

Elif YENİLMEZ

**THE INVESTIGATION OF REUSE OF
DRIED ACTIVATED SLUDGE FOR
ADSORPTION OF Cd, Cr AND Pb METALS**

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M.S. Thesis in Chemistry

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APPROVAL PAGE

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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Supervisor: Assoc. Prof. Abdülhadi BAYKAL

ABSTRACT

The main objective of this study was to investigate the feasibility of using textile sludge as activated sludge based adsorbents for the removal of the metal ions which are Pb, Cd and Cr from aqueous solutions. Since the textile treatment sludge was not appreciable to dispose on sanitary landfill sites according to the analysis given on Regulation on Sanitary Landfill of Wastes, it was aimed to use it as an adsorbent for metal purification from wastewaters. By this way, two different types of wastewater-treatment sludge and wastewater- will be disposed.

In this study, also comparative adsorption studies of heavy metal ions, Cr (III), Pb (II), Cd (II), on activated sludge were performed to investigate the uptake performances. Batch adsorption experiments were performed at five different initial heavy metal ion concentrations (50, 75, 100, 150, 250 mg/L) with different adsorbent weights, time period ranging from 5 minutes to 90 minutes.

The adsorption characteristics of Pb (II), Cd (II), Cr (III) were studied by various models, such as Freundlich and Langmuir isotherm equation. Adsorption capacity (q_m) of the activated sludge were found to be decreased in the order of Pb(II)>Cd(II)>Cr(III). The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to determine kinetics parameters of adsorption of Pb(II) and Cd(II). It was found that the pseudo-first-order model fitted the adsorption process of lead while the pseudo-second-order model fitted well the adsorption of cadmium.

Both of the Freundlich and Langmuir adsorption isotherms are seem to adequately represent the adsorption data obtained in this study.

Keywords: Adsorption, heavy metals, treatment sludge, wastewater.

KURUTULMUŞ AKTİF ÇAMURUN Cd, Cr ve Pb METALLERİNİN ADSORPSİYONUNDA KULLANILMASININ ARAŞTIRILMASI

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ÖZ

Bu çalışmanın ana amacı kurutulmuş aktif çamurun atıksulardaki Pb, Cd ve Cr metallерinin adsorpsiyonunda kullanılmasıdır. Adsorban olarak kullanılan tekstil çamuru Atıkların Düzenli Depolanmasına İlişkin Yönetmeliğinde verilen parametreleri sağlamadığından düzenli depolama yapılamaz. Bu yüzden bu atığın adsorban olarak değerlendirilmesi amaçlanmıştır. Aynı zamanda bu şekilde iki atık türü tek bir yöntemle bertaraf edilmiş olacaktır.

Bu çalışmada Pb (II), Cd (II), Cr (III) metallерinin aktif çamur üzerindeki adsorplama kapasitelerini belirlemek için çalışılmıştır. Beş farklı başlangıç konsantrasyonuna (50, 75, 100, 150, 250 mg/L) sahip metal solüsyonları, farklı adsorban miktarları ve 5 dakikadan 90 dakikaya kadar karıştırma zaman aralığında çalışmalar yapılmıştır.

Pb (II), Cd (II) ve Cr (III) metallерinin farklı adsorpsiyon kapasitelerinin tayini için Langmuir ve Freundlich isotermleri çalışılmıştır. Aktif çamurun metalleri adsorplama kapasitesinin Pb(II)>Cd(II)>Cr(III) doğrultusunda azaldığı görülmüştür. Pb (II) ve Cd (II) için pseudo-second order, pseudo first order ve partiküller içi uzaklık belirlenmesi için kinetic çalışmalar yapılmıştır Pseudo-first order modelinin kurşun adsorpsiyonuna, pseudo-second-order modelinin ise cadmium adsorpsiyonuna uygun olduğu görülmüştür.

Freundlich ve Langmuir isotermleri de bu çalışmada elde edilen adsorpsiyon verilerini yeterince temsil ettiği görülmüştür.

Anahtar Kelimeler: Adsorpsiyon, ağır metallер, arıtma çamuru, atıksu.

This dissertation is dedicated to my dear father and mother
Ali & Fatma Yenilmez

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CHAPTER 1

INTRODUCTION

1.1. BACKGROUND

The earth faces with environmental pollution due to the rapid increase in population in consequence of the problem from developing technology and industrialization. Environmental pollution has emerged for the first time as a result of the start of urban life and increased in parallel with industrial development. Especially in the second half of the twentieth century, environmental pollution rising with the increasement in population led to living sources more polluted and ultimately ecosystem degradation become gradually more serious. Indeed, since the water environment a part of the ecosystem is used as a receiver and repellent region for used water and other wastes; it is the most suffered part of the ecosystem from pollution in proportion to the air and soil.

The pollutants disrupting the natural balance can be as follows: radioactivity, organic substances, industrial wastes, inorganic salts, petroleum derivatives, and organic chemicals synthetic agricultural fertilizers, detergents, and pesticides, synthetic and waste heat. According to this classification, heavy metals take place within industrial wastes and some pesticides and reach to become a threat to the ecosystem balance [1].

Everyday, many new industrial plants are added to the current plants dependent on the process of the industrial development. Depending on the branches of a developing industry, various pollutants raise the effect on air, water and soil ecosystems which are essential for our lives. In this respect, the type of environment polluting industrials and their pollutant concentrations make difficult to solve the problems

resulting from the interaction between pollutants. That's why; it is needed to treat all industrial pollution at source by using effective and new technologies.

It is estimated that as in nowadays, the increase in the output of the treatment sludge both from the domestic and industrial wastewater treatment plants cause significant environmental problems in the future in parallel with the increased standards for environmental investments [2].

Despite the trace amounts of heavy metals in the marine environment, their natural levels and deposits are different in organism. Heavy metal expression covers all the metals and metalloids in nature. These metals have a continuous impact on marine ecosystem because of the toxic effects on humans and marine organisms though very low concentrations and because of causing environmental pollution. In parallel with the rapid development of industry and raising the living standards, usage areas of heavy metals also increase gradually. Being indispensable for life, being used in every aspect of life and being used consistently of water demonstrates the importance of water quality needed for drinking and using, and the protection of water resources. All kinds of substances which could be found in water are harmful to health over a certain concentration. Therefore, contaminants in water must be removed. For this, biological or chemical methods are appealed such as chemical precipitation, ion exchange, membrane filtration, reverse osmosis, adsorption and co-precipitation [3].

Disposing of heavy metals randomly causes the contamination of water resources, and therefore it becomes important all around the world. It is well known that some metals can have toxic or harmful effects on many forms of life. In the Water Framework Directive, Chromium (Cr), Copper (Cu), Lead (Pb), Cadmium (Cd) and Mercury (Hg) are one of 11 hazardous substances in the list of pollutants contained and they are the most toxic metals among other heavy metals [4]. One or more of these toxic heavy metals are involved in wastewaters produced from many industries such as metallurgical, tannery, chemical manufacturing, mining, battery manufacturing industries. The concentration of metals is sometimes higher than permissible discharge levels in effluents. Hence, these toxic heavy metals should be removed from wastewaters to a applicable extent by a suitable treatment [5]. Activated carbon has

been widely used to remove heavy metals from wastewater. However, activated carbon is a very expensive material.

The importance of using wastes as production starting materials is put forward by trends on new materials. Reusing or recycling the wastes decreases the environmental problems combined with their build-up and decline the use of noble starting materials [6].

European Union Member Countries are recommended by European Directive 91/271 that cities with an equivalent population over 2000 should have a wastewater treatment plant by 2006. Because of that an increasing number of wastewater treatment plants are being open under this directive [2,7,8]. Since Turkey is in the European Union accession process, it must also perform this regulation. Environmental improvements have begun with this, but, at the same time, the amount of sludge produced has increased.

Heavy metal contamination of natural resources including water has become a great concern today. Quick industrialization producing large volumes of waste are one of the main reasons for water and other environmental resources contamination by heavy metals [9]. Nearly 46 % industrial waste consists of sludge. Activated sludge from wastewater treatment processes makes up the greater part of the waste sludge. Hence, it is necessary to generate a system for recycling the activated sludge. Using sludge as a fertilizer, as building materials or sometimes as a fuel are the recycling systems created so far [10].

It is presumed that the colloidal nature of the material, the rapidity of action, and the absence of replaceable anions provide sludge to perform as a zeolite [11]. Microorganisms accumulating heavy metals on their cell walls or in their cell membranes are present in sludge [12,13], and therefore sludge sometimes concentrates these heavy metals influencing crops and humans negatively [14]. Most of the experiments on the storage of a number of chemical species in activated sludge have only taken into consideration the equilibrium state between aqueous phase and sludge within short time periods (several hours) [12], presuming mediately adsorption event. In this work, textile sludge was used as an adsorbent for metal purification.

1.2. PURPOSE

The main objective of this study was to investigate the feasibility of using textile sludge as activated sludge based adsorbents for the removal of the metal ions which are Pb, Cr and Cd from aqueous solutions.

Since the textile treatment sludge was not appreciable to dispose on sanitary landfill sites according to the analysis given on Regulation on Sanitary Landfill of Wastes, it was aimed to use it as an adsorbent for metal purification from wastewaters. By this way, two different types of wastes- treatment sludge and wastewater- will be disposed.

1.3. HEAVY METALS

The term heavy metal refers to the elements with high atomic weights (atomic number is often greater than 20) and transition metals in periodic table. They are generally considered as a metal with density exceeding 5 g/cm^3 [15,16]. Some toxic heavy metals are cadmium (Cd^{2+}), copper (Cu^{2+}), lead (Pb^{2+}), mercury (Hg^{2+}), nickel (Ni^{2+}), chromium (Cr^{2+}) and zinc (Zn^{2+}) etc. Heavy metal ions are among the most important pollutants of water. The toxic heavy metals cause significant effect on the aqueous environment, animals and humans.

Since heavy metals are not biodegradable and tend to store in living organisms, its higher amounts result in several diseases and disorders [17]. As a consequence of artifactitious industrial activities, rock minerals and basic soil materials heavy metals have scattered into huge areas [18]. Heavy metals are found in the environment due to the waste disposal and industrial activities involving the mining industry, metal industry, coating/electroplating industry, production and deposition of batteries, burning of fossil fuels, the use of phosphate fertilizers, waste incineration, leaching from waste deposits [19].

1.3.1. Lead (Pb)

Native lead is rare in nature. Currently lead is usually found in ore with zinc, silver and copper and it is extracted together with these metals. The main lead mineral in Galena (PbS) and there are also deposits of cerrussite (PbCO₃), chrome yellow (PbCrO₄) and anglesite (PbSO₄) which are mined [20]. Galena has a cubic crystal structure and is bright and metallic mineral [21]. Lead is a silver-gray in color and the most soft and heavy one among the all known metals. It is named as Blei, Plumbum, and Lead. Atomic weight is 82, and appears in 4A group in periodic table. Lead melts at 327°C, boils at 1740°C. It is the most found heavy metal [3]. Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead isotopes are the end products of each of the three series of naturally occurring radioactive elements.

Some practices of lead, one of the most commonly used non-ferrous metals, and its compounds are building constructions, ammunition, solder, cable sheathing and pipework, storage batteries, , storage tank lining, corrosive liquid containers, catalysers, antibacterial substances, for radiation shielding, , as pigments in paints and ceramics, and wood preservatives [22]. Lead occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline an unnatural lead-cycle has consisted. In car engines lead is burned, so that lead salts (chlorines, bromines, and oxides) will originate. These lead salts enter the environment through the exhausts of cars. The larger particles will drop to the ground immediately and pollute soils or surface waters, the smaller particles will travel long distances through air and remain in the atmosphere. Part of this lead will fall back on earth when it is raining. This lead-cycle caused by human production is much more extended than the natural lead-cycle. It has caused lead pollution to be a worldwide issue.

Not only leaded gasoline causes lead concentrations in the environment to rise. Other human activities, such as fuel combustion, industrial processes and solid waste combustion, also contribute. Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints.

It cannot be broken down; it can only be converted to other forms. Lead accumulates in the bodies of water organisms and soil organisms. These will experience health effects from lead poisoning. Health effects on shellfish can take place even when only very small concentrations of lead are present. Body functions of phytoplankton can be disturbed when lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it [20]. All lead compounds are cumulative poisons that normally affect the gastrointestinal tract, the nervous system and sometimes both [23]. Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present. Soil organisms then suffer from lead poisoning, too. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains. For more effects on freshwater ecosystem take a look at lead in freshwater.

