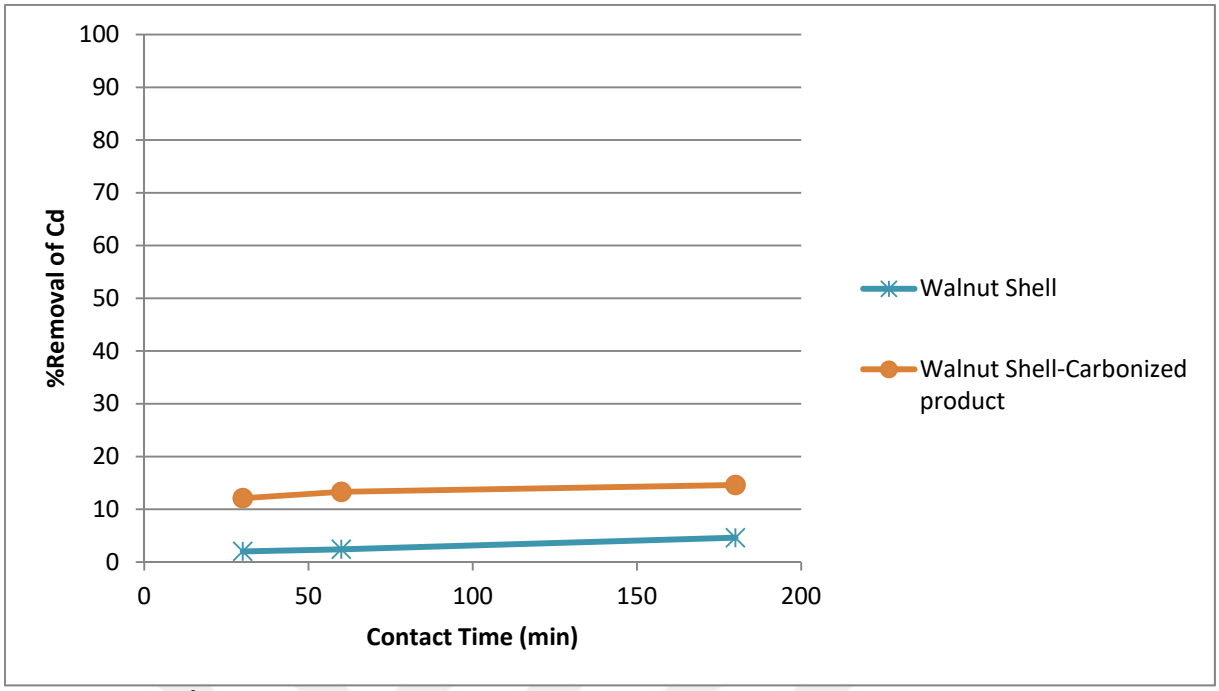

Figure 31. Cd^{+2} ion uptake by walnut shell and walnut shell carbonized-product as a function of contact time

Performances of their carbonized products were found to be better than their untreated natural form for the removal of Cd^{+2} ions from the solution. It was observed that the best adsorbent for Cd^{+2} is olive stone carbonized product. The second good adsorbent was walnut shell and the last one was coconut shell carbonized product. For instance, when the contact time is increased from 30 min to 180 min the removal of Cd^{+2} ions increased from 10.0% to 16.3% for olive stone carbonized product (Figure 30). It can be said that the carbonized products of the tested adsorbent almost double performed when compared to their untreated natural forms with the change of their structure by carbonization process.

Removal percentages of Pb^{+2} ions verse the contact time were shown graphically in Figure 32, 33 and 34.

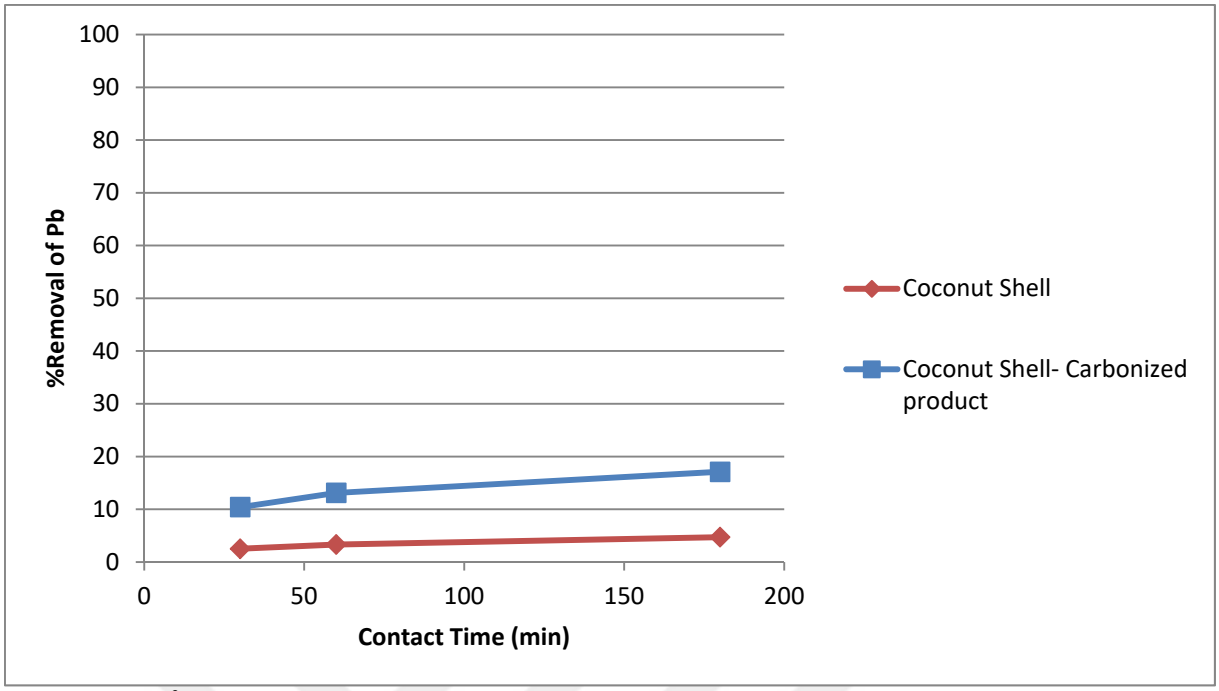

Figure 32. Pb^{+2} ion uptake by coconut shell and coconut shell carbonized product as a function of contact time

As could be seen from Figure 32, 33, and 34, while carbonized products showed the best performance, untreated natural organic adsorbents remained in the background. Good performers among these adsorbents are walnut shell, olive stone, and coconut shell, respectively. For Pb^{+2} ion, it was observed that the best adsorbent is olive stone carbonized products.

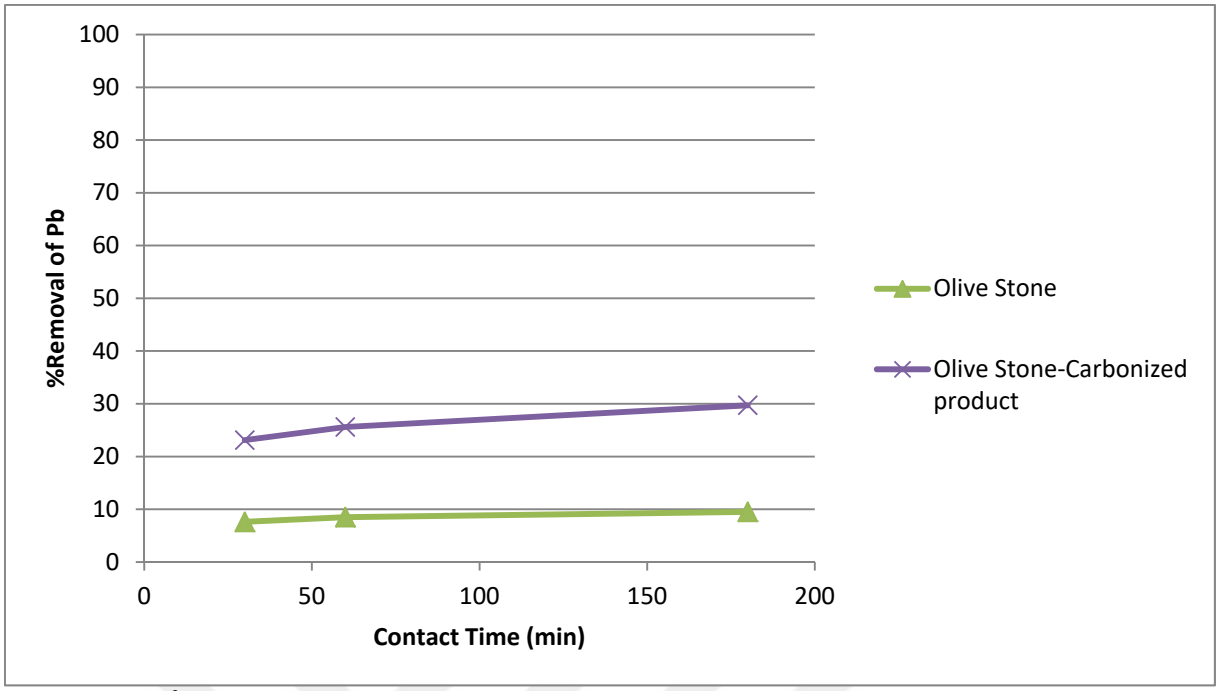

Figure 33. Pb^{+2} ion uptake by olive stone and olive stone carbonized product as a function of contact time

It is observed that the removal of Pb^{+2} ions with the use of olive stone carbonized product is dramatically higher compared to others. This is most probably due to the high pore structure, found and shown in Figure 21 D, E, and F of the olive stone carbonized product. Besides is explained by researchers that the reason of the behind of this phenomenon is the smaller hydration energy and hydration radius of the lead ion (Colella, 1996; Mobasherpour et al., 2012; Golomeova & Zendelska, 2016). Therefore, the adsorption of Pb^{+2} ions is expected to be better than other ions.

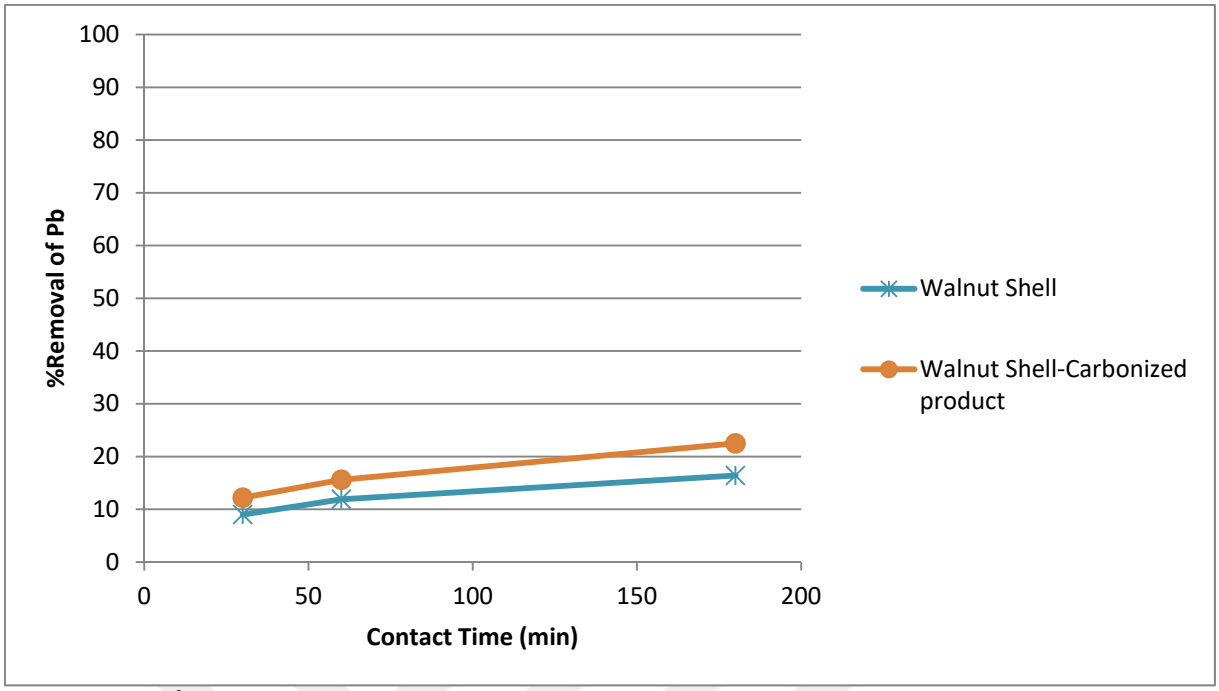

Figure 34. Pb^{+2} ion uptake by olive stone and olive stone carbonized product as a function of contact time

According to figures above, it appears that the increase in contact time from 30 min to 180 min for all adsorbent types significantly increases the removal per cent of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions.

When the performances for the removal of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions for the untreated natural forms and their carbonized products of the adsorbents of all three types examined; the carbonized products of the adsorbents well performed for all the tested heavy metal types. As said before the reason for this is the porous structure due to carbonization process (Claoston et al., 2014; Abdul Rahim et al., 2020). Therefore, the carbonization of the all three type adsorbents has more and open pore structure in their physical bodies, as seen from SEM images (Figure 23) and the higher porosity is responsible for the higher heavy metal removal from the solution.

According to these findings and data, while examining the effects of the other independent variable parameters below, the contact time was chosen constant as 180 min for the adsorption experiments.

4.1.2 Effect of Adsorbent Dose

The effect of adsorbent dose on the adsorption of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions of coconut shell, olive stone, walnut shell and their carbonized products were investigated and the results are given below.

0.5, 1, and 2 g of coconut shell, olive stone, walnut shell and their carbonized products were taken and mixed with 100 mL, 100 ppm Zn^{+2}, Cd^{+2}, and Pb^{+2} mix solution at 180 rpm for 180 min at room temperature. At the end of the adsorption experiment periods, samples were taken and filtered with a Macherey-Nagel brand filter paper, and the concentrations of Zn^{+2}, Cd^{+2}, and Pb^{+2} remaining in the filtrate were determined by AAS.

The removal percentages of Zn^{+2} ion versus the adsorbent amounts/doses of coconut shell, olive stone, walnut shell and their carbonized products were presented in Figure 35, 36,and 37.

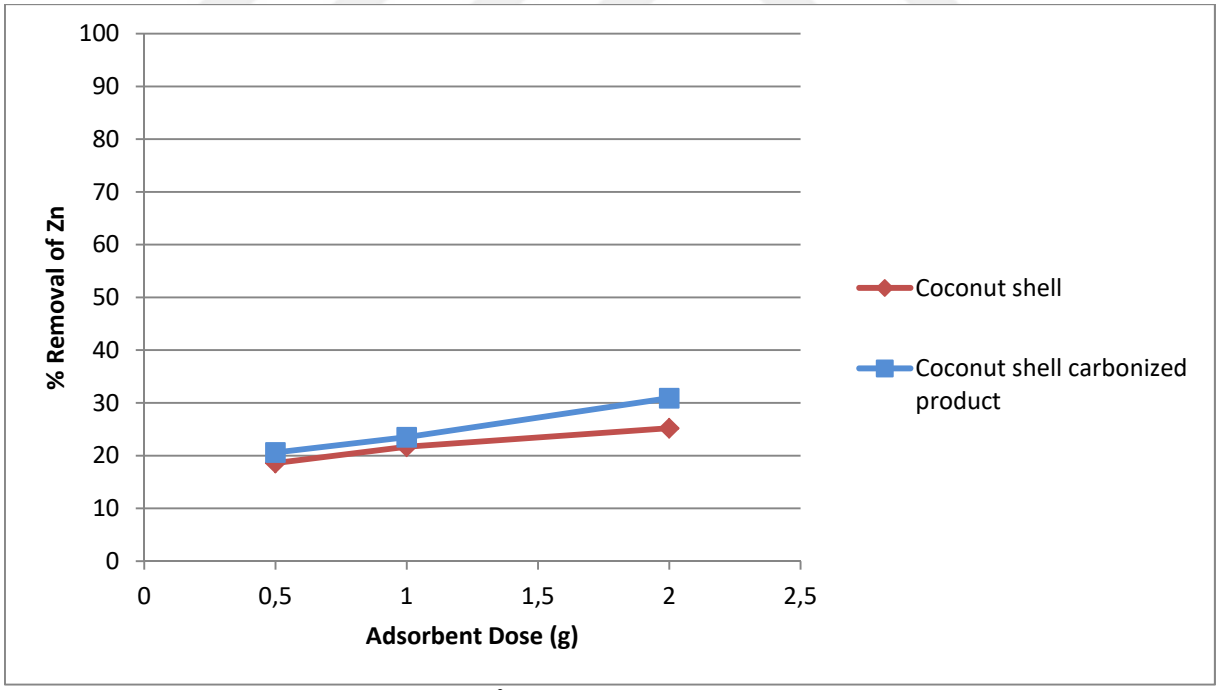

Figure 35. Adsorbent dose effect on Zn^{+2} removal by coconut shell and coconut shell carbonized product

According to Figure 35, 36, and 37 when the adsorbent dose per 100 mL solution is increased from 0.5 g to 2.0 g, the removal percentages for Zn^{+2} ion increased for all

adsorbent types. Although, it was observed that the performances of the untreated natural adsorbents were almost equal to each other around 20%, the performances of their carbonized products were found to be better for the removal of Zn^{+2} ion.

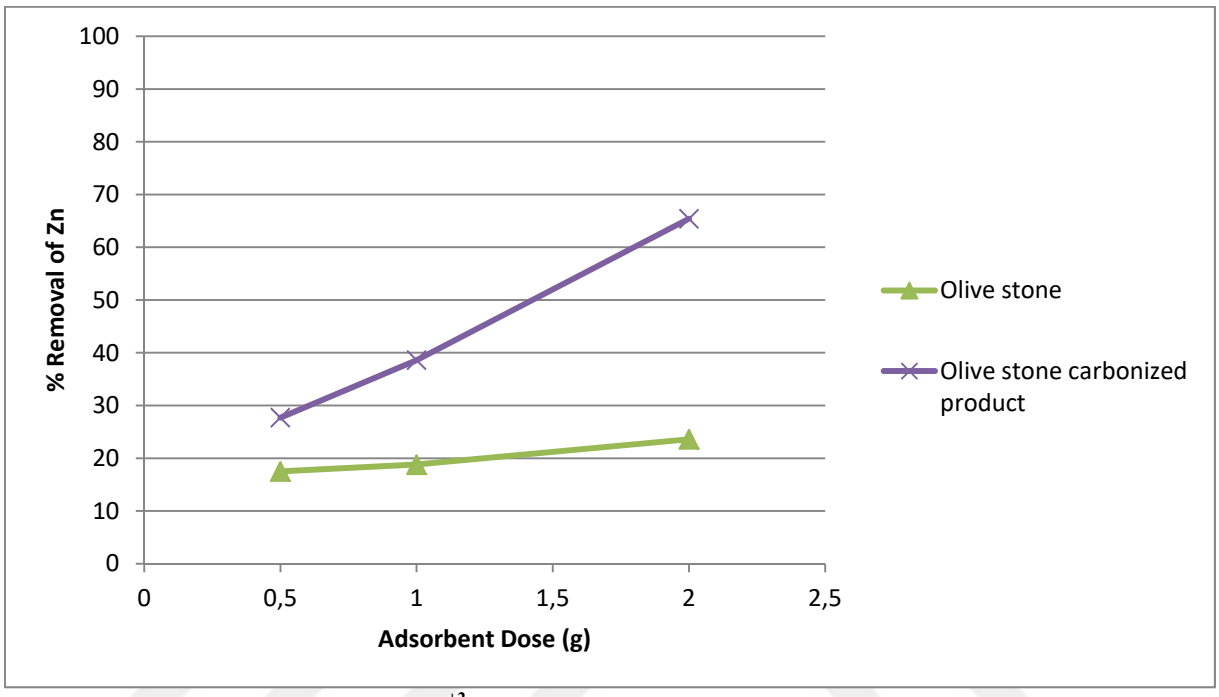

Figure 36. Adsorbent dose effect on Zn^{+2} removal by olive stone and olive stone carbonized product

The best removal efficiency for Zn^{+2} ion was achieved using olive stone carbonized product and the removal value was increased from 27.7% to 65.4% when the adsorbent dose was increased from 0.5 g to 2.0 g.

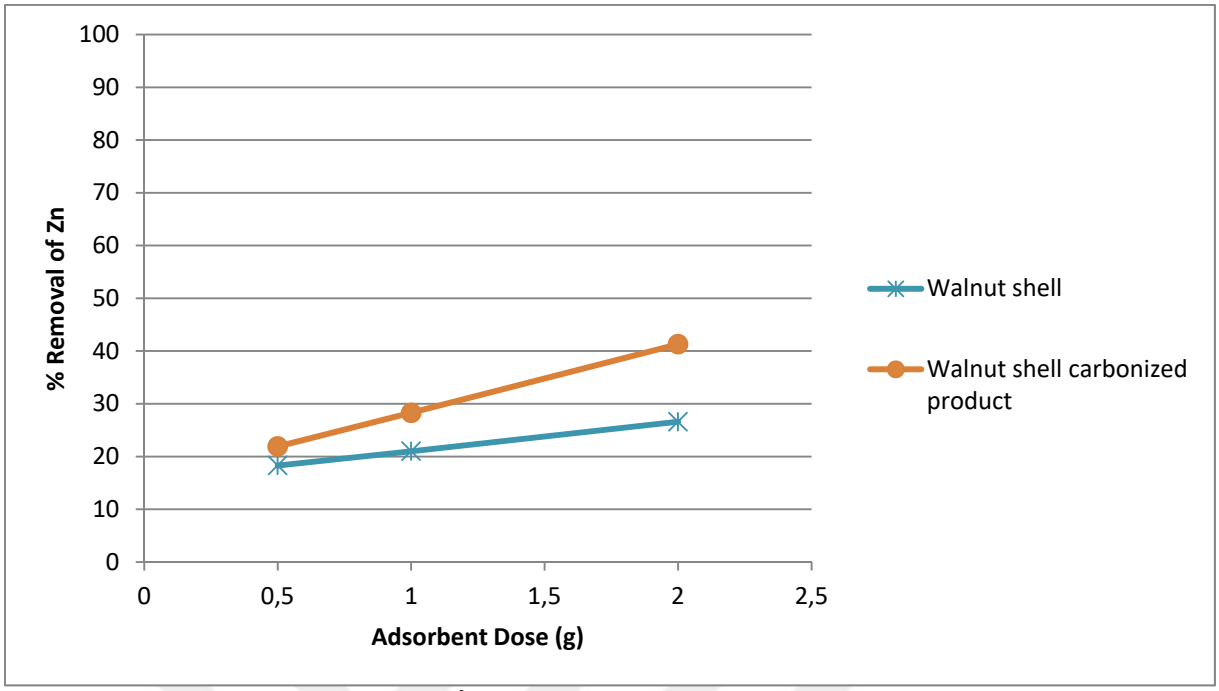

Figure 37. Adsorbent dose effect on Zn^{+2} removal by walnut shell and walnut shell carbonized product

In Figure 38, 39, and 40 the removal percentages of Cd^{+2} ion versus the adsorbent amounts of coconut shell, olive stone, walnut shell and their carbonized products were shown.