Lead is used in battery and accumulator production and dye industry. It is generally found in dust produced from melting, wastewater from dye preparation industry, stored or disposed batteries, emission from exhaust fume. Its amount in soil and plant is in trace amounts. Lead has many outcomes to human health. Despite slow lead adsorption, it favors to stock the place where it goes into. Red blood cells actuate the lead stored in liver and kidney, scattered to bone tissue, teeth and brain. Toxic effects of lead are not observed instantly on bones; however, at advanced age or in cortison treatment its harmful appears effectively. The main symptoms are nervous system disorders, anemia and calitis pain. Lead taken from the roots of plants results in plant poisoning. By respiration or eating leaded plants, animals get lead. Anemia is the first symptom of lead poisoning in animals and central nervous system disorders is for in children [24,25].

1.3.2. Chromium (Cr)

Chromium is a lustrous, brittle, hard metal. Its color is silver-gray and it can be highly polished. It does not tarnish in air, when heated it burns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below.

Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts color glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make molds for the firing of bricks. Cr^{4+} oxide (CrO_2) is used to manufacture magnetic tape. Chromium is mined as chromite (FeCr_2O_4) ore.

Chromium is found in effluent waters from various industries. It is used in metal alloys, metal coatings, resistance, stainless steel, automotive and equipment accessories as a preservative, nuclear research and inorganic pigment compounds. It exists as Cr^{3+} and Cr^{6+} in leather industry wastewaters. Cr^{3+} is less toxic and since it compensates the chloroplast structure, it has a positive outcome on the growth of plants [26]. The main human activities that increase the concentrations of Chromium (III) are steel, leather and textile manufacturing. The main human activities that increase Chromium (VI) concentrations are chemical, leather and textile manufacturing, electro painting and other Chromium (VI) applications in the industry. These applications will mainly increase concentrations of Chromium in water. Through coal combustion Chromium will also end up in air and through waste disposal Chromium will end up in soils [27]. It influences human physiology, gathers in the food chain and results in various ailments. Getting in touch with chromium can cause serious health problems ordering from simple skin irritation to lung [26].

There are several different kinds of Chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the Cr^{3+} and Cr^{6+} form through natural processes and human activities. Most of the Chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater. In water Chromium will absorb on sediment and become immobile. Only a small part of the Chromium that ends up in water will eventually dissolve. Chromium (III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when the daily dose is too low. Chromium (VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer [27]. Crops contain systems that arrange the Chromium-uptake to be low enough not to cause any harm. But when the amount of Chromium in the soil rises, this

can still lead to higher concentrations in crops. Acidification of soil can also influence Chromium uptake by crops. Plants usually absorb only Chromium (III). This may be the essential kind of Chromium, but when concentrations exceed a certain value, negative effects can still occur. Chromium is not known to accumulate in the bodies of fish, but high concentrations of Chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals Chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation.

1.3.3. Cadmium (Cd)

Cadmium is a naturally occurring metallic element, found in rocks, soils and sediments, which comprise part of the earth's crust at levels of approximately 0.2 ppb. Cadmium and cadmium compounds are always derived as by-products of the refining of both zinc and lead, because the ores of cadmium (sphalerite, CdS) and zinc (greenockite, ZnS) are geologically closely associated. An estimated 90-98% of cadmium present in zinc ores is recovered in the mining and extraction process. In cadmium recovery furnaces, cadmium is reduced using carbon, vaporised and then condensed. Most of the resulting cadmium metal is shipped to Ni-Cd battery manufacturers for use in new batteries (batteries have an average cadmium content of 12%-15% by weight). The cadmium is cast into small flattened discs (4mm to 6mm in diameter) to facilitate handling and reduce erratic rolling [28].

Cadmium is a soft metal shining like silver. Atomic number is 48 and molecular weight is 112,41 g/mol. Its density is 8,64 g/cm³, melting point is 320,9°C ve boiling point is 767,3°C and its vapors are monoatomic. It is scarcely soluble in non-oxidizing acids, simply soluble in dilute nitric acid. It is impervious to air however, not resistant to heat and is oxidized to CdO. Cadmium is generally used for electrolytic coatings, and also for producing bearing metal and solder in significant amounts [3]. Due to its high toxicity and great solubility in water Cd²⁺ is a notably dangerous pollutant. At low concentrations, Cd²⁺ is not toxic to plants but at higher concentrations it is toxic. Being subjected to high Cd²⁺ concentration have been found to be carcinogenic, mutagenic and teratogenic for a large number of animal species, including human beings.

Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing. Cadmium is released into the environment by human activities such as phosphate fertilizers, disposal of household, municipal and industrial wastes such as pigments, batteries, plastics and metal coatings [29,30]. About three-fourths of cadmium is used in Ni-Cd batteries, most of the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadmium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission.

The most common use area of cadmium is electroplating. In nickel plating it is used as deoxidized. In light solder and aluminum solder, easy fusible alloy productions, carving processes, cadmium vapor lamps, paint, ink and plastics, power transfer strings, the basic colourants used in ceramics, photoelectric cells, ultraviolet solar radiation photometer and Ni-Cd batteries, cadmium is widely used. In dental, its powder form is used as amalgam (1Cd:4Hg). The most important waste source among the Cd usage area is metal plating industry [31]. Cadmium can mainly be found in the earth's crust. It always occurs in combination with zinc. Cadmium also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides. Cadmium waste streams from the industries mainly end up in soils. The causes of these waste streams are for instance zinc production, phosphate ore implication and bio industrial manure. Cadmium waste streams may also enter the air through (household) waste combustion and burning of fossil fuels. Because of regulations only little cadmium now enters the water through disposal of wastewater from households or industries. Another important source of cadmium emission is the production of artificial phosphate fertilizers. Part of the cadmium ends up in the soil after the fertilizer is applied on farmland and the rest of the cadmium ends up in surface waters when waste from fertilizer productions are dumped by production companies.

Cadmium can be transported over great distances when it is adsorbed by sludge. This cadmium-rich sludge can pollute surface waters as well as soils. Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. This is a potential danger to the animals that are dependent upon the plants for survival. Cadmium can accumulate in their bodies, especially when they eat multiple plants.

Cadmium is one of the most toxic elements, critically impacting human health. The diffusion of cadmium into the environment results from the industrial processes, domestic activities, agricultural practices (use of fertilizers), use of cadmium containing goods, and disposal of wastes [32]. In aquatic ecosystems cadmium can bioaccumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms [33]. Through natural processes such as weathering and erosion, small amounts of cadmium are released naturally into the atmosphere and water systems. Table 1.1 shows the levels in each major environmental compartment [28].

Table 1.1. Natural Cadmium Levels in Environment [34].

Compartment	Levels
Atmosphere	0.1 – 5 ng / m ³
Earth's Crust	0.1 – 5 mg / kg
Marine Sediment	~ 1 mg / kg
Sea Water	~ 0.1 g / l

Cadmium does not present in nature as the native metal but principally as the sulphide ore greenockite (CdS) strongly associated with zinc sulphide ore sphalerite. Wastewaters produced from industries operating cadmium, the release from iron and steel industry brings about the cadmium get into the environment [22].

1.3.4. Effects of Heavy Metals

Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms. Lately, the heavy metal compounds in wastewater from high industry activities have caused environmental pollution and serious symptoms of poisoning. Heavy metal pollution caused by cadmium, chromium, copper, lead, mercury, nickel and arsenic is most serious to the human body. Concentrations of 0.005 mg/L (for Pb^{2+} and Cr^{3+}), 0.001 mg/L (for Cd^{2+} , Ni^{2+} and As^{5+}) and 0,1 mg/L (for Cu^{2+}), will cause illness in humans and can even be fatal [35]. The removal of heavy metal ions is an important problem in the field of water purification.

Heavy metals interfusing living environment by chemical substances and products produced by air, water, food, people enter human body by inhalation, engulfment, absorbing by skin. If the entry speed of heavy metals to human body is lower than exit speed of heavy metals from human body, they accumulate on human body in the process of time [36]. Due to the compact use of heavy metals in the production of industrial products, heavy metal exposure rate of people has increased seriously in the last fifty years. Because of mercury amalgam fillings, paints and lead in tap water, processed goods, cosmetics, shampoos, hair products, chemical residuals in toothpastes, people live with heavy metals at any moment [3].

Some heavy metals are required for the growth of biological life and when they were not present in sufficient amounts for example, limits the growth of algae. Any of these metals being found at large quantities affects the use of water effectively because of their toxicity by aquatic organisms and human. For the protection of human health maximum permissible concentrations of heavy metals in natural waters are shown in Table 1.2 [36].

Table 1.2. Maximum Permissible Concentrations of Various Metals in Natural Waters [18].

Metal	mg / m³	μmol / m³
Mercury (Hg)	0,144	0,72
Lead (Pb)	5	24
Cadmium (Cd)	10	89
Nickel (Ni)	13,4	228
Chromium (Cr)	50	962
Iron (Fe)	300	5372
Barium (Ba)	1000	7281

1.4. ADSORPTION

The phenomenon of adsorption is essentially an attraction of adsorbate molecules to an adsorbent surface. The preferential concentration of molecules in the proximity of a surface arises because the surface forces of an adsorbent solid are unsaturated. Both repulsive and attractive forces become balanced when adsorption occurs. Adsorption is nearly always an exothermic process [37]. Adsorption is useful in most natural physical, biological and chemical systems. In industrial applications such as charcoal, synthetic resins and water purification, adsorption is widely used.

If a gas under constant pressure or vapor is contacted with a surface cleaned solid by heating, it is seen that the volume of gas or vapor decreases. If the same procedure is carried out under constant volume, it is seen that the pressure of gas or vapor decreases. In that case a portion of gas or vapor is retained by solid. This retention could be possible in two ways. First one is that gas or vapor molecules dissolve in solid homogeneously, second one is that gas or vapor molecules hold on to the surface of solid. First one is called absorption; the second one is called adsorption [3].

Adsorption differs by chemical characteristics of active centers, adsorbate and adsorption circumstances. The main feature of a good adsorbent is having a wide

surface area per unit mass [38]. There are three types of adsorption which are physical, chemical and ionic adsorption.

1.4.1. Physical Adsorption

In physical adsorption, the identity of the adsorbate and the adsorbent are preserved. Physical adsorption from a gas occurs when the inter-molecular attractive forces between molecules of the solid adsorbent and the gas are greater than those between molecules of the gas itself. In effect, the resulting adsorption is like condensation, which is exothermic and thus is accompanied by the release of heat [37]. Physical adsorption occurs quickly and may be mono-molecular (unimolecular) layer or monolayer, or 2, 3 or more layers thick (multi-molecular). As physical adsorption takes place, it begins as a monolayer. It can then become multi-layer, and then, if the pores are close to the size of the molecules, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the maximum capacity of a porous adsorbent can be more related to the pore volume than to the surface area.

In physical adsorption, there is a van der Waals interaction (dispersion or a dipolar interaction) between the adsorbate and the substrate. Van der Waals interactions have a long range but are weak, and the energy released when a particle is physically adsorbed is some of the order of magnitude as the enthalpy of condensation. Such small energies can be absorbed as vibrations of the lattice and dissipated as thermal motion, and a molecule bouncing across the surface will gradually lose its energy and finally adsorb to it in the process called accommodation. The enthalpy of physical adsorption can be measured by monitoring the rise in the temperature of a sample of known heat capacity, and typical values are in the region of 20 kJ mol^{-1} . This small enthalpy change is insufficient to lead to bond breaking, so a physically adsorbed molecule retains its identity, although it might be distorted by the presence of the surface [39].

Physical adsorption generally occurs at low temperature and fast, the event can be recycled. Therefore, the adsorbed molecules are easily displaced by lowering the gas pressure or concentration. In physical adsorption of gases, forces such as condensation occur. The value of heat adsorption of same molecules generally is close to the heat of condensation [3].

1.4.2. Chemical Adsorption

In chemisorption, there is a transfer or sharing of electron or breakage of the adsorbate into atoms or radicals which are bound separately.

The molecules or atoms stick to the surface by forming a chemical (usually covalent) bond, and tend to find sites that maximize their coordination number with the substrate. The enthalpy of chemisorption (abbreviated as chemical adsorption) is very much greater than that for physical adsorption, and the typical values are in the region of 200 kJ mol^{-1} . The distance between the surface and the closest adsorbate atom is also typically shorter for chemisorption than physical adsorption. A chemisorbed molecule may be torn apart at the demand of unsatisfied valencies of surface atoms, and the existence of molecular fragments on the surface as a result of chemisorptions is one reason why solid surfaces catalyse reactions. Except in special cases, chemisorption must be exothermic [39].