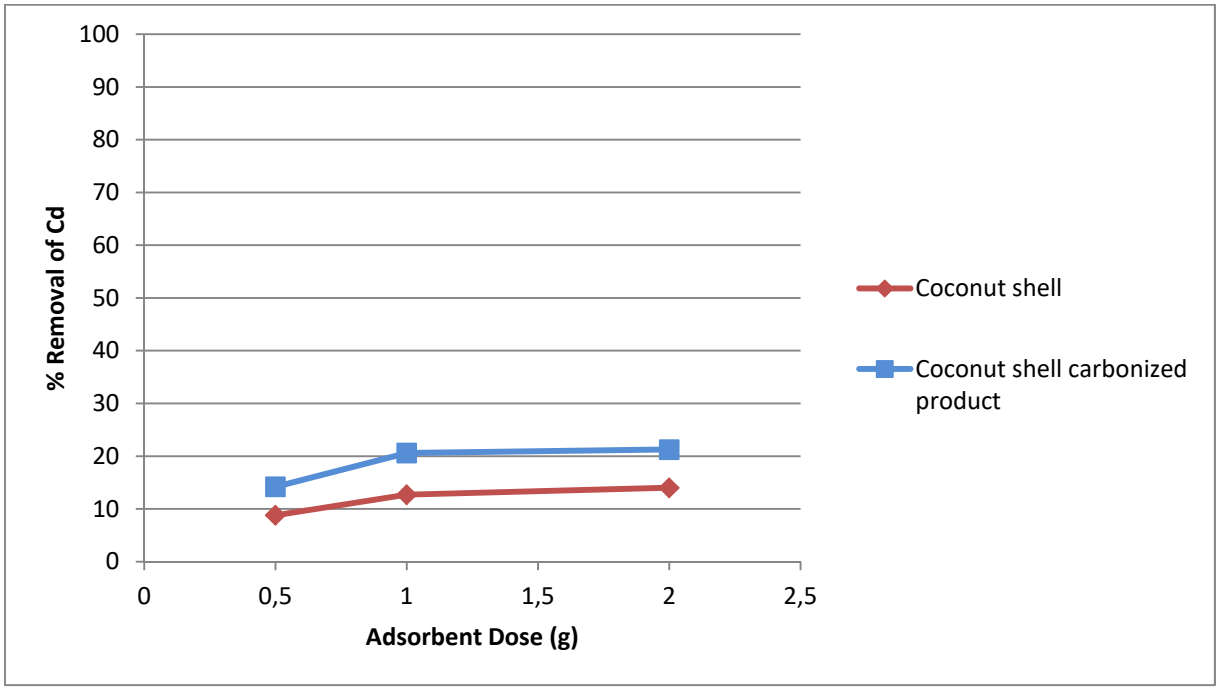

Figure 38. Adsorbent dose effect on Cd^{+2} removal by coconut shell and coconut shell carbonized product

It can be seen from Figure 38, 39, and 40 when the adsorbent dose was increased from 0.5 to 2.0 g, the removal of the Cd^{+2} ions was also increased for all types of adsorbents. The removal results for the Cd^{+2} ions were found about same and about 10% for the untreated natural adsorbents. On the other hand, the performances of their carbonized products were found to be better for the removal of Cd^{+2} ions.

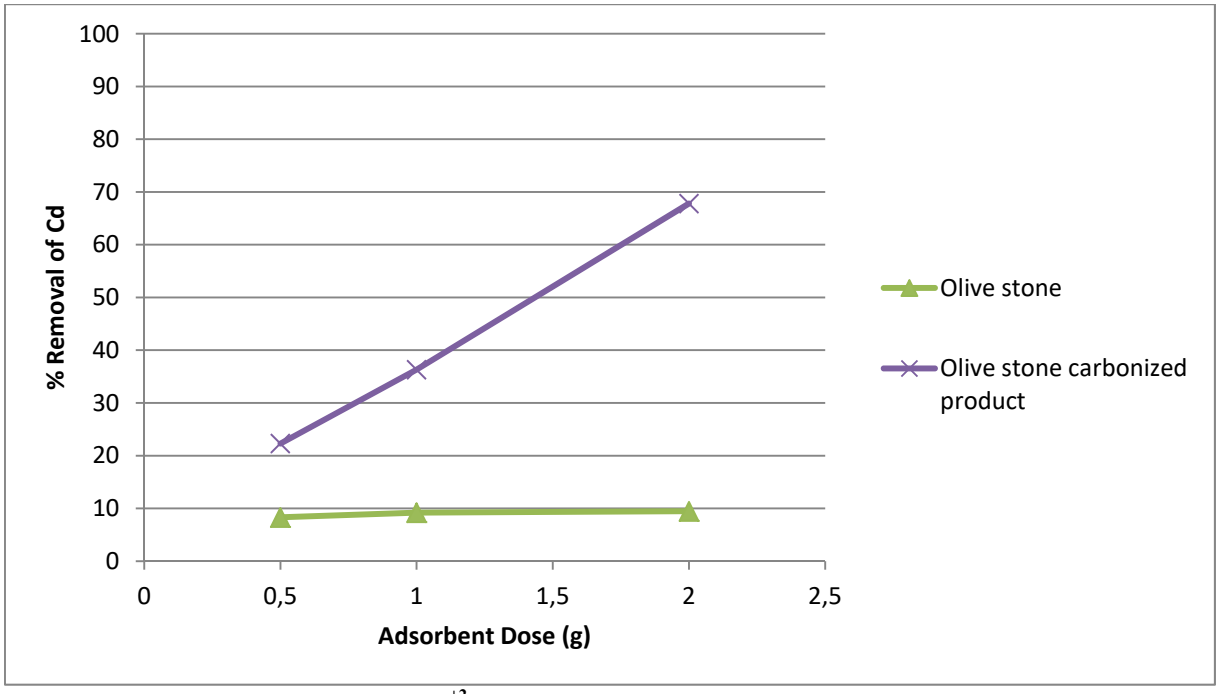

Figure 39. Adsorbent dose effect on Cd^{+2} removal by olive stone and olive stone carbonized product

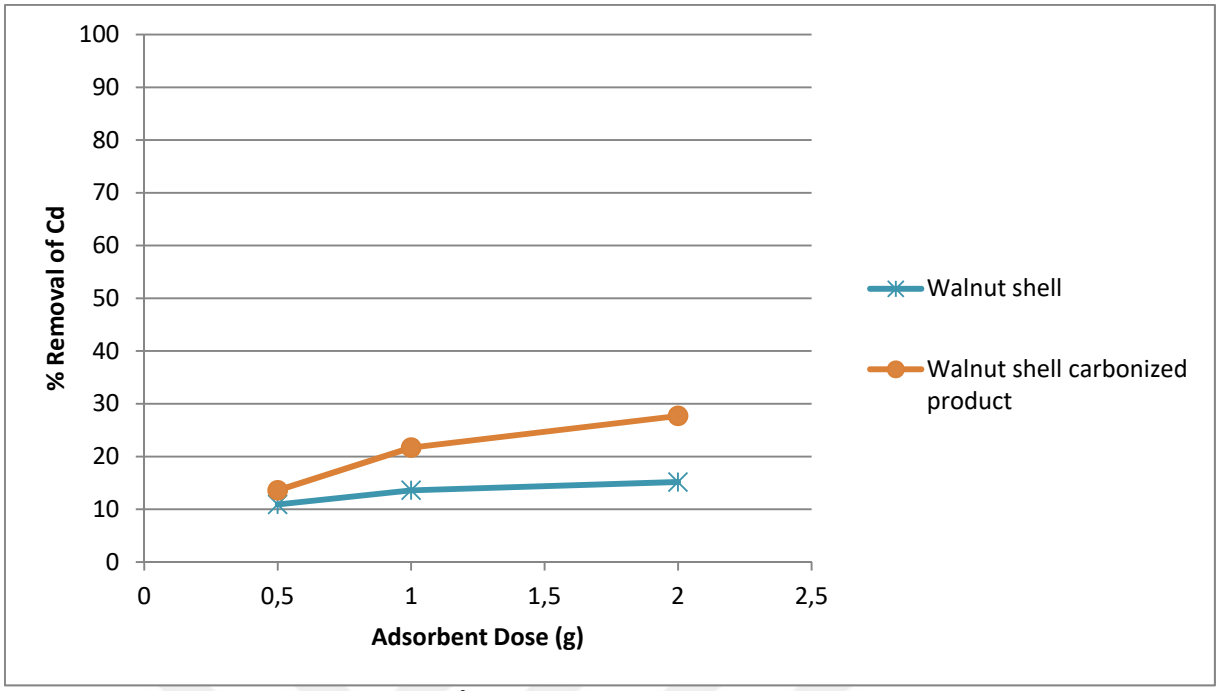

Figure 40. Adsorbent dose effect on Cd^{+2} removal by walnut shell and walnut shell carbonized product

The best adsorbent for the removal of Cd^{+2} ions was found as olive stone carbonized product. The other better performed adsorbents were walnut shell carbonized product and coconut shell carbonized products following olive stone carbonized products.

In Figure 41, 42, and 43; removal percentages of Pb^{+2} ions verse the adsorbent amounts of coconut shell, olive stone, walnut shell and their carbonized products were graphically shown.

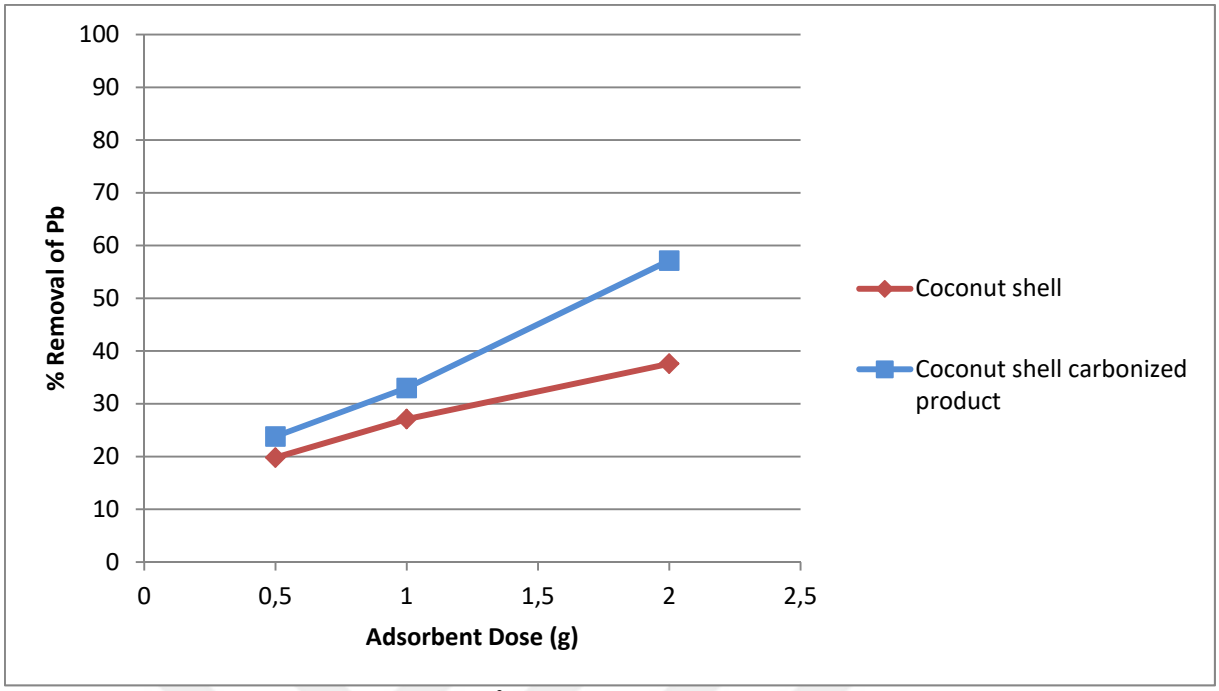

Figure 41. Adsorbent dose effect on Pb^{+2} removal by coconut shell and coconut shell carbonized product

As shown in Figure 41, 42, and 43, almost similar trends on the curves are observed in figures of other metals for Pb^{+2}. When the adsorbent dose was increased the removal of Pb^{+2} ions was also increased. The best Pb^{+2} ions removal was achieved using the olive stone carbonized product as adsorbent again as happened similar for the other heavy ions namely Zn^{+2} and Cd^{+2} ions.

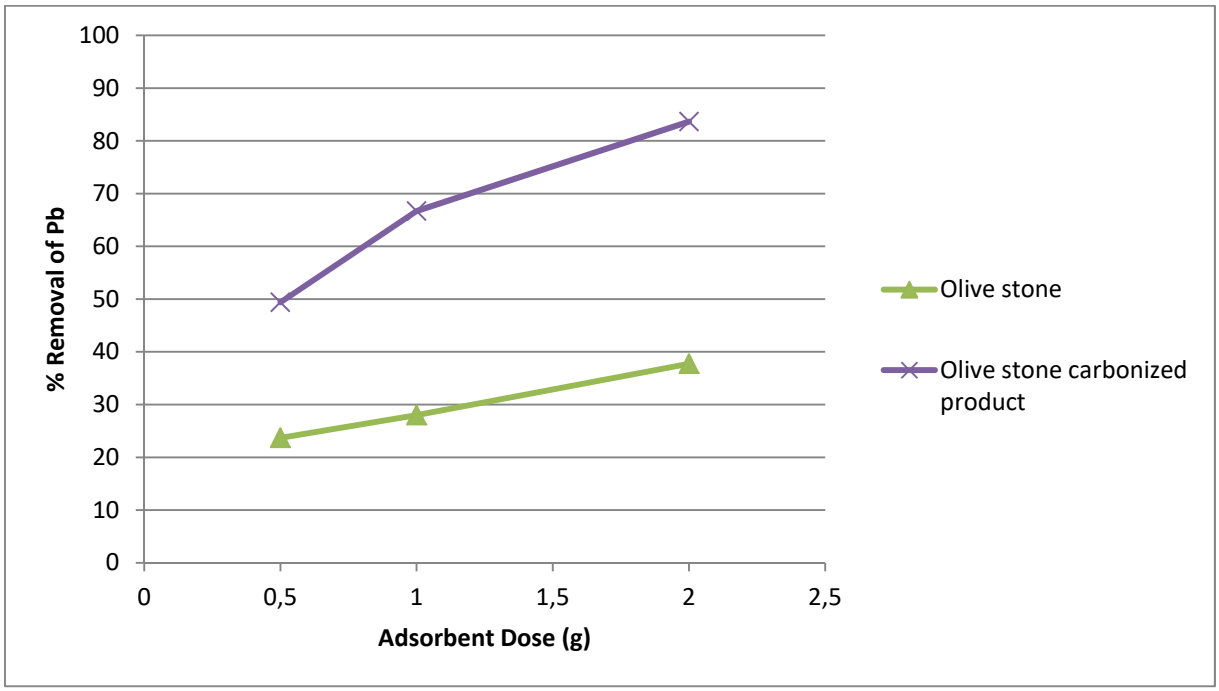

Figure 42. Adsorbent dose effect on Pb^{+2} removal by olive stone and olive stone carbonized product

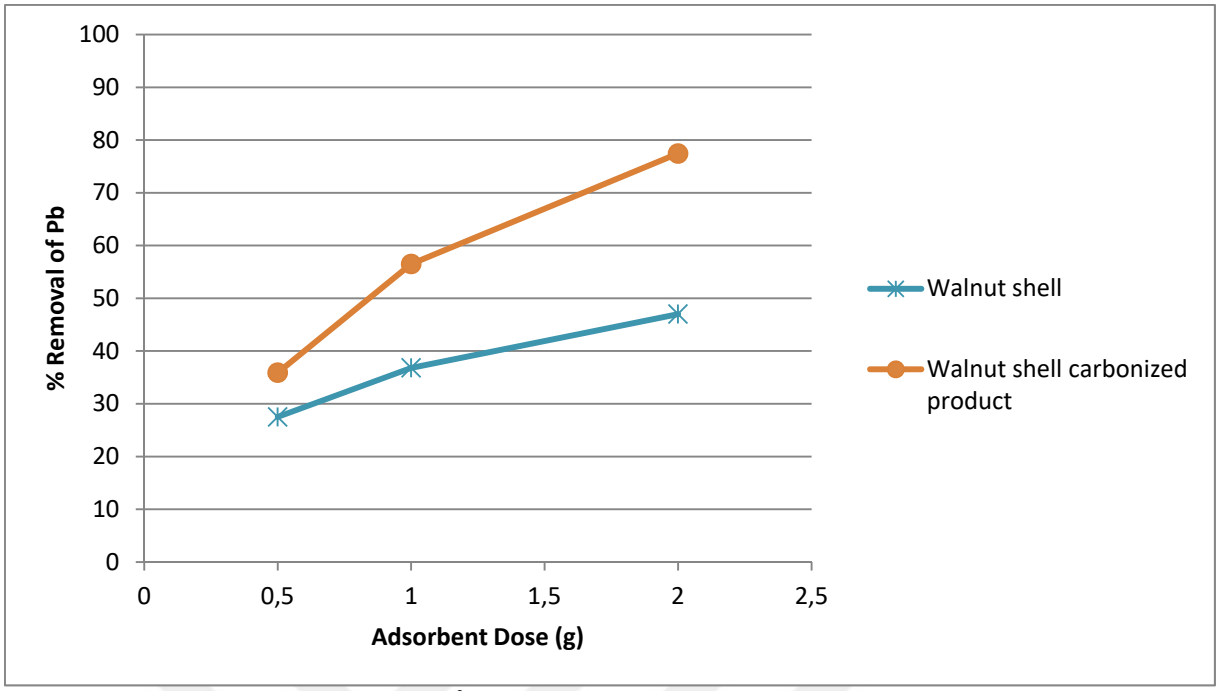

Figure 43. Adsorbent dose effect on Pb^{+2} removal by walnut shell and walnut shell carbonized product

The removals of Pb^{+2} ions were determined between about 20% and 47% when untreated natural coconut shell, walnut shell and olive stone shell used as adsorbent. On the other hand, these values were increased from 25% to 84% when their carbonized products used as adsorbents.

According to results shown in figures above, the removal (adsorption percentage of adsorbents) of Zn^{+2}, Cd^{+2} and Pb^{+2} ions increased as the amount of adsorbent increased for all adsorbent type. As the number of adsorption sites or specific surface area is increased with the amount of the adsorbent, higher metal removal percentage was achieved at higher doses. This result is consistent with the results obtained in the similar literature (Amarasinghe & Williams, 2007; Garg et al., 2008; Bansal et al., 2009; Gündoğdu, 2010). At the same time, it has been observed that the adsorbent carbonized products adsorb more Zn^{+2}, Cd^{+2}, and Pb^{+2} ions because of their high porosity structure than their untreated natural forms. Another result is that olive stone carbonized product is determined as the best adsorbent since it adsorbed the highest Zn^{+2}, Cd^{+2}, and Pb^{+2} ions.

Based on these results, adsorbent dose was chosen as 2 g while examining the effect of initial concentration parameter below.

4.1.3 Effect of Initial Ion Concentration

The effect of initial concentration of mix solution (heavy metal including synthetically prepared wastewater) on the adsorption of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions of coconut shell, olive stone, walnut shell and their carbonized products were investigated.

A certain amount (2 g as determined before) of coconut shell, olive stone, walnut shell and their carbonized products mixed with 100 mL 50-100-200 ppm of Zn^{+2}, Cd^{+2}, and Pb^{+2} mix solution, at 180 rpm at room temperature for optimum adsorption period (180 min as determined before). At the end of the adsorption experiment periods, samples were taken and filtered with a Macherey-Nagel brand filter paper, and the concentrations of Zn^{+2}, Cd^{+2}, and Pb^{+2} remaining in the filtrate were determined by AAS.

In Figure 44, 45, and 46; removal percentages of Zn^{+2} ions verse initial heavy metal concentration of mix solution were shown.

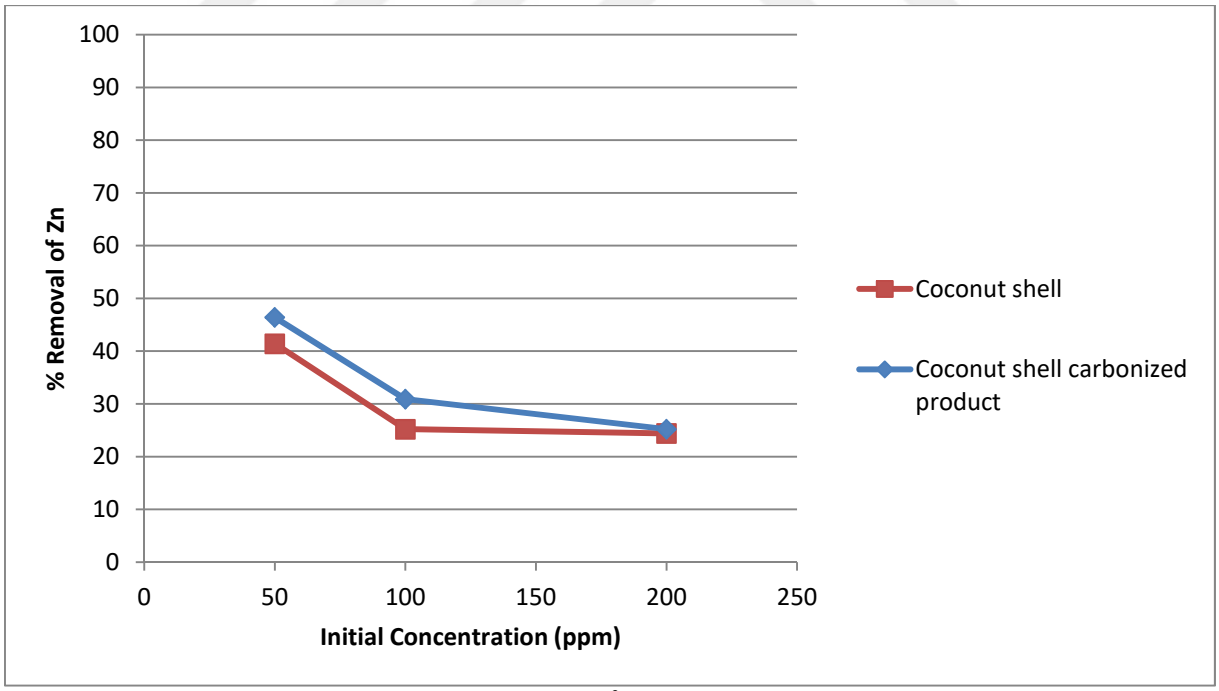

Figure 44. Effect of initial ion concentration on Zn^{+2} ion removal by coconut shell and coconut shell corbonized product

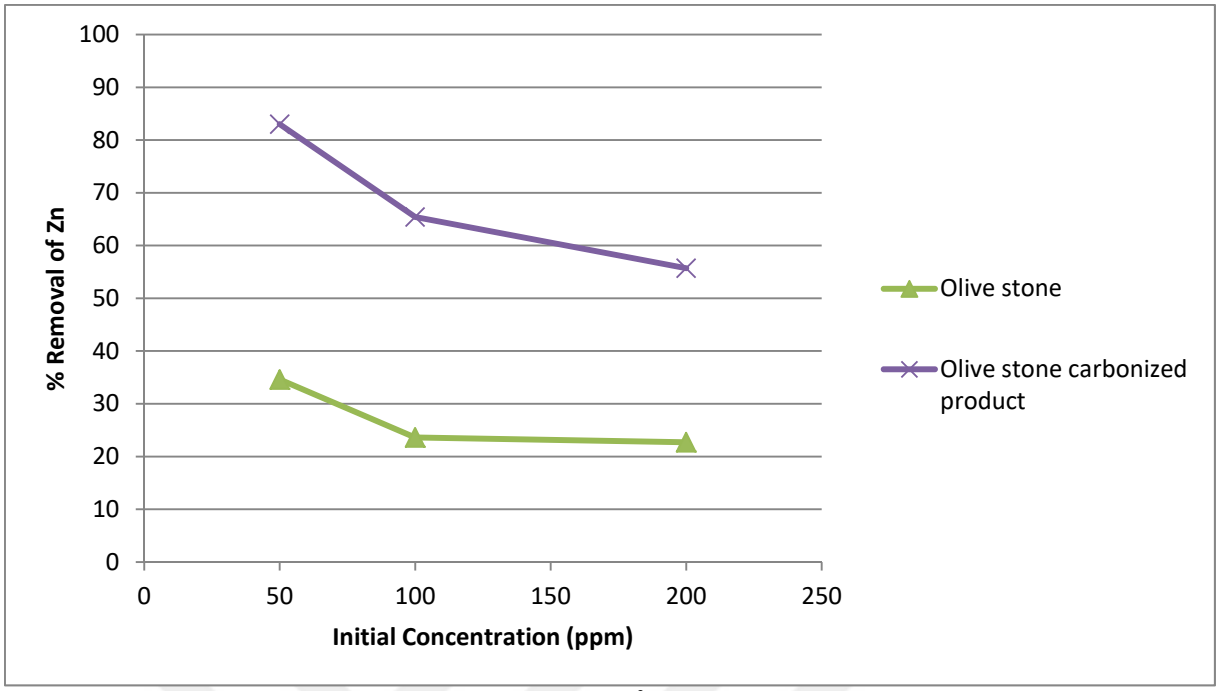

Figure 45. Effect of initial ion concentration on Zn^{+2} ion removal by olive stone and olive stone corbonized product