At casual areas on the surface specific chemical bonds take place in chemical adsorption. The adsorbed molecules do not lean to occupy adjacent areas and adsorption is finished when the surface is totally covered. The bonds are weaker in physical adsorption. Chemical adsorption can be only one layer. Before the first layer has achieved second layer starts to form since the adsorbed molecules are connected to each other. All the surface areas have maintained to link [40,41]. In chemical adsorption, chemical bonds occur between the solid and the adsorbed material. Between the solid surface and adsorbed material, there exists a surface complex. The stability of this complex depends on the electron density and electron exchange between the interacting molecules [38].

1.4.3. Ionic Adsorption

Ionic adsorption occurs by electrical shooting between the adsorbate and the adsorbed surface. Ion exchange is also included in this class. Here, the attraction of adsorbent surface and adsorbed material with opposite electrical charges becomes important. Ions with high electrical charge and ions with small diameters are better adsorbed [42].

By the results of electrostatic attraction forces, ions keep on loaded areas on surface. Here ionic strength of the adsorbent and adsorbed material is important. If the ions are same charged the smaller one is initially hold on the surface [43].

1.4.4. Factors Affecting Adsorption

There are any factors affecting adsorption phenomena. Most important ones are; surface area, adsorbate structure – particle size, contact time, solubility, polarity, carbon atoms, ionized molecules- pH, and temperature.

1.4.4.1. Surface Area

Larger sizes of adsorbent surface area imply a greater adsorption capacity. Adsorption is a surface event and adsorption degree is proportional to the specific surface area. Specific surface area can be expressed as the ratio of the area used in adsorption to the total surface area. Adsorbent unit weight versus amount of adsorbed material increases depending on the porosity of solid material. Active area changes according to the particle shape of the surface area. As an example of 1 m³ of global material has 4,8 m² active area. Depending on the size of particles, if the material with cm³ is separated into the 0,1 cm sized small pieces, it has a surface area of 600 cm², if separated into the 0,001 cm sized small pieces, it has a surface area of 600 m² [3].

Adsorption with small particle size, wide surface area and porous structure increases the adsorption. Since the adsorption is a surface event, the most important feature of adsorbent is surface area. Each solid material can be adsorbent; but surface structure of the adsorbent changes the capacity of adsorption. Suitable adsorbent is the material with wide surface area and porous structure. As the porosity increases, adsorption also increases. Another important feature affecting the adsorption is particle size of the adsorbate. Many studies show that as the particle size decreases, the capacity of adsorption increases [44].

1.4.4.2. Adsorbate Structure

Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained). However, wastewater drop across columns packed with powdered material is too high for use of this material in packed beds. Addition of powdered adsorbent must be followed by their removal. The longer the contact or residence time the more complete the adsorption will be. However, the equipment will be larger [45]. Substances slightly soluble in water will be more easily removed from water (i.e., adsorbed) than substances with high solubility. Also, non-polar substances will be more easily removed than polar substances since the latter have a greater affinity for water. The surface of activated carbon is only slightly polar. Hence non-polar substances will be more easily picked up by the carbon than polar ones.

For substances in the same homologous series a larger number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed (e.g., the degree of adsorption increases in the sequence formic-aceticpropionic-butyric acid). Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes. More highly ionized molecules are adsorbed to a smaller degree than neutral molecules [45]. In the event of any adsorption, it is known from solution that adsorption is a sudden event and solubility of solute material controls the adsorption balance in high ratio. In adsorption, there is an inverse correlation between the adsorption degree of dissolved substance and its solubility. In solubility-adsorption relations, it is necessary to break the bonds between solvent and solute before adsorption occurs. The degree of adsorption decreases with resolution capability and increase in bond forces between solute and solvent [3].

One of the most important factors in the case of adsorption is adsorbent solubility controlling the adsorption equilibrium. There is an inverse relation between adsorption of the substance and solubility of the medium where adsorption occurs. Adsorption occurs subject to the breakage the bonds between adsorbent and solvent. In other words, as the solubility increases the bond between the adsorbent and solvent becomes

stronger, adsorption decreases. The size of adsorbent affects the adsorption. If the adsorbate molecules are bigger than the pore of adsorbent, it causes the pores clogged and cause active centres on pores not function. In this circumstances adsorption decreases. Another feature affecting adsorption is ionization of adsorbate. Most water and wastewater compounds are in ionic form. Ionized substances are less adsorbed than neutral ones. Adsorption polarity has also effect on adsorption. A polar adsorbent is more strongly adsorbs the polar substance in a solvent than apolar ones [44].

1.4.4.3. pH

The degree of ionization of a species is affected by the pH (e.g., a weak acid or a weak basis). This, in turn, affects adsorption [45]. The pH of adsorbed solution affects the speed of adsorption in some factors. Since hydrogen and hydroxyl ions adsorb strongly, other ions adsorption processes are prevented by the pH of solution. Therefore, ionization ratio of acidic and basic compounds and accordingly since controlling ionization degree of solution, the pH affects adsorption occurring in solution [3,43].

1.4.4.4. Temperature

Adsorption process is generally in the form of exothermic reactions. For this reason, the size of adsorption increases with decreasing temperature. It is known that the emitted heat is generally in the stage of condensation or crystallization heat in physical adsorption, and in chemical adsorption it is in the stage of chemical reaction heat [43]. The change in the enthalpy of adsorption processes is due to the adsorption being exothermic reaction or due to the crystallization reactions. Thus, small changes in temperature do not cause significant changes in adsorption process [3].

The dependence of adsorption speed to the temperature is expressed by activation energy (E_a). Adsorption type is determined according to the Arrhenius equation with activation energy. However, energy parameters (ΔE_a , ΔH ve ΔS) are the parameters affecting adsorption processes in water and wastewater treatment processes and are important parameters to consider [3].

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (1.1)$$

$$\Delta G = -RT \ln k \quad (1.2)$$

$$\Delta G = \Delta H - T\Delta S \quad (1.3)$$

1.4.5. Adsorption Agents

In order to increase effectiveness of adsorption, it is important to choose the appropriate adsorbent. Appropriate adsorbent is an adsorbent able to adsorb the material in environment at maximum level and has high sensitivity, capacity and long servicing life [38].

In adsorption, many adsorbents are used; however, the most used one among them is activated carbon. Due to the high cost, it has limited use. Activated carbon gain different chemical activity and physicochemical property according to the sources from where it is obtained. According to the shape and size of the activated carbon, it is divided into four groups as powder, granular, fibrous and cloth activated carbon. It is used in output water treatment, in drinking water treatment, in solvent recovery, in removing color, in metal mining processes and various household applications [44].

Adsorbents obtained from natural, industrial or agricultural wastes are used as the alternative to activated carbon. These low-cost adsorbents draw attention because of showing high efficiency in treatment and having high metal binding capacity. Known and often found in application of removal of heavy metals adsorbents are chitosan, zeolite, clay, waste sludge, lignin, lignite, peat, citrus peel, wood wastes, agricultural wastes, and industrial wastes.

Etched plant peat is a complex solid material composing of lignin and cellulose. Plant peat has a large surface area (>200 m²/g) and has great pores. Eutropic and oligotropic type of plant peat show an important role on treatment of industrial wastewater including Cu⁺², Cd⁺², Zn⁺², Ni⁺² metals [38].

Chitin, the raw material of chitosan, is the second most abundant natural polymer among biosorbents after cellulose. Due to an active holder for heavy metals, chitosan usage in research is gradually increasing [38].

1.4.6. Adsorption Isotherms

Upon contacting an amount of activated carbon with a wastewater containing an adsorbable substance adsorption will take place. Adsorption will continue until equilibrium will be established between the substance in solution and the same substance in the adsorbed state.

When the temperature is held constant as well as adsorbate and adsorbent, adsorption by gasses only depends on pressure, adsorption by solution only depends on concentration. In this case, the lines giving the alteration in adsorbate substance amount with pressure or concentration is called adsorption isotherms. In adsorption isotherm, the amount of substance adsorbed is a function of the concentration of adsorbed substance and temperature [46].

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm, etc.

1.4.6.1. Langmuir Isotherm

Langmuir's isotherm describing the adsorption of adsorbate (A) onto the surface of the adsorbant (S) requires four assumptions [47]:

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism.

- At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

For liquids (adsorbate) adsorbed on solids (adsorbent), the Langmuir isotherm can be expressed by;

$$q = q_m K_A C \frac{1}{1 + K_A C} \quad (1.4)$$

where,

q = the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent – mol.g^{-1}

q_m = the maximal substance amount of adsorbate per gram (or kg) of the adsorbent – mol.g^{-1}

K_A = constant (function of enthalpy of adsorption and temperature) – $\text{mol}^{-1} \cdot \text{dm}^3$

C = the concentration of adsorbate in liquid – mol.dm^{-3}

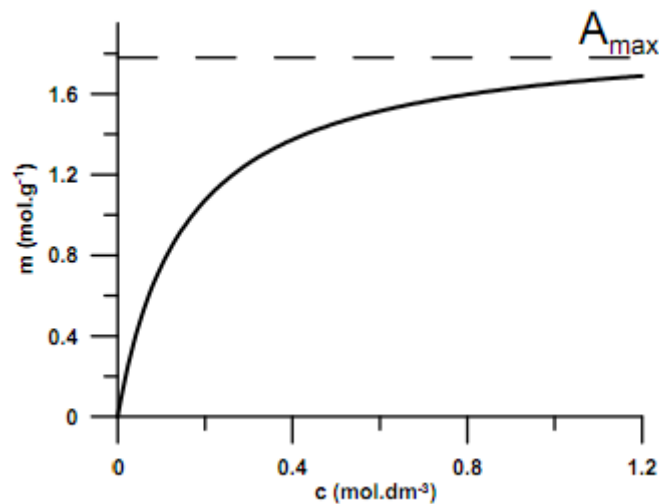


Figure 1.1. General Form of the Langmuir Isotherm [47].

1.4.6.2. Freundlich Isotherm

The Freundlich equation can be mathematically represented by:

$$\frac{x}{m} = kC^{1/n} \quad (1.5)$$

where,

x =the quantity adsorbed

m =the mass of adsorbent

C =concentration of adsorbent

k and n empirical constants for each adsorbent-adsorbate pair at a given temperature

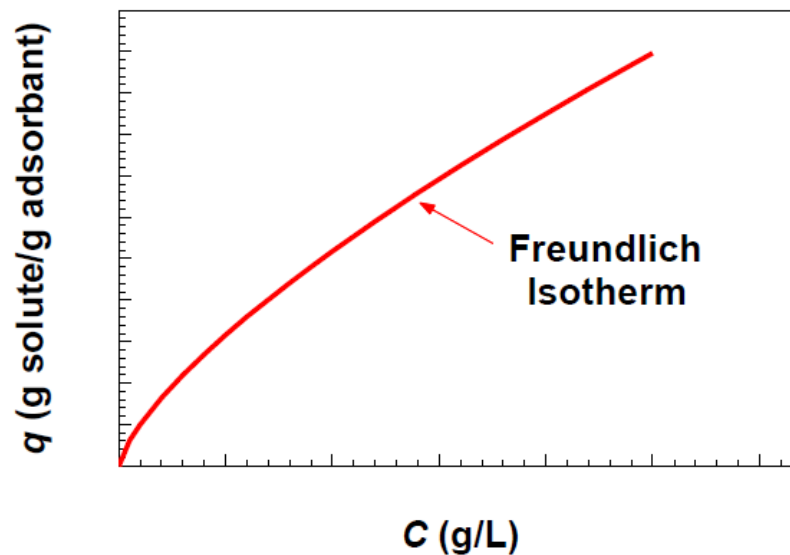


Figure 1.2. General Form of the Freundlich Isotherm [45].

1.4.6.3. BET Isotherm

In the Langmuir model, it was assumed that adsorption could only occur on the unoccupied substrate adsorption sites. But here this restriction is removed. If the initial adsorbed layer can act as a substrate for further adsorption then, instead of the isotherm leveling off to some saturated value at high pressures, it can be expected to rise

indefinitely. The most widely used isotherm dealing with multiplayer adsorption was derived by Stephen Brunauer, Paul Emmet and Edward Teller, and is called the BET isotherm.

The assumptions made in the derivation of the BET model are [45]:

- The adsorbed molecules are arranged in multiple layers on the surface of the adsorbent
- The adsorbed molecules do not move on the surface of the adsorbent
- A layer does not need to be completed before the next layer starts to fill up
- The enthalpy of adsorption is the same for all molecules in a given layer
- All molecules in layers other than the first have the same adsorption energy

The BET equation can be mathematically represented by:

$$q = \frac{q_m K_B C}{(C_s - C) \left[1 + (K_B - 1) \frac{C}{C_s} \right]} \quad (1.6)$$

where

q_m = maximum adsorbable value of q

K_B = constant (function of energy of adsorption and temperature)

C_s = concentration of solute when all layers are saturated

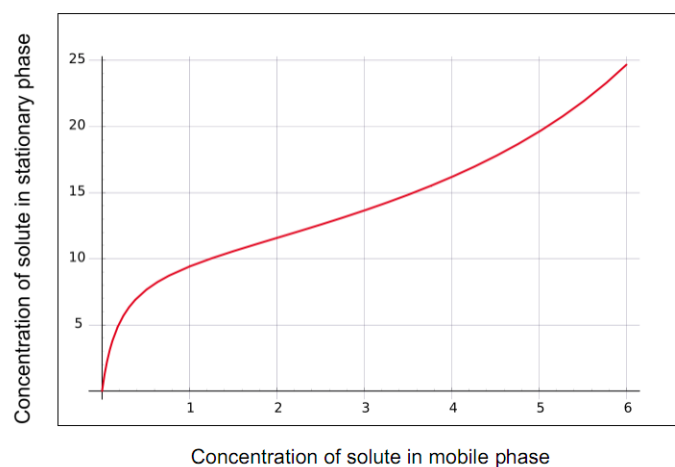


Figure 1.3. General Form of the BET Isotherm [48].

1.4.7. Adsorption Kinetics

The kinetic study of the adsorption processes provides useful data regarding the efficiency of adsorption and feasibility of scale-up operations. To evaluate the effectiveness of an adsorbate, studies of kinetics of adsorption equilibria are also needed. Several kinetic models are available to examine the controlling mechanism of the adsorption process and to test the experimental data [49].

1.4.7.1. Lagergren pseudo-first order equation

The Lagergren pseudo-first order equation is;

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (1.7)$$

where

q_e = the amount of metal adsorbed per unit weight of the adsorbent (mol/g) at equilibrium time

q_t = the amount of metal adsorbed per unit weight of the adsorbent (mol/g) at equilibrium time t

k_1 = the rate constant for the first order kinetic

C_s = concentration of solute when all layers are saturated

The values of adsorption rate constants are determined from the plots of $\ln(q_e - q_t)$ against t . In many cases, the above equation does not fully describe the adsorption kinetics. In such cases, a pseudo-second-order equation can be used.

1.4.7.2. Pseudo-second-order equation

The pseudo-second order equation is often successfully used to describe the kinetics of the fixation reaction of pollutants on the adsorbent. The equation can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1.8)$$

where

q_e = the amount of metal adsorbed per unit weight of the adsorbent (mol/g) at equilibrium time

q_t = the amount of metal adsorbed per unit weight of the adsorbent (mol/g) at equilibrium time t

k_2 = the rate constant for the second order kinetic

C_s = concentration of solute when all layers are saturated

The equilibrium adsorption capacity (q_e) and the second order rate constant k_2 (g/mol min) can be determined experimentally from the slope and intercept of plot of t/q_t versus t .

1.5. WASTEWATER TREATMENT SLUDGE

Wastewater treatment sludge is in the liquid or semi-solid form as a result of wastewater treatment, it is odorous, and consists of solid material with 0,5 – 12 % by weight depending on the treatment process [50]. Due to the significant portion of the sludge is water, the volume they occupy is very high. Especially, since the organic content of treatment sludge coming from biological treatment is very high, this type of sludge tends to decompose and putrefaction.

Using the treatment sludge as in fertilizer, raw material, building material and fuel are in examination in our country and in many developing countries which could be a solution to reappraisal of waste treatment sludge. Assessment of the treatment sludge as a raw material, using in building material, in cement raw material, and as adsorbents get ahead. These examinations are focused on incineration and pyrolysis processes and evaluating the obtained pyrolysis products in treatment processes are examined [8].

According to data of the State Institute of Statistics in 2003, In Turkey, in municipal wastewater treatment plants 600 million m^3 wastewaters are treated annually and nearly 500.000 tonnes treatment sludge are produced. In Fig. 1.4 and Fig.1.5 examples to treatment sludge are given.



Figure 1.4. Industrial Wastewater Treatment Sludge [51].



Figure 1.5. Industrial Wastewater Treatment Sludge [52].

Treatment sludge includes compounds with agricultural value as well as pollutant compounds. The ones having agricultural value are organic substances, nitrogen, phosphorous, and potassium along with small amounts of calcium, sulfur, and magnesium. The pollutants are heavy metals, organic pollutants and pathogens.

The components of treatment sludge vary depending on the treatment waste sources and pre-treatment processes. The information obtained by looking only the source of treatment sludge is qualitative. Various measurement techniques and methods are developed on the basis of many important parameters and to determine the specific properties of sludge. These developed methods have been standardized under the name of European Committee for Standardization (CEN/TC308/WG1) by Technical Committee

308. Nowadays, the amount of treatment sludge coming from the wastewater treatment plants whose establishment and operation are necessary are increasing with increasing environmental consciousness [53].

1.5.1. Sludge Types and Their Characters

Treatment sludge can be examined in three titles according to the sources of them [53]:

- Sludge from wastewater treatment plants operated by local governments; wastewater treatment plants where only domestic wastewater or domestic, industrial and raining waters treated
- Sludge from industrial wastewater treatment plants
- Sludge from drinking water treatment plants; it is a must to treat drinkign water prior to use and the amount of sludge produced in drinking water treatment plants is significantly lower than the amoun of sludge produced from wastewater treatment plants.

Sludges can be classified depending on the treatment type and the goal, such as preliminary setting wastes produced by settleable solids, chemical sludges as a result of chemical treatment and coagulation, biologic sludges from biological treatment plants, and alum sludges as a result of drinking water treatment plants [53].

1.5.1.1. General Characters of Treatment Sludge

Component of treatment sludge vary quite large according to the sources of wastewater. The bases for these differences are the input required in the process of industrial production or used chemicals in the course of wastewater treatment.

Total solids in sludge are equal to the sum of suspended and dissolved solids. These three types of solids (total, suspended and dissolved), each one is volatile and have constant parts. The part oxidized at 600°C is volatile solid material, the remainings are constant. Organic content of sludge mainly consists of hydrocarbons, aminoacids, small proteins and fats. The amount of nitrogen and phosphorus takes first place among

the nutrients in treatment sludge. In addition, potassium, sulfur, magnesium, sodium and oligo-elements (boron, cobalt, selenium, iodine, etc.) which have agricultural importance and supporting the growth of plants are found in sludge. Nitrogen is found in sludge in the form of organic compounds and a little in the form of ammonia. Other mineral forms are found in trace amounts. Nitrogen ratio in sludge varies between a wide ranges 4-60 %. Phosphorus in sludge is generally in the form of minerals and depending on the type of sludge, 30-98 % of total phosphorus could be mineral phosphorus.

In order to stabilize treatment sludge lime addition is applied. Calcium concentration is high in sludges lime added.

Treatment sludges consist of many heavy metals. Heavy metals in wastewaters are caused by industries, domestic wastewaters and the corrosion and erosion of pipes carrying wastewaters. Heavy metals accumulate within the sludge on the course of wastewater treatment. Heavy metals in sludge are in the form of hydroxides, carbonates, phosphates, silicates and sulphates.

In Table 1.3, heavy metals concentrations in treatment sludge and their limit values are given [54].

Table 1.3. Heavy Metal Concentration of Treatment Sludge and Their Limit Values [54].

	Heavy Metal Concentration mg/kg dry matter	EU Directive 86/278/EEC mg/kg dry matter
Cd	0.4 – 3.8	20 – 40
Cr	16 - 275	1000 – 1750
Cu	39 – 641	1000 - 1750
Hg	0.3 - 3	16 – 25
Ni	9 - 90	300 – 400
Pb	13 – 221	750 – 1200
Zn	142 – 2000	2500 – 4000

Organic pollutants varying according to the physical and chemical properties can exist in sludge. Some of them are PAH (polynuclear aromatic hydrocarbon), PCBs (polychlorinated biphenyls), AOX (adsorbable organic halogen), LAS (linear alkyl benzenesulfonates), etc. [55].

Pathogens types as viruses, bacteria, protozoa and helminths can be found in treatment sludges. Amount of pathogens varies with time. Treatment sludge contains microorganism especially in systems where biological treatment is carried out [53].

Treatment sludge from classical wastewater treatment plants are produced from primary, secondary and advanced processes. Each treatment process has different effects wastewater pollution. Accordingly, produced sludges are in different structures. Six different treatment sludge characters are given on Table 1.4 [56].

Table 1.4. Six Different Treatment Sludge's Characterization [56].

	Sector A*	Sector B*	Sector C*	Sector D*	Sector E*	Sector F*
% Humidity	26.86	73.93	87.47	73.69	58.17	75.7
% LOI**	70	51	81	68	31	19
Cu – mg/kg	20.385	20.101	62.67	5.765	13.715	1.239
Cr – mg/kg	44.309	6.062	68.147	370.5	32.217	7.151
Pb – mg/kg	7.932	38.869	55.467	38.025	20.325	78.294
Cd – mg/kg	0.151	0.418	0.539	1.512	0.737	1.057

*Sector A: A paint company carrying chemical and biological treatment (after filter press)

Sector B: A food company with high organic content of wastewaters carrying biological treatment (thickening tank output)

Sector C: A food company with high organic content of wastewaters carrying biological treatment (thickening tank)

Sector D: A chemical company with a high organic content of wastewaters carrying prechemical and biological treatment (after filter press)

Sector E: A chemical company carrying prechemical and biological treatment (after filter press)

Sector F: A metal plating company with a high inorganic and organic content of wastewaters carrying chemical treatment (thickening tank output)

** LOI: Loss on Ignition (Organic Material Content)

1.5.1.1.1. Sludge From Primary Treatment

The basic principle of primary treatment is the removal of settleable solid materials from wastewater. Solids with inorganic characters and self-settleable are kept in grill, sand traps and pre-settling ponds. Since the settleable solids with rough nature kept in grills have the characteristic of domestic solid waste, without any requirements they could be disposed with urban solid wastes. Organic matter of this sludge known as raw sediment sludge is between 60-80 % and water content is considerable high [50].

1.5.1.1.2. Sludge From Secondary Treatment

This is the treatment sludge from biological oxidation of settleable organic substances (removal of BOD) in secondary treatment. In secondary treatment, BOD is removed by biological processes but physical and chemical treatments can also be used for this purpose. Biomass in ventilation tank is settled on final sedimentation tank, some part is sent to the beginning of the plant in order to reuse. Discarded biomass waste is named as activated sludge. Solid particles detached from filter beds separate from treated water in last sedimentation pond. This sludge is known as humus and quantity is less. Filter humus and active waste sludge is generally mixed with raw pre-sedimentation sludge and putrefied in anaerobic futrefacient. Final material is named as decayed sludge [53].

1.5.1.1.3. Sludge From Advanced Treatment

Sludges from advanced treatment plants are formed in systems constituted in additon to secondary treatment processes in order to remove undesirable nutrients (nitrogen and phosphorus) resulted by chemical processes and bacterial activities. Nitrogen removal is a biological process proceeding with the formation of N_2 . Each step is carried out with specific bacteria and different conditions are needed for their growth. Phosphorus removal is applied together with chemical and biological processes. The amount of sludge produced in the removal of phosphorus by phsical and chemical treatment in activated waste plants are increased by 30 %. Biological treatment is carried out with appropriate specific microorganisms for phosphorus removal.

Phosphorus accumulated within the bacteria during the treatment makes sludge difficult to treat [57].

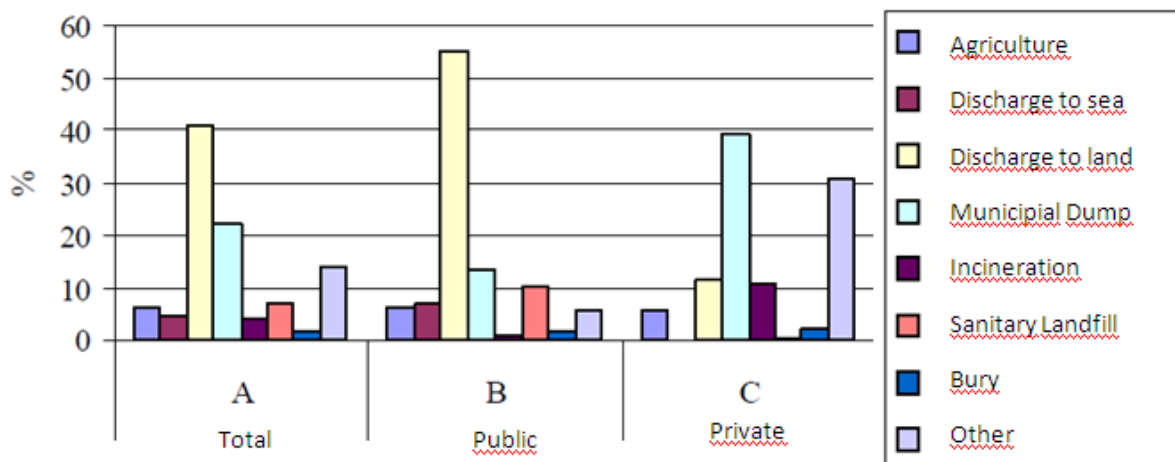


Figure 1.6. Disposal Methods of Treatment Sludges From Manufacturing Industry.