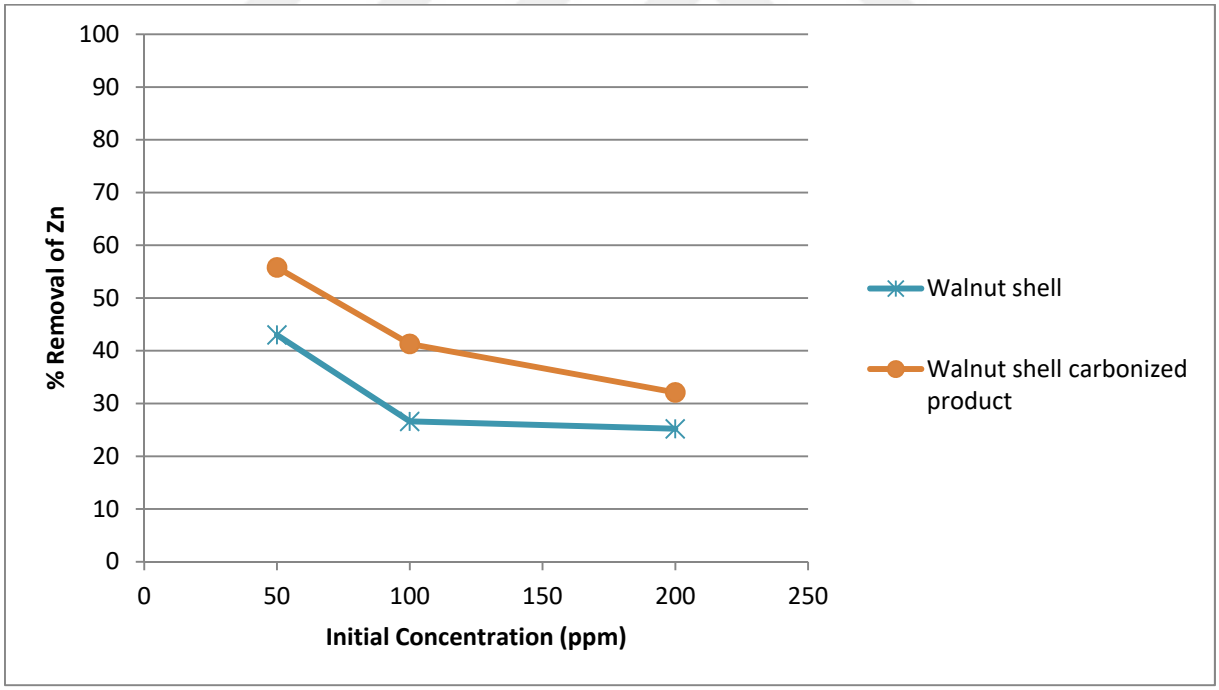

Figure 46. Effect of initial ion concentration on Zn^{+2} ion removal by walnut shell and walnut shell corbonized product

According to Figure 44, 45, and 46 the decreasing trend of the removal percentages of Zn^{+2} heavy metal ions while the solution concentration increased can be seen. When the initial concentration of mix solution was increased from 50 ppm to 200 ppm, the removal

percentages of Zn^{+2} was decreased about 20% for untreated natural adsorbents and their carbonized products.

In Figure 47, 48, and 49; removal percentages of Cd^{+2} ions verse the initial concentration of mix solution were shown graphically.

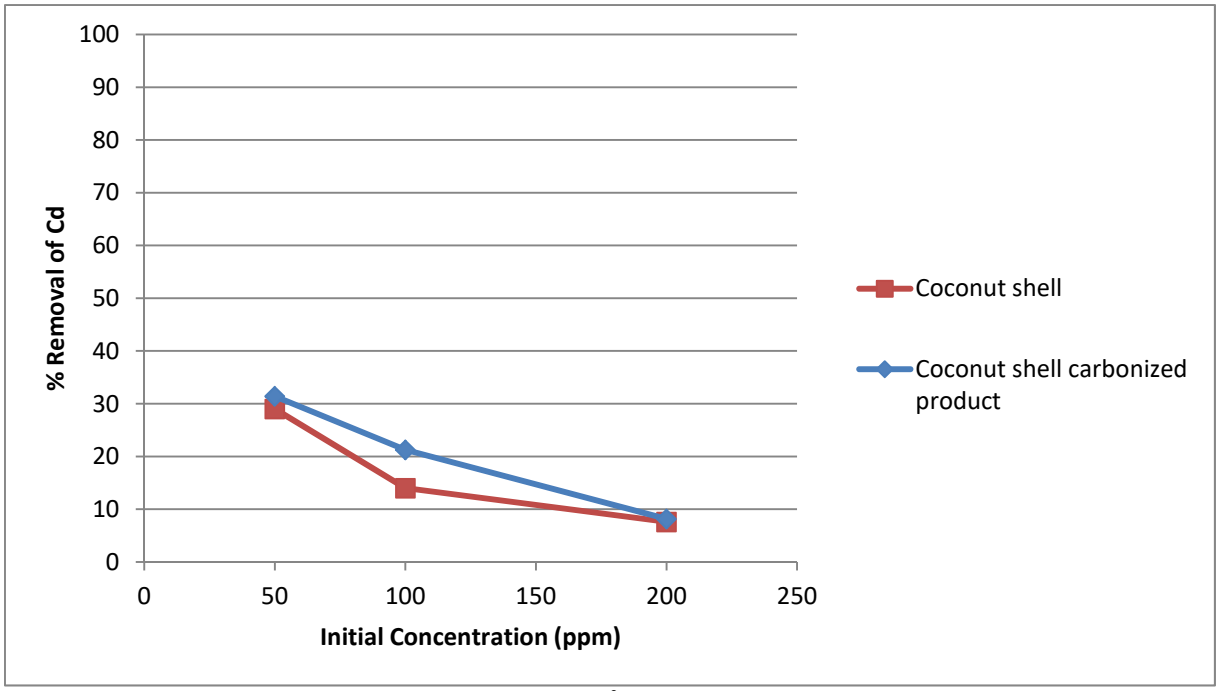

Figure 47. Effect of initial ion concentration on Cd^{+2} ion removal by coconut shell and coconut shell corbonized product

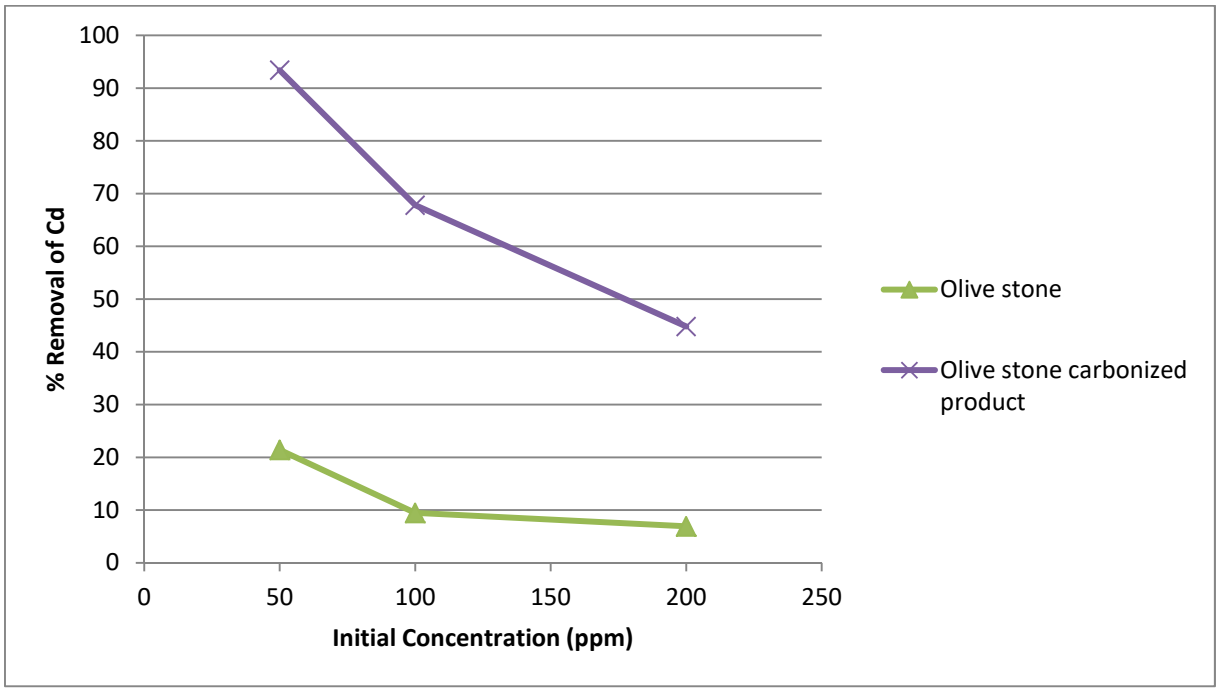

Figure 48. Effect of initial ion concentration on Cd^{+2} ion removal by olive stone and olive stone corbonized product

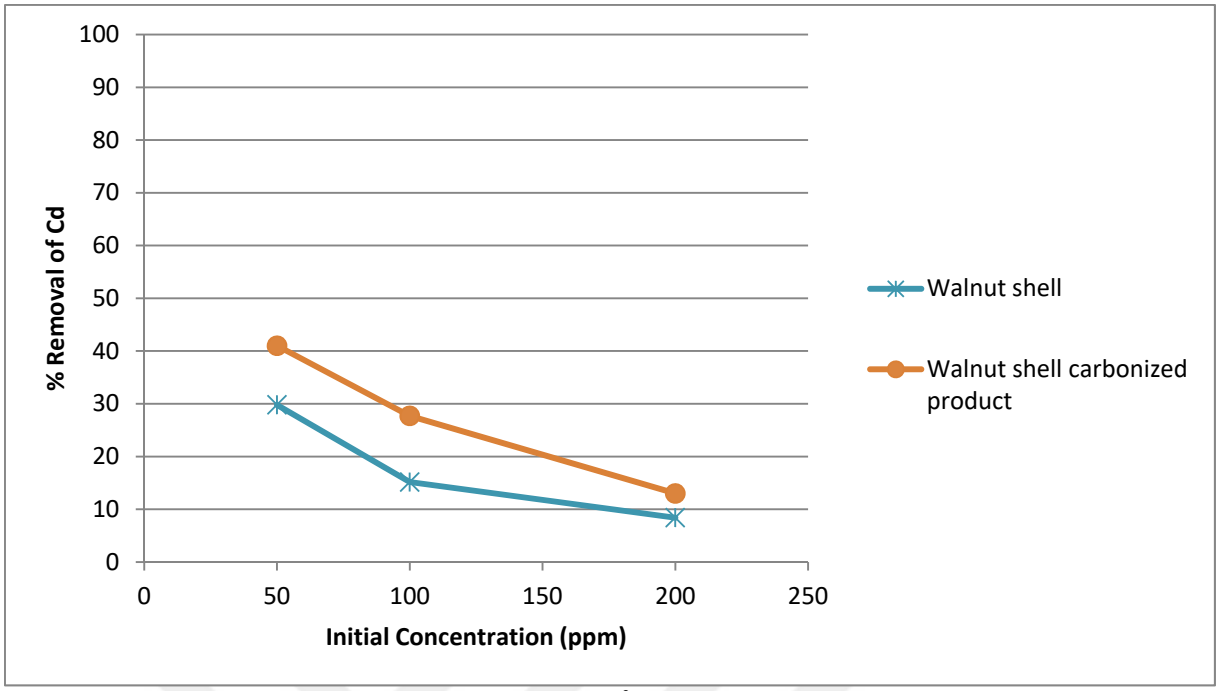

Figure 49. Effect of initial ion concentration on Cd^{+2} ion removal by walnut shell and walnut shell corbonized product

As could be seen from Figure 47, 48, and 49, when the initial concentration of the mixing solution was increased, natural untreated adsorbents and their carbonized products showed similar declining behaviour in the percentage of Cd^{+2} removal.

Removal percentages of Pb^{+2} ions verse initial concentration of mix solution were shown in Figure 50, 51, and 52.