1.5.2. Sludge Processing and Disposal Techniques

It is necessary to dispose sludges from water and wastewater treatment plants by applying appropriate treatment and fulfilling the environmental health criteria. Economic and effective processing of sludge is based on the determination of physical and chemical structures by appropriate analysis methods.

Disposal methods percentages of treatment sludges from manufacturing industry are given on Fig. 1.6 [58]. In the determination of sludge treatment and disposal methods, it is very important to know the feature and the content of sludge and solid material. This is also closely related to the solid waste source, sludge age in the system and process type [59].

Various alternatives can be presented for final disposal of sludge. Applied final disposal method with respect to current economic and technical opportunities differs from the properties of treatment sludges.

1.5.2.1. Incineration

Incineration is an oxidation reaction. Sludge incineration is carried out directly or indirectly. In direct incineration, sludges are generally incinerated together with domestic wastes; in indirect incineration it is used as fuel in energy production or in cement production it is used together with another fuel in the input for energy and raw material.

Today, the most recent method used in the treatment of waste sludge is incinerating them alone or together with other wastes. Some limitations for agricultural usage and sanitary landfill have led to an increase in disposing waste sludge by incineration [53]. In some countries, treatment sludge disposal are 40 % of disposal methods and since it is the method providing the largest volume reduction in organic wastes, it seen to be suitable method for countries having shortness land [60]. But this method is 2-3 times more expensive than landfill. Moreover, air pollution resulting from incineration have negative effects on environment unless advanced flue gas technologies are used [61]. In Fig. 1.7 an example to incineration plant is given.



Figure 1.7. Incineration Plant [62].

1.5.2.2. Landfill

Landfill is a final disposal method applied to the wastes not recycled, not other usage area, to remainings resulting in recovery plants and to ash and slag produced in incineration. Sanitary landfill should be seen a disposal technique as the least desirable and the lowest priority in solid waste management. In spite of the fact that since it is cheaper and simpler than other disposal techniques, sanitary landfill is the most widely used solid waste disposal system with some exceptions [61].

There are two options for landfill of treatment sludges. In single landfill, the site is used only for treatment sludges. In mixed landfill, the site is used for domestic solid wastes and there is no special technical precautions for treatment sludges. Sludges sent to the landfill sites are generally discredited, dried in drying beds and dehydrated. Sludge with a water content higher than 50 % cause problem in landfill but sludge with high solid matters are disposed in landfill sites without creating any problem. After the treatment sludges are disposed on landfill sites, their surface are covered with soil in order to minimize their effects on the environment [53]. There is a regulation for wastes in order to be disposed on landfill sites, which is Regulation for Sanitary Landfill of Wastes (26.03.2010 / 27533). There are three types of landfill sites which are primary, secondary and tertiary landfill sites. According to this regulation some parameters limit values for sludge to dispose on different landfill sites are given on Table 1.5.

Table 1.5. Limit Values of Some Parameters for Sanitary Landfill of Wastes [63].

	Wastes treated as inert wastes	Wastes treated as nonhazardous wastes	Wastes treated as hazardous wastes
TOC (mg/kg)	-	30000	60000
LOI (%)	-	-	10
Solid Matter (%)	50	50	50
Cd (mg/L)	0,004	0,1	0,5
Total Cr (mg/L)	0,05	1	7
Cu (mg/L)	0,2	5	10
Pb (mg/L)	0,05	1	5

According to the Regulation for Sanitary Landfill of Wastes, in order to dispose treatment sludges on sanitary landfill sites, its humidity should be lower than 50 %. Besides that, according to the relevant regulation other heavy metals, salts and ions, organic content is to be determined and according to this appropriate disposal methods will be determined. In Fig. 1.8 an example of sanitary landfill site is given.



Figure 1.8. Sanitary Landfill Site [64].

1.5.2.3. Composting

The other method for treatment sludge disposal is composting. Composting is an anaerobic biological stabilization method for sludges which is a ventilation system for sludges mixed with secondary products such as wood powder and animal manure.

Composting is a conversion of organic wastes to the hummus like stabilized sludge by airy thermophilic decay. In the resulting hummus, there may present dead or living organisms up to 25 %. The most important parameters that must be checked in practice are carbon/nitrogen ratio, temperature and ventilation [65].

1.6. WASTEWATER

Today, water a key component of life is the most exposed to the pollution. With industrialization, wastewater production and its diversity have increased.

Waste is a solid, liquid or gas substance causing directly or indirectly harmfulls by leading the media where physical, chemical and bacteriological properties are faced with at the end of production and consumption acitivities to change its natural composition and properties and affects the usability potential of environment [3]. Wastewater is water with partly or completely altered properties or polluted as a result of domestic, industrial, agricultural or other usages. Waters from mines and mineral processing plants, waters resulting from conversion of raining to surface or subsurface flow from built-coated and uncoated areas of city street, car park and similar areas are also wastewaters [66].

In Turkey, 930 million cubic meters of wastewater containing toxic and heavy metals are produced per year. 22 % of these wastewater are treated, 78 % is directly disposed to the lakes, rivers and seas [3]. Treating only the 5 % of wastewaters in developing countries, discharging the remaining industrial and domestic wastes into the environment, especially to the rivers and underground waters in uncontrolled ways is a big problem in itself. One-thirds of the world's populations, in other words 2.4 billion people, do not have wastewater treatment plants. In developing countries, 70 % of industrial wastes and 90 % of sewer are discharged directly to the natural water resources. Scientist have identified that every day two million tons of waste is discharged into the rivers, lakes and streams, one liter wastewater contaminates eight liters of clean water, 12000 km³ contaminated water exits in the world and this occupies up to the 10 largest river basin area, if the pollution is not prevented it will cause 18000 km³ of cleaned water loss by the year 2050 [7].

Many industrials do not work without water. In industry, in washing, vaporization, drying, energy consumption, and cooling processes consume so much water. This waters consist of many substances and properties according to the usage areas. These are organic substances, acids, alkalines, corrosive substances, toxic substances and high temperature, colority, bad odor [3].

The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost and land, simple design and easy operation, and no effect of toxic substances compared to conventional biological treatment processes [67]. Industrial waters should be treated by various methods before discharge into the rivers or seas. Moreover, toxic materials are to be cleaned from inhibitors. Otherwise, they damage the living organisms on rivers, lakes and seas by toxicity or consuming water oxygen [36]. A wastewater storage reservoir example is given on Fig. 1.9.



Figure 1.9. Wastewater Storage Reservoir [68].

1.6.1. General Character of Wastewater

For purposes of comparison, it is useful here to recall that road transport and combustion installations, mainly of the energy sector, are the most important sources of air pollutants. In the case of water bodies, it is obvious that agriculture and the metal industry, plus the activities in the production of inorganic chemicals and fertilizers, constitute the major polluters [19]. In Table 1.6 the direct releases of the most important pollutants into water are presented in association with the corresponding main industrial source.

Table 1.6. The Releases of the Main Pollutants Charged Directly into Water From the Industrial Sector in Europe 2001 [69].

Compound	Tones/year	Main Source
Phenols	1,419,344	Basic Inorganic Chemicals or Fertilizers (47%)
Total Organic Carbon	246,524	Industrial Plants for Pulp from Timber or Other Fibrous Materials, and Paper or Board Production (70%)
Nitrogen	22,317	Basic Inorganic Chemicals or Fertilizers (29%)
Phosphorous	1662	Basic Inorganic Chemicals or Fertilizers (25%)
Chromium	864	Metal Industry (45%)
BTEX	82.5	Basic Inorganic Chemicals (56.1%)
Nickel	71.5	Metal Industry (45%)
Copper	45.8	Metal Industry (23%)
Lead	41.7	Metal Industry (40%)
Polycyclic Aromatics	10.3	Metal Industry (74%) Hydrocarbons
Cadmium	8.1	Metal Industry (74%) Hydrocarbons
Arsenic	5.1	Metal Industry (22%)
Mercury	0.5	Metal Industry (23%)

Most of the heavy metals in wastewaters present in treatment sludge. Dissolved parts remain on these sites by reaching to the surface water and seas. From there, heavy metals reach to the drinking water and food chain by mobilising again. Heavy metals reaching to the food chain cannot be discharged from the body by chemically or biologically and accumulates in the body [25,70].

1.6.2. Wastewater Sources

In every branch of the industry, different production processes are carried out, various materials are used and some part of these used chemicals are mixed with wastes. Each industrial wastes according to the its nature have some features and disrupt the life balance by affecting the environment in different ways [44]. Sectors producing industrial wastewater are classified according to the production types and many several sectors are created. These sectors are mining industry, oil industry, food industry, metal industry, wood products and furniture industry, beverage industry, chemical industry, pulp, paper and cardboard industry, other industrial facilities that produce wastewater quality, the serial manufacture of machinery, electrical machinery and equipment, food components industry, textile industry, glass industry, coal preparation, business and power generation, leather and leather products industry, blended industries.

Some common metals used in various industries and wastewaters are given on Table 1.7 [25].

Table 1.7. Heavy Metals Used and Discharged Industries [25].

Industry	Cd	Cr	Cu	Pb	Zn	Ni
Metal Alloy	X		X	X	X	X
Chemistry, Drug,	X	X	X	X	X	
Plating	X	X	X	X	X	
Fertilizer	X	X		X	X	X
Fossil Fuel Incineration	X			X		
Mining	X	X		X	X	X
Dye and Pigments	X	X	X	X	X	X
Petroleum Refining		X	X	X	X	X
Machine			X	X		
Plastic Production	X			X		
Paper Production		X	X	X		
Textile		X	X			

1.6.3. Wastewater Treatment

Removal of heavy metals from aqueous solutions is necessary because of the frequent appearance of heavy metals [Zn^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} etc.] in waste waters from many industries, including electroplating, metallurgical, chemical manufacturing, mining and battery manufacturing industries [67].

The main objective of wastewater treatment is to decrease the effect of wastewaters to public health and ecological balance. The basic steps that occur in wastewater treatment are removal of suspended solids, removal of harmful and toxic heavy metals and their compounds, removal of biodegradable organic matter, removal of nitrogen and phosphorus depending on the receiving media, and destruction of pathogenic organisms [71].

Wastewater parameters to what extent they are treated are determined by laws and regulations. Depending on the capabilities of receiving media to adsorb, determined discharge standards vary from country to country. Discharge criteria to a sea, to a lake or a river media differs from each other.

Wastewater treatment plants are designed in order to decrease the negative effects of discharge of domestic and industrial wastewaters to the receiving media on the environment. Because of the different wastewater characteristics, treatment methods for each wastewaters will be different [50].

Wastewater treatment methods are mainly divided into three groups; physical, chemical and biological treatment methods. Different treatment methods can be used for wastewater with different characteristics. While physical and chemical methods are preferred for domestic wastewaters, chemical methods are preferred for industrial wastewater treatment. But, the systems where all of them are used together are also available. In Fig. 1.10 and Fig. 1.11, wastewater treatment plant is shown.



Figure 1.10. A Wastewater Treatment Plant [64].

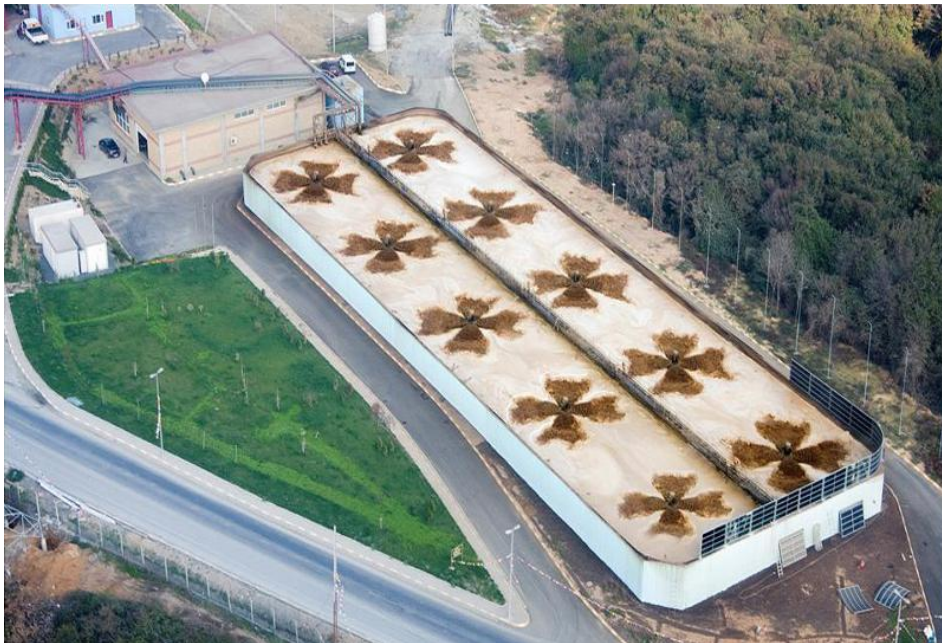


Figure 1.11. A Wastewater Treatment Plant [64].

1.6.3.1. Physical Treatment Methods

Physical treatment method is a treatment method depending on the physical properties of pollutant such as the size of the substance, viscosity and specific gravity. Physical treatment methods are grids, sand arresters, sedimentation tanks, filtration pools, color removal, odor removal [71].

1.6.3.2. Chemical Treatment Methods

Chemical treatment methods are applied in order to provide sedimentation by changing physical state of substances causing pollution presenting as dissolved or suspended or colloidal. In chemical treatment processes the materials needed to be sedimented are separated from water as sludge as a result of adding chemical substances like coagulant, polyelectrolyte at optimum pH value to wastewater. Chemical precipitation in water treatment is used in the removal of hardness [44]. Examples to chemical treatment are acid-base neutralization, removal of organic compounds, cyanide removal, and heavy metal removal. Chemical-physical treatment flow chart is given on Fig. 1.12.

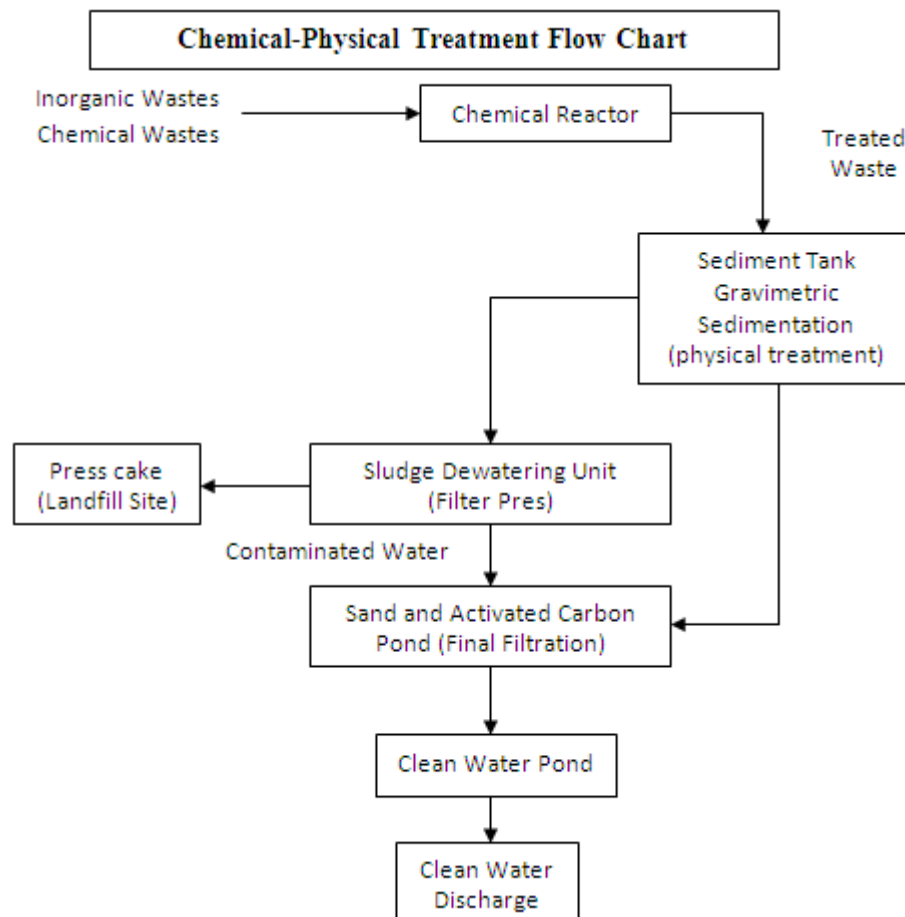


Figure 1.12. Chemical-Physical Treatment Flow Chart [51].

1.6.3.3. *Biological Treatment Methods*

Biochemical reactions are the methods where the dissolved organic pollutants are removed from wastewater. Biological treatment is divided into two as aerobic and anaerobic. Treatment occurring in oxygenated environment is called aerobic processes. Here, treatment is carried out by activated sludge systems, trickling filters and aerobic stabilization ponds systems. On the other hand anaerobic processes occur on airless environment. Examples to biological treatment are biological filters, activated sludge and its modifications, stabilization ponds and modifications.

The percentage of wastewater treatment plants according to the treatment type in Turkey is given in Fig.1.13 [72].

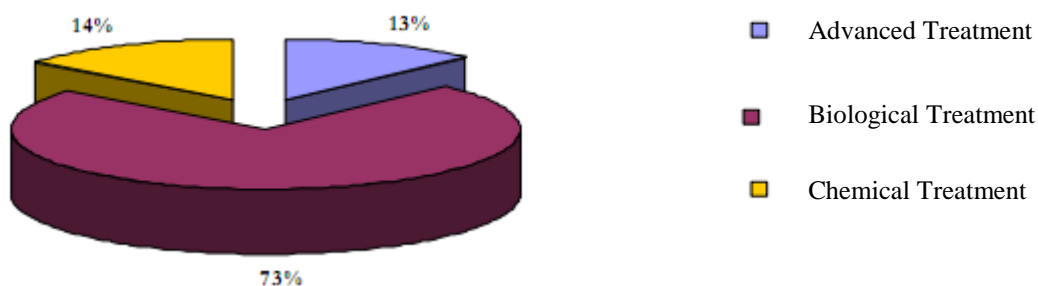


Figure 1.13. The Percentage of Wastewater Treatment Types.

1.7. Other Metal Purification Methods from Wastewater

Several treatment methods for metal ions removal from aqueous solutions have been published, principally reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption [73]. Most of these methods are affected from the disadvantages such as high capital and operational costs or the disposal of the residual metal sludge [74].

Many reports have appeared on the development of low-cost activated carbon adsorbents developed from cheaper and readily available materials [17,75,76]. Activated carbons have large surface area, microporous character. Chemical natures of

the surface with these characters have made them potential adsorbents for heavy metals removal from industrial wastewater [74].

Reverse osmosis is a membrane technical filtration method that removes many types of large molecules and ions from solutions by applying pressure to the solution when it is on one side of a selective membrane. Disadvantage of this method is being expensive.

Ultrafiltration is a variety of membrane filtration in which hydrostatic pressure forces a liquid against a semipermeable membrane. Suspended solids and solutes of high molecular weight are retained, while water and low molecular weight solutes pass through the membrane. Disadvantage of this method is the high amount of sludge produced as a result.

Ion exchange is based on displacement of metal ions in solution with ions held by electrostatic forces over the ion exchange resins. High cost and only certain ions removal are disadvantages of the system.

1.7.1. Filtration

Filtration is commonly used method for removal of suspended solid substances remained in water treatment. It is used mainly for removal of suspended solids such as clay and silt particles produced during treatment processes, colloidal and decayed humic substances, particles formed by putrefying, calcium carbonate used in water softening, and magnesium hydroxide sediments [77].

1.7.2. Coagulation

1.7.2.1. Chemical Coagulation

Chemical coagulation is an event to provide the sedimentation by gathering together by neutralization of charged ions by mutually colliding charged ions within colloidal suspension with opposite charged ions. For this reason chemical substances are added. Alum like chemical substances has long been used to a large extent for wastewater treatment.

The most widely used coagulant in wastewater treatment applications is aluminum sulfate. (Alum - $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). Coagulation becomes faster by shock formation precipitated faster by addition of some chemicals [7].

1.7.2.2. Electrocoagulation

In this method, aluminum hydroxide shocks are produced with electrochemical hydrolysis by using aluminum anodes. Recently, due to the limitations for discharge outlets of wastewater treatment, electrocoagulation has come on the agenda again.

The precipitates produced during electrocoagulation generally arise from many hydroxide formations. These hydroxides is due to the soluble electrode material. If aluminum electrodes are used, the precipitates produced in the result are disposed into garbage dump site. Because of that iron electrodes are preferred more. Because in landfill sites heavy metal pollution can exist [7].

Direct current and direct current power suppliers are generally used in electrocoagulation processes. It is used in paper and paper industry and mining and metal processing industry. Also, it is used in wastewater treatment of food, oil, paint, metal industry wastewater, leaking water containing organic matter, fluoride removal, textile, synthetic detergent and mining processes.

Initial and final concentrations of metal plating wastewaters treated by electrocoagulation method are given on Table 1.8. From these results it is clearly seen that electrocoagulation is an effective method for metal purification.

Table 1.8. Initial and final concentrations of metal plating wastewater treated by electrocoagulation.

Element	Entrance (ppm)	EC Output (ppm)	Purification (%)
Cd	31	0.34	98.90
Cr	210	0.0216	99.99
Cu	287	0.48	99.80
Pb	24	0.010	99.95
Zn	221	0.14	99.90

1.7.3. Biosorption

Biosorption is the accumulation of waste substances on the cell surface or within the cell in aqueous solutions by biological materials, bacteria, algae, fungi, molds and so on species [78]. While choosing the biomass that is used in metal biosorption, the most important factor to be considered is the origin of biomass. It should be selected from industrial wastes or obtainable from nature and rapig growing microorganisms [43]. Some pretreatment processes killing the cells of microorganisms are carried out such as killing by heat treatment, the use of organic chemicals as formaldehyde, detergents, and the use of inorganic chemicals (NaOH, HCl, HNO₃, H₂SO₄, NaHCO₃, and CaCl₂). These pretreatments, drying and grinding processes increase significantly the capacity of biosorption [79]. From many studies about biosorption, it is seen that microorganisms decontaminated from metal ions could be reused and metal recovery capacity of this reused microorganism decreases.

1.8. LITERATURE SURVEY

1.8.1. Comparison of adsorption capacity of different adsorbents for heavy metals ions

In this study, it is aimed to investigate the usability of tea waste and gey and brown clays, collected from Erzurum region, as an adsorbent in removing metal ions such as Zn (II), Cd (II), Pb (II) and Cu (II).

Tea contains polyphenols, lignin, tannin and organic compounds in cellulose structure. Because of that, it is considered to be used as an adsorbent. After the tea waste was washed with pure water, then with heated pure water at 70-80°C until having a colorless extract, it was dried in oven 110°C. Then it is used as adsorbent. Grey and brown Erzurum clays were used after meshing through different sized meshes. In this study the effect of treatment time, mixing speed, amount of adsorbent, particular size, ionic strength, single ionic adsorption, pH, temperature and concentration of Zn (II), Cd (II), Pb (II) and Cu (II) on adsorption capacity were examined. After ascertaining the optimum adsorption conditions for these adsorbents, desorption of these ions was also studied. The concentrations of Zn (II), Cd (II), Pb (II) and Cu (II) adsorbed and desorbed from tea waste and Erzurum clays was determined by DPP-ASV method.

It is found in the study that the optimum adsorption conditions for selected metal ions were 30 min. treatment times, 500 rpm mixing speed, 1.00 g adsorbent, 1000 mesh particular size, pH 5.00 and 30°C temperature. The adsorption capacity of tea waste on Zn (II), Cd (II), Pb (II) and Cu (II) was found 15.66, 18.83, 22.53, and 21.51 mg/g, respectively. For Zn (II), Cd (II), Pb (II) and Cu (II) adsorption on grey Erzurum clay, studied optimum conditions were same as in tea waste except treatment time and pH, which were 10 min. treatment times, and pH 4.00. The adsorption capacity of tea waste on Zn (II), Cd (II), Pb (II) and Cu (II) was found 16.40, 16.77, 18.40, and 19.38 mg/g, respectively. For Zn (II), Cd (II), Pb (II) and Cu (II) adsorption on brown Erzurum clay, studied optimum conditions were same as in tea waste and grey Erzurum clay except treatment time, pH and temperature which were 15 min. treatment times, pH 6.00 and 20°C temperature. The adsorption capacity of tea waste on Zn (II), Cd (II), Pb (II) and Cu (II) was found 12.93, 13.05, 17.80, and 17.40 mg/g, respectively.