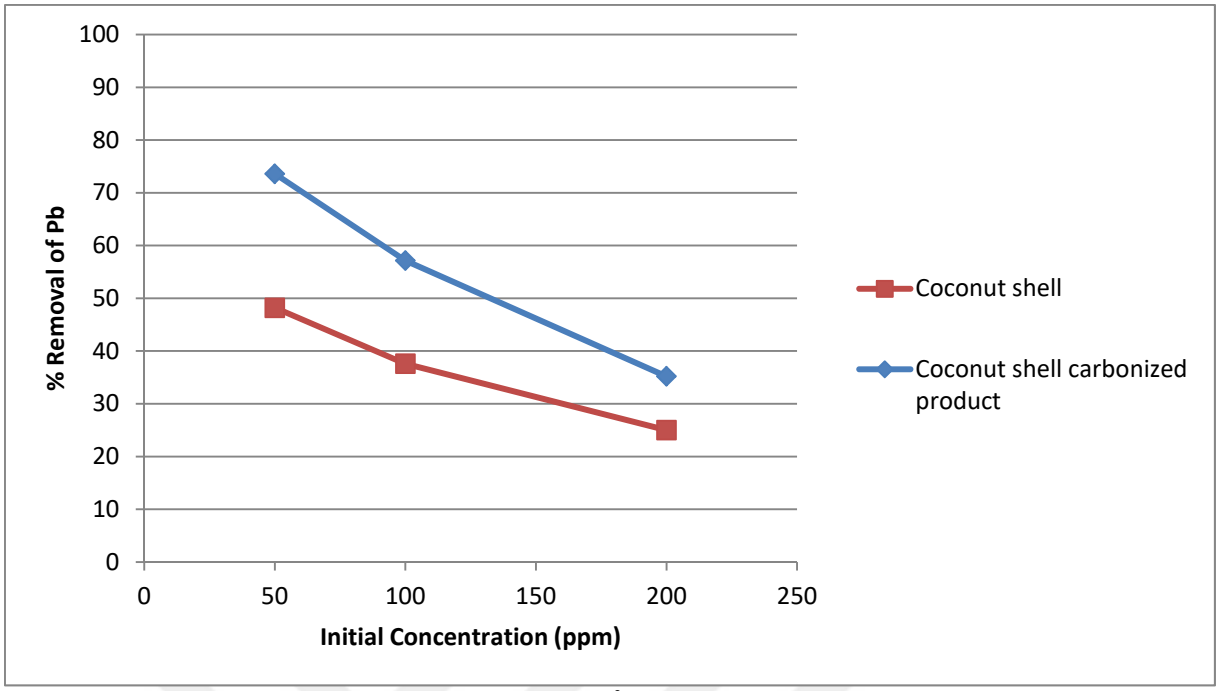

Figure 50. Effect of initial ion concentration on Pb^{+2} ion removal by coconut shell and coconut shell corbonized product

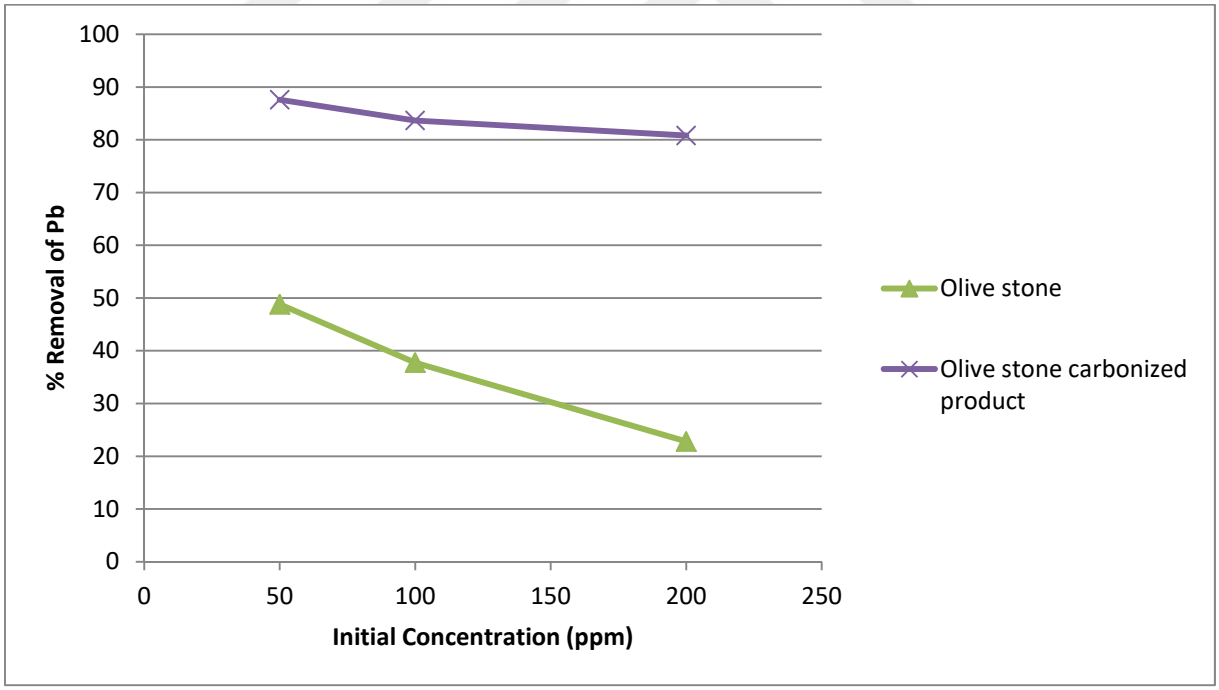

Figure 51. Effect of initial ion concentration on Pb^{+2} ion removal by olive stone and olive stone corbonized product

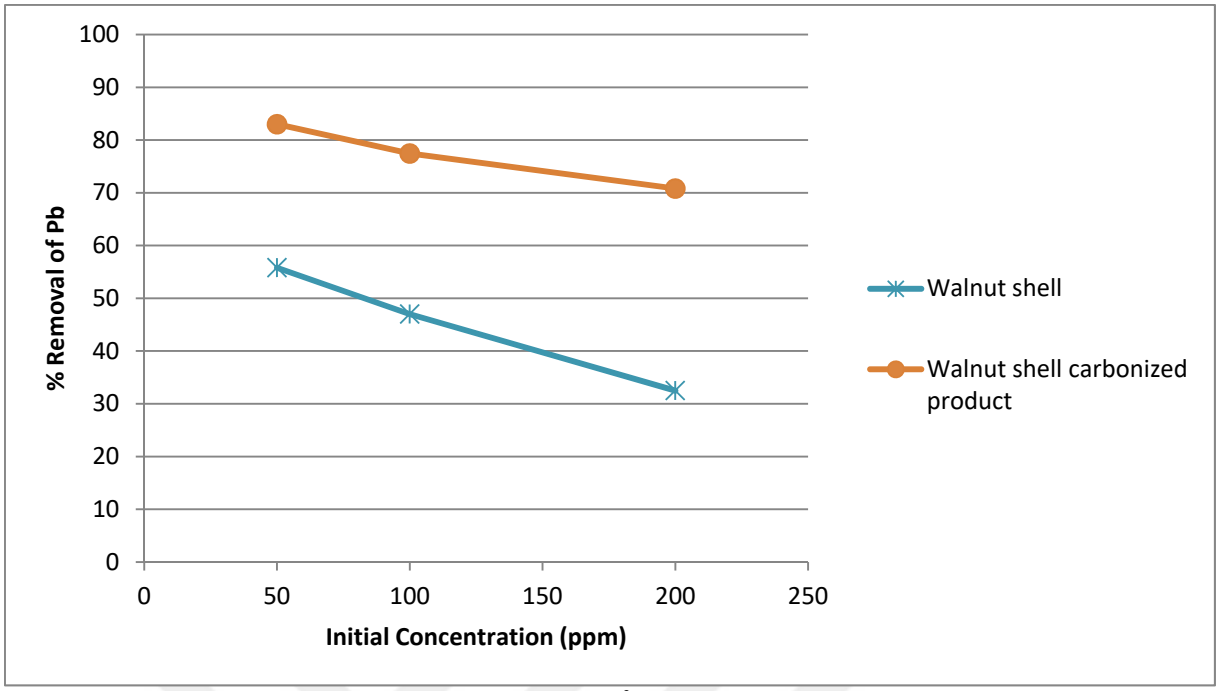

Figure 52. Effect of initial ion concentration on Pb^{+2} ion removal by walnut shell and walnut shell corbonized product

As shown in Figure 50, 51, and 52, for untreated adsorbent and their carbonized products, it is seen that the percentage of Pb^{+2} removal increases at 50 ppm, which is the initial concentration of the mixture solution, and the percentage of Pb^{+2} removal decreases when the initial concentration is increased to 200 ppm.

In the present study, in which the amount of untreated natural adsorbent and their carbonized products were kept constant, as shown in the figures above, for the removal of Zn^{+2}, Cd^{+2} and Pb^{+2} ions by using coconut shell, olive stone, walnut shell and their carbonized products, it was observed that the % removal of heavy metal ions decreased as the initial ion concentration increased. These results show that adsorption is affected by the initial concentration of metal ions. Since the ratio of surface, pores and cracks of adsorbent sites to total metal ions in solution is high at tested low ion concentrations, all metal ions can interact with the adsorbent and be removed from the solution (İpek, 2014). On the other hand, when the initial metal concentration is high, the suitable surface, pores and cracks of adsorbent is occupied with the potential heavy metal ions found in the solution. Therefore, decreases in metal removal are observed as the initial ion concentration increases. This finding is well consistent with the results published in the similar literature (Garg et al., 2008; Bansal et al., 2009; Gündoğdu, 2010; Al-Qahtani, 2015).

5. CONCLUSION

The increase in mining activities and industrialization may cause hazardous effects for the environment. One of these is heavy metal pollution in underground and surface waters, which has a toxic effect on living things. In this study; coconut shell, olive stone, walnut shell, and their carbonized products as adsorbents were investigated for the removal of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions from the synthetically prepared wastewater. Effect of adsorbent type, contact time, adsorbent dose, and initial ion concentration were selected as independent variables. Heavy metal removal percentage was selected as dependent variables.

The following results were obtained from the present study.

- The dose of adsorbent and the initial ion concentration were kept constant in the beginning experiments and the contact time was tested for different times: 30, 60 and 180 min. The contact time which is 180 min was determined as maximum contact time.
- It was found that the removal percentages of all tested heavy metal ions increased regularly when the contact time increased.
- The best removal for Zn^{+2} ion was 27.4%, for Cd^{+2} ion was 16.3 %, for Pb^{+2} ion was 29.7 % and these values were provided with olive stone carbonized product.
- The contact time and initial ion concentration were kept constant and the effect of the adsorbent doses on adsorption percentage was investigated and the maximum adsorbent dose was determined as 2.0% adsorbent amount (g)/solution volume (mL).
- It was determined that when the adsorbent dose was increased the removals of heavy metal ions were also increased.
- It was determined that the olive stone carbonized products have the maximum adsorption percentage for Zn^{+2}, Cd^{+2}, and Pb^{+2} ions (65.4%, 67.8%, and 83.7%, respectively).
- The effects of the initial ion concentration on the adsorption percentage were investigated for 50, 100, and 200 ppm by keeping the maximum adsorbent dose (2.0% adsorbent amount (g)/solution volume (mL)) and contact time (180 min).

Results showed that the lower initial ion concentration (50 ppm) provided better heavy metal removal than others. These results show that adsorption is affected by the initial ion concentration of metal ions. Since the ratio of surface, pores and cracks of adsorbent sites to total metal ions in solution is high at tested low ion concentrations, all metal ions can interact with the adsorbent and be removed from the solution.

- The performances of the carbonized products of tested adsorbents were found to be better than their untreated natural forms for the removal of heavy metal ions. The carbonization of the all three type adsorbents provides more and open pore structure in their physical bodies, and the higher porosity is responsible for the higher heavy metal removal from the solution. This was proven via micro images examination.

As a result, it was concluded that the coconut shell, olive stone, walnut shell and their carbonized products can be used as adsorbent for the removal of heavy metal ions from industrial wastewaters.