The desorption of adsorbed Zn(II), Cd(II), Pb(II) and Cu(II) from drunk tea waste in 0.1 M HNO₃ were 68.69 %, 44.41 %, 56.36 % and 53.42 % respectively, from grey Erzurum clay in 0,1 M HCl were 97.14 %, 65.18 %, 65.61 % and 68.50 % respectively and from brown Erzurum clay in 0.1 M HCl were 64.65 %, 64.80 %, 51.53 % and 48.84 % respectively.

From these results it could be concluded that these adsorbents can be used to remove metal ions.

1.8.2. Lead Removal From Wastewaters By Natural Zeolites

In this study, the capacity of natural zeolite clinoptilolite brought from Manisa City as a low cost ion exchange material for lead removal from industrial wastewaters were evaluated. In the experiment activated and not activated zeolites were used as adsorbents. The zeolite sample activated with 1 M NaCl solution at a flow rate of 2 mL/min.

Batch experiment with different mixing time, mixing speed and Pb (II) concentration was used for ion exchange study and maintains column experiment using lead-zinc mining raw wastewaters. It is found from the experimental study that the activated zeolites have higher removal efficiency than the non-activated zeolites. When the mixing time was chosen between 5 and 10 minutes, lead removal efficiency by activated zeolites was increases by 11-15 %. By using activated zeolite, maximum removal efficiency was obtained at 30 minutes mixing time.

1.8.3. Removal of Heavy Metal Ions from Aqueous Solutions by Keratin

In this study, the capacity of chicken feathers in heavy metal ions removal from wastewater were investigated. Untreated an treated chicken feathers were used for Cd (II), Ni (II), Cu (II) ions removal from their dilute aqueous solutions. In order to raise the heavy metal ions removal, chicken feathers were modified with sodium hydroxide, acetic acid and citric acid. The highest uptake capacity was achieved for all heavy metal ions with chicken feathers modified with citric acid.

Pseudo-first order, pseudo-second order and Weber-Morris intra-particle diffusion kinetics models were studied to assess the adsorption kinetics mechanism. For the sorption of metal ions onto chicken feathers modified with citric acid, the pseudo-second order kinetic model is found to be more appropriate. When the modified chicken feathers are compared with unmodified chicken feathers, it is seen that heavy metal removal capacities were increased by 85, 80, 79, 72 for Cd (II), Ni (II), Zn (II) and Cu (II), respectively.

1.8.4. Investigation of Applicability of Clay Minerals in Wastewater Treatment

It is aimed in this study to utilize the clay minerals in wastewater treatment. Therefore, kaolinite is used as an adsorbent to remove certain metals (i.e. Cu, Fe, Ni, and Zn) from aqueous solutions. In batch adsorption experiments, the effects of pH, particle size, adsorbent dosage, contact time and initial metal concentrations were studied for synthetic and industrial wastewaters. It can be deduced from the results that kaolinite is a very strong adsorbent. The pH of metal solution has a strong effect on metal removal. The pH 10 was found to be optimum condition for maximum adsorption of Cu (II), Ni (II) and Zn (II).

By 99.4 % removal efficiency, copper concentration was reduced from 1000 $\mu\text{g/L}$ to 5 $\mu\text{g/L}$. The maximum efficiency for Ni and Zn ions were 98% and 97%, respectively. Nevertheless pH 5 was found to be more appropriate for iron removal by 99 % efficiency. Despite the fact that adsorption efficiency was not importantly affected from the particle size, the smallest particle size was determined as an effective diameter for the kaolinite. Although 0.1 g adsorbent was required for copper and zinc ions, higher amounts of adsorbent were required for nickel and iron adsorption. Moreover, metal removals were achieved very quickly which 15 minutes contact time was enough for effective metal removal. In addition to this, adsorption kinetics was also examined. Adsorption data for copper, iron and nickel was adjusted to Freundlich equation which shows that physical adsorption mechanism is effective in the process.

CHAPTER 2

EXPERIMENTAL

2.1 INSTRUMENTATION

In the study, the surface structure was determined by SEM (Scanning Electron Microscopy). The pH was measured using a NEL 890 pH meter. A rotary shaker was used to mix the samples. Hermle Z 300 model centrifuge was used for centrifugation. Solutions were digested by CEM MARS Xpress. The concentration of heavy metals in the solutions was determined by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) using standard methods 3120B.

2.1.1 Spectroscopic Measurements

2.1.1.1 ICP-OES

An analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element [10-11]. The intensity of this emission is indicative of the concentration of the element within the sample.

The basic aim of analytical atomic spectroscopy is to identify elements and quantify their concentrations in various media. The procedure consists of three general steps: atom formation, excitation, and emission. Before excitation, an element that is bound in a specific matrix must be separated from that matrix so that its atomic emission spectra are free from interferences. For UV and visible spectroscopy, the input energy must be sufficient to raise an electron from the ground state to the excited state. Once the electron is in the excited state, the atom emits light, which is characteristic of

that particular element. This tutorial will compare the Inductively Coupled Plasma (ICP) excitation source to other techniques while covering methods of sample introduction, detection, and fundamental plasma processes [81].

In Fig. 2.1, the steps involved in the analysis of aqueous samples by inductively coupled plasma are shown. It consists of 6 basic steps.

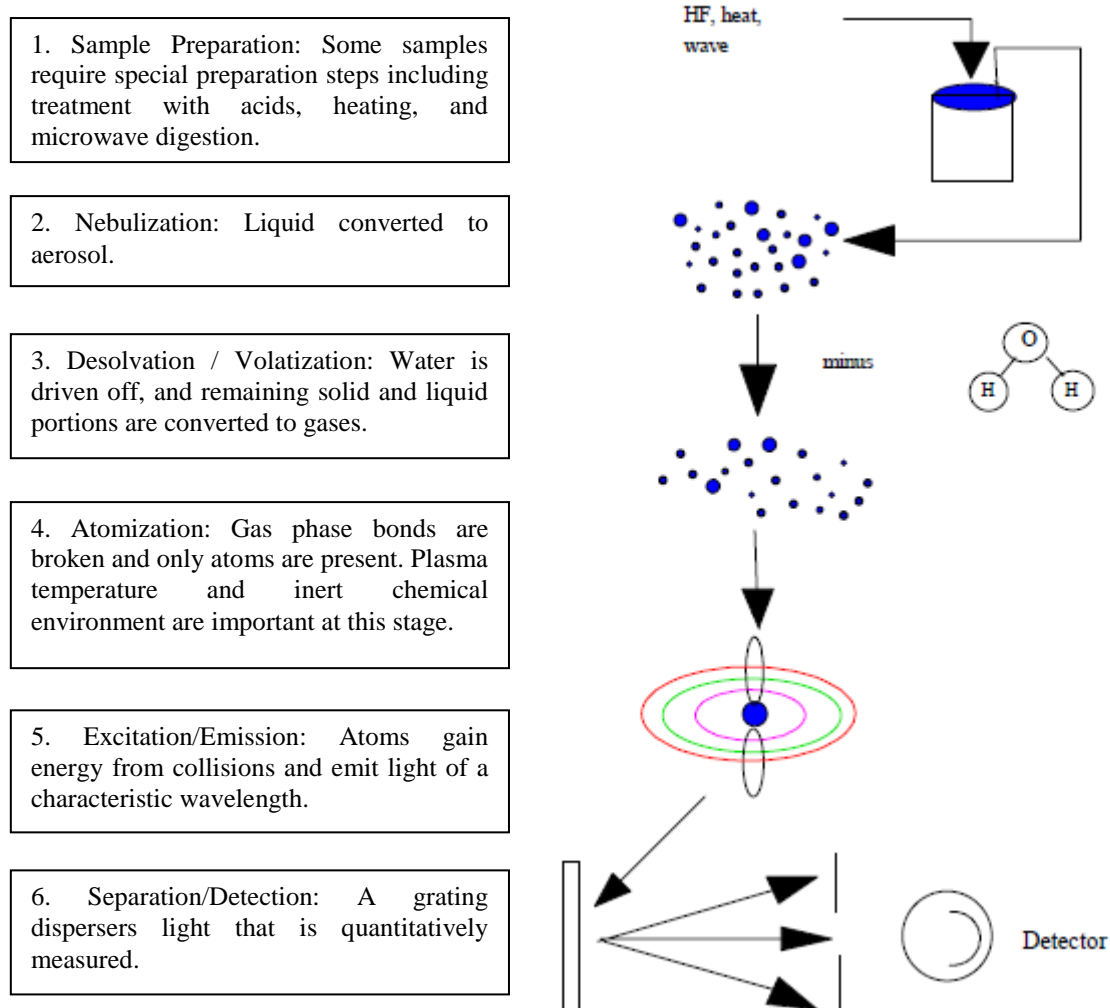


Figure 2.1. Steps Involved in The Analysis of Aqueous Samples by ICP-OES.

2.1.2 SEM

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. The electron beam, which typically has

an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high-resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disk [82].

In this study, Scanning Electron Microscopy (SEM) analysis was performed on a FEI XL40 Sirion FEG Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to SEM analysis.

2.1.3 Microwave

To perform an atomic absorption or atomic emission measurement the sample must be dissolved prior to analysis. It is often the case that the sample is not easily dissolved. In such situations fusion or acid digestion may be used, microwave digestion is a form of acid digestion. Microwave digestion offers high-pressure and temperature systems in order to increase reaction rates and decrease digestion times for sample preparation for trace metal analysis.

In this study, microwave digestion was performed on CEM MARS Xpress. Sample digestion was carried out on that instrument according to the EPA 3015 AND 3051 method.

2.2 COLLECTION OF SLUDGE SAMPLES

Activated sludge from a textile industry wastewater treatment plant was used in this work.

2.3 METAL ADSORPTION AT FIXED PH

The initial pH of the textile sludge was 11. Because of the effect of pH on the adsorption of Pb (II), Cd (II) and Cr (III) onto textile sludge it was studied in the range $7 < \text{pH} < 8$ according to the previous studies. Its pH was adjusted to 7.2 by adding H_2SO_4 .

2.4 ADSORPTION PROCESS

The adsorption of heavy metals onto activated sludge was studied in batch operation mode. The general method used for this study was the following. A known weight of the corresponding adsorbent was equilibrated with 50 mL of the heavy metals solution of known initial concentration (C_0) in stopped borosil glass flasks at a room temperature (22°C) in a thermostatic mechanical stirrer. The metal solutions of Pb, Cd and Cr were prepared from $\text{Pb}(\text{NO}_3)_2$; $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ respectively. In each case and for each adsorbent, flasks containing solutions with different initial metal concentrations were used. Stirring was kept until reaching steady concentration of metal in solution (C_e), i.e. until equilibrium. After equilibration, the corresponding adsorbent was separated from solution by centrifuge. The remaining metal concentration in solution was analyzed by VARIAN 710-Series Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) instrument. In all cases, experiments were carried out by duplicate. Control solutions without adsorbent and blanks without metal were run simultaneously with experiments for control purposes.

2.4.1 Metal Salts

Cadmium Nitrate Tetrahydrate - $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Lead Nitrate - $\text{Pb}(\text{NO}_3)_2$, Chromium Nitrate - $\text{Cr}(\text{NO}_3)_2$ and all other chemicals were analytical grade and purchased from Merck and used as received without further purification.

2.4.2 Preparation of Metal Solutions

The metal solutions of Pb, Cd and Cr were prepared from $\text{Pb}(\text{NO}_3)_2$; $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ respectively.

2.4.2.1 Preparation of Lead Solutions

A stock solution of 1000 mg/l Pb solutions was prepared. 1598,5 mg lead nitrate salt was dissolved in 1-L distilled water. From this stock solution 75, 100, 150 and 250 ppm, 100 ml stock solutions were prepared.

2.4.2.2 Preparation of Cadmium Solutions

A stock solution of 1000 mg/l Cd solutions was prepared. 2744,2 mg cadmium nitrate tetrahydrate salt was dissolved in 1-L distilled water. From this stock solution 50, 75, 100, 150 and 250 ppm, 100 ml stock solutions were prepared.

2.4.2.3 Preparation of Chromium Solutions

A stock solution of 1000 mg/l Cr solutions was prepared. 7692,9 mg chromium nitrate salt was dissolved in 1-L distilled water. From this stock solution 75, 100, 150 and 250 ppm, 100 ml stock solutions were prepared.