The best performed adsorbent for the adsorption of Zn^{+2}, Cd^{+2}, and Pb^{+2} ions among tested adsorbents was olive stone carbonized product. This should be investigated deeply in a separate research.

6. RECOMMENDATIONS

- In the adsorption studies of olive stone carbonized product, the removal of different heavy metals or other parameters affecting the adsorption can be studied.
- It can be studied on the recovery of heavy metal ions captured by using olive stone carbonized product.
- Kinetic studies or adsorption isotherms of olive stone carbonized product can be studied.

REFERENCES

Abdolali, A., Ngo, H. H., Guo, W., Lu, S., Chen, S. S., Nguyen, N. C., Zhang, X., Wang, J., & Wu, Y. (2016). A breakthrough biosorbent in removing heavy metals: Equilibrium, kinetic, thermodynamic and mechanism analyses in a lab-scale study. *Science of the Total Environment*, *542*, 603–611. https://doi.org/10.1016/j.scitotenv.2015.10.095.

Abdul Rahim, A. R., Mohsin, H. M., Thanabalan, M., Rabat, N. E., Saman, N., Mat, H., & Johari, K. (2020). Effective carbonaceous desiccated coconut waste adsorbent for application of heavy metal uptakes by adsorption: Equilibrium, kinetic and thermodynamics analysis. *Biomass and Bioenergy*, *142*(October), 105805. https://doi.org/10.1016/j.biombioe.2020.105805.

Aboudi Mana, S. C., Hanafiah, M. M., & Chowdhury, A. J. K. (2017). Environmental characteristics of clay and clay-based minerals. *Geology, Ecology, and Landscapes*, *1*(3), 155–161. https://doi.org/10.1080/24749508.2017.1361128.

Ahluwalia, S. S., & Goyal, D. (2007). Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology*, *98*(12), 2243–2257. https://doi.org/10.1016/j.biortech.2005.12.006.

Ahmaruzzaman, M. (2011). Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science*, *166*(1–2), 36–59. https://doi.org/10.1016/j.cis.2011.04.005.

Al-Qahtani, K. M. (2015). Water purification using different waste fruit cortexes for the removal of heavy metals. *Journal of Taibah University for Science*, *10*(5), 700–708. https://doi.org/10.1016/j.jtusci.2015.09.001.

Al-Rub, F. A. A., Kandah, M., & Al-Dabaybeh, N. (2002). Nickel Removal from Aqueous Solutions Using Sheep Manure Wastes. *Engineering in Life Sciences*, *2*(4), 111. https://doi.org/10.1002/1618-2863(200204)2:4<111::aid-elsc111>3.3.co;2-h.

Alalam, S., Marciniak, A., Lessard, M.-H., Berube, A., Chamberland, J., Pouliot, Y., Labrie, S., & Doyen, A. (2021). Evolution of Bacterial Communities during the Concentration and Recirculation of Dairy White Wastewater by Reverse Osmosis. *International Dairy Journal*, 118490. https://doi.org/10.1016/j.idairyj.2021.105283.

Ali, H., Khan, E., & Ilahi, I. (2019). Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. *Journal of Chemistry*, *2019*(Cd), 1–14. https://doi.org/10.1155/2019/6730305.

Aman, T., Kazi, A. A., Sabri, M. U., & Bano, Q. (2008). Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent. *Colloids and Surfaces B: Biointerfaces*, *63*(1), 116–121. https://doi.org/10.1016/j.colsurfb.2007.11.013.

Amarasinghe, B. M. W. P. K., & Williams, R. A. (2007). Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, *132*(1–3), 299–309. https://doi.org/10.1016/j.cej.2007.01.016.

Ayala, J., Blanco, F., García, P., Rodriguez, P., & Sancho, J. (1998). Asturian fly ash as a heavy metals removal material. *Fuel*, *77*(11), 1147–1154. https://doi.org/10.1016/S0016-2361(98)00027-1.

Ayten, Ş. (2006). *Farklı Adzorbanların Ağır Metal İyonlarını Tutma Kapasitelerinin Karşılaştırılması*. Celal Bayar Üniversitesi.

Babel, S., & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*, *97*(1–3), 219–243. https://doi.org/10.1016/S0304-3894(02)00263-7.

Babel, S., & Kurniawan, T. A. (2004). Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, *54*(7), 951–967. https://doi.org/10.1016/j.chemosphere.2003.10.001.

Badawi, A. K., & Zaher, K. (2021). Hybrid treatment system for real textile wastewater remediation based on coagulation/flocculation, adsorption and filtration processes: Performance and economic evaluation. *Journal of Water Process Engineering*, *40*(December 2020), 101963. https://doi.org/10.1016/j.jwpe.2021.101963.

Bakar, C., & Baba, A. (2009). Metaller VeİnsanSağliğiYirminci Yüzyildan Bugüne Ve GeleceğeMiras Kalan Çevre Sağliği Sorunu. *1. Tıbbi Jeoloji Çalıştayı*, 162–185.

Bansal, M., Garg, U., Singh, D., & Garg, V. K. (2009). Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: A case study of rice husk. *Journal of Hazardous Materials*, *162*(1), 312–320. https://doi.org/10.1016/j.jhazmat.2008.05.037.

Begum, S. A. S., Tharakeswar, Y., Kalyan, Y., & Naidu, G. R. (2015). Biosorption of Cd (II), Cr (VI) & Pb (II) from Aqueous Solution Using Mirabilis jalapa as Adsorbent. *Journal of Encapsulation and Adsorption Sciences*, *05*(02), 93–104. https://doi.org/10.4236/jeas.2015.52007.

Bohli, T., Ouederni, A., Fiol, N., & Villaescusa, I. (2015). Evaluation of an activated carbon from olive stones used as an adsorbent for heavy metal removal from aqueous phases. *Comptes Rendus Chimie*, *18*(1), 88–99. https://doi.org/10.1016/j.crci.2014.05.009.

Bolatkhan, K. (2009). *Kurutulmuş Alg Hücresi ile Metal Adsoprsiyonu*. Yıldız Teknik Üniversitesi.

Calero, M., Iáñez-Rodríguez, I., Pérez, A., Martín-Lara, M. A., & Blázquez, G. (2018). Neural fuzzy modelization of copper removal from water by biosorption in fixed-bed columns using olive stone and pinion shell. *Bioresource Technology*, *252*(December 2017), 100–109. https://doi.org/10.1016/j.biortech.2017.12.074.

Casiday, R., Noelken, G., & Frey, R. (1999). Treating the Public Water Supply: What Is In Your Water, and How Is It Made Safe to Drink. *Washington University*, 1–9. http://www.chemistry.wustl.edu/~edudev/LabTutorials/Water/PublicWaterSupply/PublicWaterSupply.html.

Çevre Kirliliği. (n.d.). Retrieved December 6, 2019, from http://cevreonline.com/cevre-kirliligi/

Chandana, L., Krushnamurty, K., Suryakala, D., & Subrahmanyam, C. (2018). Low-cost adsorbent derived from the coconut shell for the removal of hexavalent chromium from aqueous medium. *Materials Today: Proceedings*, *26*, 44–51. https://doi.org/10.1016/j.matpr.2019.04.205.

Chemical Precipitation. (n.d.). Retrieved February 17, 2021, from http://www.chemcollective.org/chem/ubc/exp01/index.php.

Claoston, N., Samsuri, A. W., Ahmad Husni, M. H., & Mohd Amran, M. S. (2014). Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. *Waste Management and Research*, *32*(4), 331–339. https://doi.org/10.1177/0734242X14525822.

Coagulation and Flocculation Process. (n.d.). Retrieved March 1, 2021, from https://pubs.acs.org/doi/pdf/10.1021/acs.iecr.5b04703.

Colella, C. (1996). Ion exchange equilibria in zeolite minerals. *Mineralium Deposita*, *31*(6), 554–562. https://doi.org/10.1007/s001260050062.

Das, N., Vimala, R., & Karthika, P. (2008). Biosorption of heavy metals - An overview. *Indian Journal of Biotechnology*, *7*(2), 159–169.

De Gisi, S., Lofrano, G., Grassi, M., & Notarnicola, M. (2016). Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustainable Materials and Technologies*, *9*, 10–40. https://doi.org/10.1016/j.susmat.2016.06.002.

Dhir, B. (2014). Potential of biological materials for removing heavy metals from wastewater. *Environmental Science and Pollution Research*, *21*(3), 1614–1627. https://doi.org/10.1007/s11356-013-2230-8.

Doğu, İ. (2019). *Manganez/Nikel Oksit Partikülleri İle Sentetik Atık Sularda Krom (VI) Giderimi*. Çanakkale Onsekiz Mart Üniversitesi.

Dönmez, R. (2006). *Doğal Kil Mineralleri Kullanarak Atık Sulardan Kurşun(2) İyonunun Adsorpsiyonu*. Celal Bayar Üniversitesi.

Duranoğlu, D., Trochimczuk, A. W., & Beker, Ü. (2010). A comparison study of peach stone and acrylonitrile-divinylbenzene copolymer based activated carbons as chromium(VI) sorbents. *Chemical Engineering Journal*, *165*(1), 56–63. https://doi.org/10.1016/j.cej.2010.08.054.

Electro-Dialysis Process. (n.d.). Retrieved March 1, 2021, from https://www.fumatech.com/EN/Membrane-processes/Process%2Bdescription/Electrodialysis/index.html.

Fiol, N., Villaescusa, I., Martínez, M., Miralles, N., Poch, J., & Serarols, J. (2006). Sorption of Pb(II), Ni(II), Cu(II) and Cd(II) from aqueous solution by olive stone waste. *Separation and Purification Technology*, *50*(1), 132–140. https://doi.org/10.1016/j.seppur.2005.11.016.

Fırat, B. (2007). Atık sulardan kurşun(II) ve bakır(II) iyonlarının yumurta kabuğu ile uzaklaştırılması ve optimum koşulların belirlenmesi. In *Kimya Mühendisliği Programı* (Issue Ii). GAZİ ÜNİVERSİTESİ.

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management*. https://doi.org/10.1016/j.jenvman.2010.11.011.

Garg, U., Kaur, M. P., Jawa, G. K., Sud, D., & Garg, V. K. (2008). Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass. *Journal of Hazardous Materials*, *154*(1–3), 1149–1157. https://doi.org/10.1016/j.jhazmat.2007.11.040.

Golomeova, M., & Zendelska, A. (2016). Application of Some Natural Porous Raw Materials for Removal of Lead and Zinc from Aqueous Solutions. *Microporous and Mesoporous Materials*. https://doi.org/10.5772/62347.

González, A. G., Pokrovsky, O. S., Santana-Casiano, J. M., & González-Dávila, M. (2017). Bioadsorption of heavy metals. *Prospects and Challenges in Algal Biotechnology*, *4*(1), 233–255. https://doi.org/10.1007/978-981-10-1950-0_8.

Gunatilake, S. K. (2015). Methods of Removing Heavy Metals from Industrial Wastewater. *Multidisciplinary Engineering Scinece Studies (JMESS)*, *1*(1), 12–18. www.jmess.org.

Gündoğdu, A. (2010). *Fabrika Çay Atıklarından Aktif Karbon Üretimi, Karakterizasyonu ve Adsorpsiyon Özelliklerinin İncelenmesi*. Karadeniz Teknik Üniversitesi.

Hansen, H. K., Arancibia, F., & Gutiérrez, C. (2010). Adsorption of copper onto agriculture waste materials. *Journal of Hazardous Materials*, *180*(1–3), 442–448. https://doi.org/10.1016/j.jhazmat.2010.04.050.

Hegazi, H. A. (2013). Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. *HBRC Journal*, *9*(3), 276–282. https://doi.org/10.1016/j.hbrcj.2013.08.004.

Igwe, J. C., Ogunewe, D. N., & Abia, A. A. (2005). Competitive adsorption of Zn (II), Cd (II) AND Pb (II) ions from aqueous and non- aqueous solution by maize cob and husk. *African Journal of Biotechnology*, *4*(10), 1113–1116.

İnce, M., & Kaplan İnce, O. (2017). An Overview of Adsorption Technique for Heavy Metal Removal from Water/Wastewater: A Critical Review. *International Journal of Pure and Applied Sciences*, *3*(2), 10–19. https://doi.org/10.29132/ijpas.372335.

Ion-Exchange Process. (n.d.). Retrieved March 1, 2021, from http://jbcc-iagwsp.org/community/facts/ion_jun04.html.

İpek, B. (2014). *Kadmiyum(II) ve Nikel(II) İyonlarının Karayosunu üzerinde Adsorpsiyonla su ve atık sulardan uzaklaştırılması*. Karadeniz Teknik Üniversitesi.

Jain, C. K., Malik, D. S., & Yadav, A. K. (2016). Applicability of plant based biosorbents in the removal of heavy metals: a review. *Environmental Processes*, *3*(2), 495–523. https://doi.org/10.1007/s40710-016-0143-5.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*, *7*(2), 60–72. https://doi.org/10.2478/intox-2014-0009.

James, A., & Yadav, D. (2021). Valorization of coconut waste for facile treatment of contaminated water: A comprehensive review (2010–2021). *Environmental Technology & Innovation*, *24*, 102075. https://doi.org/10.1016/j.eti.2021.102075.

Kabuba, J., & Banza, M. (2020). Ion-exchange process for the removal of Ni (II) and Co (II) from wastewater using modified clinoptilolite: Modeling by response surface methodology and artificial neural network. *Results in Engineering*, *8*(September), 100189. https://doi.org/10.1016/j.rineng.2020.100189.

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. *Bioresource Technology*, *76*(1), 63–65. https://doi.org/10.1016/S0960-8524(00)00072-9.

Kaur, A., & Sharma, S. (2017). Removal of Heavy Metals from Waste Water by using Various Adsorbents- A Review. *Indian Journal of Science and Technology*, *10*(34), 1–14. https://doi.org/10.17485/ijst/2017/v10i34/117269.

Kobya, M., Demirbas, E., Senturk, E., & Ince, M. (2005). Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresource Technology*, *96*(13), 1518–1521. https://doi.org/10.1016/j.biortech.2004.12.005.

Lin, L. C., Li, J. K., & Juang, R. S. (2008). Removal of Cu(II) and Ni(II) from aqueous solutions using batch and fixed-bed ion exchange processes. *Desalination*, *225*(1–3), 249–259. https://doi.org/10.1016/j.desal.2007.03.017.

Lopes, T. S. de A., Heßler, R., Bohner, C., Athayde Junior, G. B., & de Sena, R. F. (2020). Pesticides removal from industrial wastewater by a membrane bioreactor and post-treatment with either activated carbon, reverse osmosis or ozonation. *Journal of Environmental Chemical Engineering*, *8*(6). https://doi.org/10.1016/j.jece.2020.104538.

Milojković, J., Stojanović, M., Mihajlović, M., Lopičić, Z., Šoštarić, T., Petrović, M., & Petrović, J. (2016). Pb(II) biosorption by selected waste biomass. *Zastita Materijala*, *57*(3), 418–423. https://doi.org/10.5937/zasmat1603418m.

Mo, J., Yang, Q., Zhang, N., Zhang, W., Zheng, Y., & Zhang, Z. (2018). A review on agro-industrial waste (AIW) derived adsorbents for water and wastewater treatment. *Journal of Environmental Management*, *227*(April), 395–405. https://doi.org/10.1016/j.jenvman.2018.08.069.

Mobasherpour, I., Salahi, E., & Pazouki, M. (2012). Comparative of the removal of Pb 2+, Cd 2+ and Ni 2+ by nano crystallite hydroxyapatite from aqueous solutions: Adsorption isotherm study. *Arabian Journal of Chemistry*, *5*(4), 439–446. https://doi.org/10.1016/j.arabjc.2010.12.022.

Moodley, K., Singh, R., Musapatika, E. T., Onyango, M. S., & Ochieng, A. (2011). Removal of nickel from wastewater using an agricultural adsorbent. *Water SA*, *37*(1), 41–46. https://doi.org/10.4314/wsa.v37i1.64105.

Murathan, A., & Koçyiğit, H. (2014). Sulu Çözeltilerden Kadmiyum İyonlarının Dolgulu Yataklarda At Kestanesi Ve Meşe Palamudu Kullanılarak Giderilmesi. *Gazi Üniversitesi Mühendislik-Mimarlık Fakültesi Dergisi*, *28*(2), 303–306. http://dergipark.gov.tr/gazimmfd/issue/6703/89088.

Öngül Bülbül, H. (2019). *Polyhipe Supported Sorbent for Selective Mercury Removal From Aqueous Solutions*. ISTANBUL TECHNICAL UNIVERSITY.

Osmanlioglu, A. E. (2018). Decontamination of radioactive wastewater by two-staged chemical precipitation. *Nuclear Engineering and Technology*, *50*(6), 886–889. https://doi.org/10.1016/j.net.2018.04.009.

Packialakshmi, S., Anuradha, B., Nagamani, K., Sarala Devi, J., & Sujatha, S. (2021). Treatment of industrial wastewater using coconut shell based activated carbon. *Materials Today: Proceedings*, *xxxx*. https://doi.org/10.1016/j.matpr.2021.04.548.

Particle Size of Colloidal Solution. (n.d.). Retrieved March 1, 2021, from https://www.api.simply.science/images/content/chemistry/states_of_matter/solutions/conceptmap/solutions.html.

Pathak, P. D., Mandavgane, S. A., & Kulkarni, B. D. (2015). Fruit peel waste as a novel low-cost bio adsorbent. *Reviews in Chemical Engineering*, *31*(4), 361–381. https://doi.org/10.1515/revce-2014-0041.

Peters, R., & Shem, L. (n.d.). *Separation of Heavy Metals: Removal From Industry*.

Pino, G. H., Souza De Mesquita, L. M., Torem, M. L., & Pinto, G. A. S. (2006). Biosorption of cadmium by green coconut shell powder. *Minerals Engineering*, *19*(5), 380–387. https://doi.org/10.1016/j.mineng.2005.12.003.

Pugazhenthiran, N., Anandan, S., & Ashokkumar, M. (2016). Removal of Heavy Metal from Wastewater. In *Handbook of Ultrasonics and Sonochemistry* (Issue July, pp. 813–839). Springer Singapore. https://doi.org/10.1007/978-981-287-278-4_58.

Qi, B., Jiang, X., Wang, H., Li, J., Zhao, Q., Li, R., & Wang, W. (2021). Resource recovery from liquid digestate of swine wastewater by an ultrafiltration membrane bioreactor (UF-MBR) and reverse osmosis (RO) process. *Environmental Technology and Innovation*, *24*, 101830. https://doi.org/10.1016/j.eti.2021.101830.

Rahman, H. L. (2017). *As (V) Removal From Aqueous Solutions With Magnetic Activated Carbon Prepared From Almond Shell, Apricot and Peach Stones Mixture*. FIRAT UNIVERSITY.

Raval, N. P., Shah, P. U., & Shah, N. K. (2016). Adsorptive removal of nickel(II) ions from aqueous environment: A review. *Journal of Environmental Management*, *179*, 1–20. https://doi.org/10.1016/j.jenvman.2016.04.045.

Reverse Osmosis. (n.d.). Retrieved March 1, 2021, from https://benjaminfranklinplumbingfortworth.com/plumbing-blog/reverse-osmosis-water-filtration-system-arlington-texas/.

Reyes-Serrano, A., López-Alejo, J. E., Hernández-Cortázar, M. A., & Elizalde, I. (2020). Removing contaminants from tannery wastewater by chemical precipitation using CaO and Ca(OH)2. *Chinese Journal of Chemical Engineering*, *28*(4), 1107–1111. https://doi.org/10.1016/j.cjche.2019.12.023.

Salman, H. A., Ibrahim, M. I., Tarek, M. M., & Abbas, H. S. (2014). Biosorption of heavy metals: A review. *Journal of Chemical Science and Technology*, *3*(4), 74–102.

Sayegh, A., Shylaja Prakash, N., Pedersen, T. H., Horn, H., & Saravia, F. (2021). Treatment of hydrothermal liquefaction wastewater with ultrafiltration and air stripping for oil and particle removal and ammonia recovery. *Journal of Water Process Engineering*, *44*(September), 102427. https://doi.org/10.1016/j.jwpe.2021.102427.

Seven, T., Can, B., Darende, B. N., & Ocak, S. (2018). Hava ve Toprakta Ağır Metal Kirliliği. *Ulusal Çevre Bilimleri Araştırma Dergisi*, *1*(2), 91–103.

Stratejik Çevresel Değerlendirme Yönetmeliği, (2017). https://www.resmigazete.gov.tr/eskiler/2017/04/20170408-3.htm.

Su Kirliliği Yönetmeliği, Pub. L. No. Resmî Gazete Sayısı: 25687 (2004). https://www.mevzuat.gov.tr/Metin.Aspx?MevzuatKod=7.5.7221&sourceXmlSearch=&MevzuatIliski=0.

Tripathi, A., & Rawat Ranjan, M. (2015). Heavy Metal Removal from Wastewater Using Low Cost Adsorbents. *Journal of Bioremediation & Biodegradation*, *06*(06). https://doi.org/10.4172/2155-6199.1000315.

Ultrafiltration Pore Size. (n.d.). Retrieved March 1, 2021, from http://www.teknikaritma.com.tr/eng/default.asp?rsm=121118000000.

Vakili, M., Deng, S., Cagnetta, G., Wang, W., Meng, P., Liu, D., & Yu, G. (2019). Regeneration of chitosan-based adsorbents used in heavy metal adsorption: A review. *Separation and Purification Technology*, *224*(May), 373–387. https://doi.org/10.1016/j.seppur.2019.05.040.

Visa, M., Isac, L., & Duta, A. (2012). Fly ash adsorbents for multi-cation wastewater treatment. *Applied Surface Science*, *258*(17), 6345–6352. https://doi.org/10.1016/j.apsusc.2012.03.035.

Wang, F. Y., Wang, H., & Ma, J. W. (2010). Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent-Bamboo charcoal. *Journal of Hazardous Materials*, *177*(1–3), 300–306. https://doi.org/10.1016/j.jhazmat.2009.12.032.

Wang, S., Li, L., & Zhu, Z. H. (2007). Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater. *Journal of Hazardous Materials*, *139*(2), 254–259. https://doi.org/10.1016/j.jhazmat.2006.06.018.

Wanyonyi, W. C., Onyari, J. M., Shiundu, P. M., & Mulaa, F. J. (2019). Effective biotransformation of reactive black 5 dye using crude protease from Bacillus cereus Strain KM201428. *Energy Procedia*, *157*, 815–824. https://doi.org/10.1016/j.egypro.2018.11.247.

Warwick, C., Guerreiro, A., & Soares, A. (2013). Sensing and analysis of soluble phosphates in environmental samples: A review. *Biosensors and Bioelectronics*, *41*(1), 1–11. https://doi.org/10.1016/j.bios.2012.07.012.

Water. (n.d.). Retrieved February 17, 2021, from https://www1.health.gov.au/internet/publications/publishing.nsf/Content/ohp-enhealth-manual-atsi-cnt-l~ohp-enhealth-manual-atsi-cnt-l-ch6~ohp-enhealth-manual-atsi-cnt-l-ch6.1.

Yakout, S. M., & Sharaf El-Deen, G. (2016). Characterization of activated carbon prepared by phosphoric acid activation of olive stones. *Arabian Journal of Chemistry*, *9*, S1155–S1162. https://doi.org/10.1016/j.arabjc.2011.12.002.

Zhai, Q., Lu, H., Liu, R., He, D., Wang, C., & Sun, W. (2021). Removal of suspended solids from weathered tungsten-ore beneficiation wastewater by electroneutralization and chemical precipitation. *Minerals Engineering*, *173*(September), 107167. https://doi.org/10.1016/j.mineng.2021.107167.

Zhang, H., Lin, H., Li, Q., Cheng, C., Shen, H., Zhang, Z., Zhang, Z., & Wang, H. (2021). Removal of refractory organics in wastewater by coagulation/flocculation with green chlorine-free coagulants. *Science of the Total Environment*, *787*, 147654. https://doi.org/10.1016/j.scitotenv.2021.147654.

Zhang, J., Weston, G., Yang, X., Gray, S., & Duke, M. (2020). Removal of herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) from saline industrial wastewater by reverse osmosis and nanofiltration. *Desalination*, *496*(May), 114691. https://doi.org/10.1016/j.desal.2020.114691.