2.4.3 Adsorption of Lead on Sludge at Various Adsorbent Amount, Time and Initial Metal Concentrations

The effect of initial metal concentration on adsorption and different weight of adsorbent was determined in the study. 25, 50, 75, 100 ve 125 mg adsorbent were added

to 75, 100, 150 ve 250 ppm 50 ml Pb solutions respectively all of them. These solutions were stirred at room temperature on mechanical stirrer for two hours. For precipitation of adsorbent the solutions were rested for 15 minutes. After that, solutions were centrifuged at 6000 rpm/rcf for five minutes. After centrifugation, solutions were taken to the bottles and kept in refrigerator for Pb analysis.

In order to determine the equilibrium time for adsorbent, various agitation periods were experienced. A known amount of adsorbent (100 mg) was added to the 150, 200 and 250 ppm solutions. Agitation times were 5, 10, 15, 20, 30, 45, 60 and 90 minutes. For precipitation of adsorbent the solutions were rested for 15 minutes. After that, solutions were centrifuged at 6000 rpm/rcf for five minutes. After centrifugation, solutions were taken to the bottles and kept in refrigerator for Pb analysis.

2.4.4 Adsorption of Cadmium on Sludge at Various Adsorbent Amount, Time and Initial Metal Concentrations

The effect of initial metal concentration on adsorption and different weight of adsorbent was determined in the study. 25, 50, 75, 100 ve 125 mg adsorbent were added to 75, 100, 150 ve 250 ppm 50 ml Cd solutions respectively all of them. These solutions were stirred at room temperature on mechanical stirrer for two hours. For precipitation of adsorbent the solutions were rested for 15 minutes. After that, solutions were centrifuged at 6000 rpm/rcf for five minutes. After centrifugation, solutions were taken to the bottles and kept in refrigerator for Cd analysis.

In order to determine the equilibrium time for adsorbent, various agitation periods were experienced. A known amount of adsorbent (125 mg) was added to the 75, 100 and 125 ppm solutions. Agitation times were 5, 10, 15, 20, 30, 45, 60 and 90 minutes. For precipitation of adsorbent the solutions were rested for 15 minutes. After that, solutions were centrifuged at 6000 rpm/rcf for five minutes. After centrifugation, solutions were taken to the bottles and kept in refrigerator for Pb analysis.

2.4.5 Adsorption of Chromium on Sludge at Various Adsorbent Amount, Time and Initial Metal Concentrations

The effect of initial metal concentration on adsorption and different weight of adsorbent was determined in the study. 25, 50, 75, 100 ve 125 mg adsorbent were added to 75, 100, 150 ve 250 ppm 50 ml Cr solutions respectively all of them. These solutions were stirred at room temperature on mechanical stirrer for two hours. For precipitation of adsorbent the solutions were rested for 15 minutes. After that, solutions were centrifuged at 6000 rpm/rcf for five minutes. After centrifugation, solutions were taken to the bottles and kept in refrigerator for Cr analysis.

2.4.6 Preparation of Mixtures for ICP-OES Readings

The solutions were digested in microwave. 2 ml sulfuric acid and 6 ml nitric acid were added to the 25 ml solution. Digestion was carried out at 1700W, 170°C for 45 minutes. After the digestion completed, the tubes were got to cool down. When the temperature of tubes down to 30°C, solutions were taken to the 100 ml volumetric flask and diluted to 100 ml with 2 % of nitric acid. These diluted solutions were than filtered from fibre glass in order to get ready for metal analysis.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 CHARACTERIZATION OF ACTIVATED SLUDGE

Analysis of the adsorbent – textile treatment sludge – was carried out by TUBİTAK according to the standards given on the Table 3.1 and results of the analysis are listed on the Table 3.2.

Table 3.1. Methods for the analysis of the sludge [63].

Analysis	The Related Standarts
TOC	SM 5310 B / Incineration On High Tem.
Cadmium, Chromium, Copper	SM 3113 AAS (Graphite Furnace)
LOI	DS/EN 12879
Lead	SM-3113 AAS (Graphite Furnace)
Solid Matter	TS 9546

SM: Standard Methods for the Examination of Water and Wastewater, 21th Edition (2005)

Table 3.2. The Chemical analysis of the used sludge in the study [83].

Parameter	
TOC (mg/kg)	32196
LOI (%)	20.78
Solid Matter (%)	17.81
Cadmium (mg/l)	< 0.0005
Chromium (mg/l)	0.009
Copper (mg/l)	0.367
Lead (mg/l)	0.013

The analysis based on the parameters is given at Annex 3 on Regulation on Sanitary Landfill of Wastes. According to the limit values for sanitary landfill of sludge given on Table 1.5, Pb, Cr, Cd parameters are suitable for inert waste sites; Cu parameter is suitable for nonhazardous waste site; according to the TOC value sludge is suitable for hazardous waste sites, however since the LOI value does not suitable for all three sites, sludge cannot be disposed on sanitary landfill sites.

3.2 MICROSTRUCTURE OF ACTIVATED SLUDGE

The morphology of activated sludge from textile industry was studied by Scanning Electron microscope (SEM). SEM images with different magnifications are shown in Figs. 3.1a and 3.1b. It can be seen that the activated sludge exhibits porous structure and, is formed agglomeration of spherical particles which have an average size about 1-2 microns. Considering the SEM images and the average particle size of the activated sludge, it can also be deduced that the effective surface area of the adsorbent might be quite high.

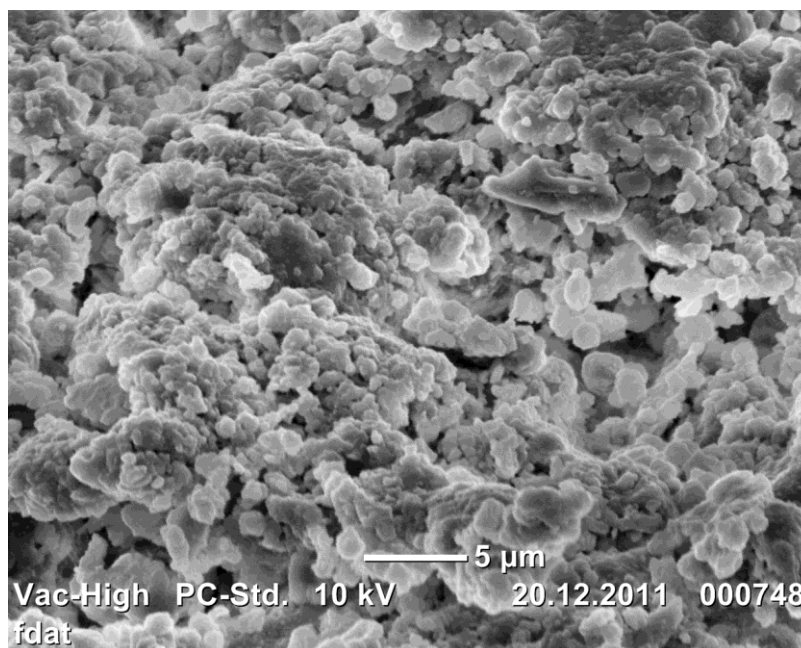


Figure 3.1a. SEM micrograph of the adsorbent.

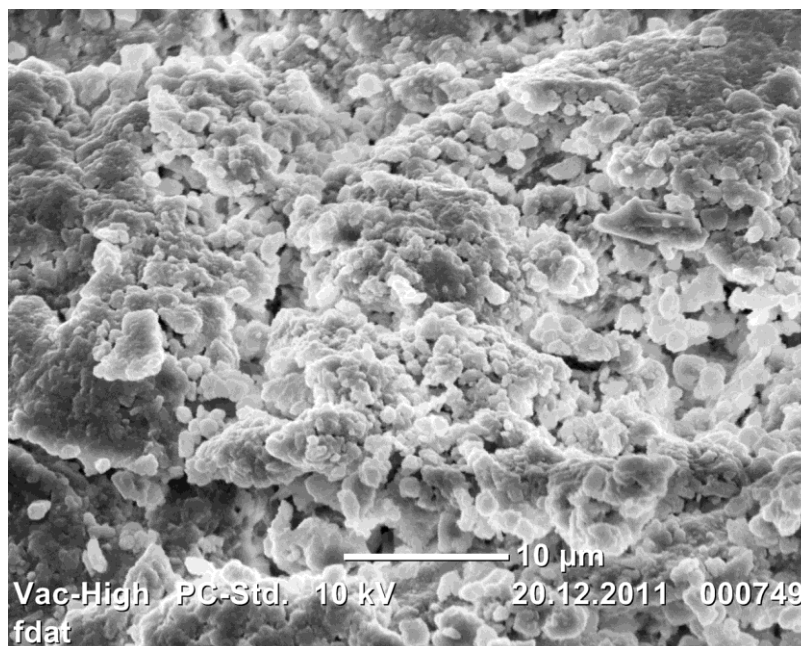


Figure 3.1b. SEM micrograph of the adsorbent.

3.3. ADSORPTION DEPENDING ON THE AMOUNT OF ADSORBENT

The effect of the amount of adsorbent on the adsorption of Pb(II), Cd(II) and Cr(III) metals with different initial concentration was investigated in the range of 25, 50, 100, 125 and 150 mg adsorbent at a constant pH value of 7.

Concentration of the adsorbed Pb(II) depending on the amount of adsorbent is given in Fig.3.2 for the different initial concentrations of metals. It was found that the 98% of the 100 mg/L of Pb(II) can be removed if the amount of adsorbent is 50 mg. Whereas, if the initial concentration of the metal solution is 150 mg/L, the amount of Pb(II) removed reduced to 87%. If the initial metal concentration is 250 mg/L, only 61% of the Pb(II) can be removed from the solution. However, if the amount of adsorbent is 75 mg, 99 % of the initial Pb(II) with a concentration of 150 mg/L can be removed. Removal of Pb(II) was found to be 98% and 84% for the initial metal concentration of 100 and 250 mg/L, respectively for the adsorbent amount of 75 mg. If the amount of adsorbent is 125 mg, 98% of the initial Pb(II) (250 mg/L) was removed. There was no change for the removal of 100 and 150 mg/L Pb(II). It can be concluded

that an effective Pb(II) removal from the aqueous metal solution was successfully performed by the activated sludge for the studied experimental conditions.

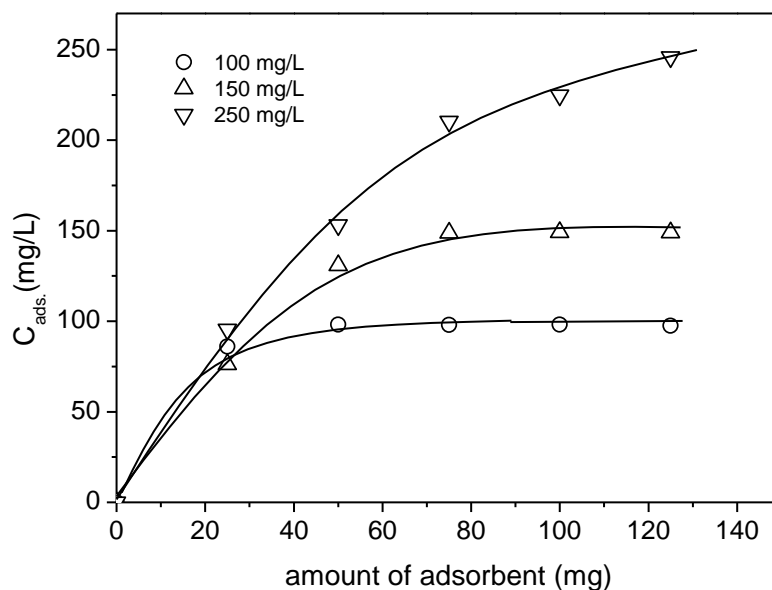


Figure 3.2. Concentration of the adsorbed Pb (II) with different initial concentration depending on the amount of adsorbent.

Concentration of the adsorbed Cd(II) depending on the amount of adsorbent is given in Fig.3.3 for the different initial concentrations of metal. It was calculated that the 65% of the initial Cd(II) (50 mg/L) can be removed if the amount of adsorbent was 50 mg. Whereas, if the initial metal concentration is 100 mg/L, the amount of Cd(II) removed reduced to 45%. For the initial metal concentration of 150 and 250 mg/L, only 33% and 27% of the Cd(II) can be removed, respectively. In the case of 75 mg of adsorbent, it was found that 85%, 62%, 45% and 35% of the initial Cd(II), concentrations of 50, 100, 150 and 250 mg/L were removed, respectively. If the amount of adsorbent is increased to the 125 mg, then the amount of Cd (II) removed increases to 95, 76, 59 and 47 % of the initial Cd(II) with a concentration of 50, 100, 150 and 250 mg/L, respectively. Small percentages of metal removal has succeed on 100, 150, and 250 mg/L Cd(II).

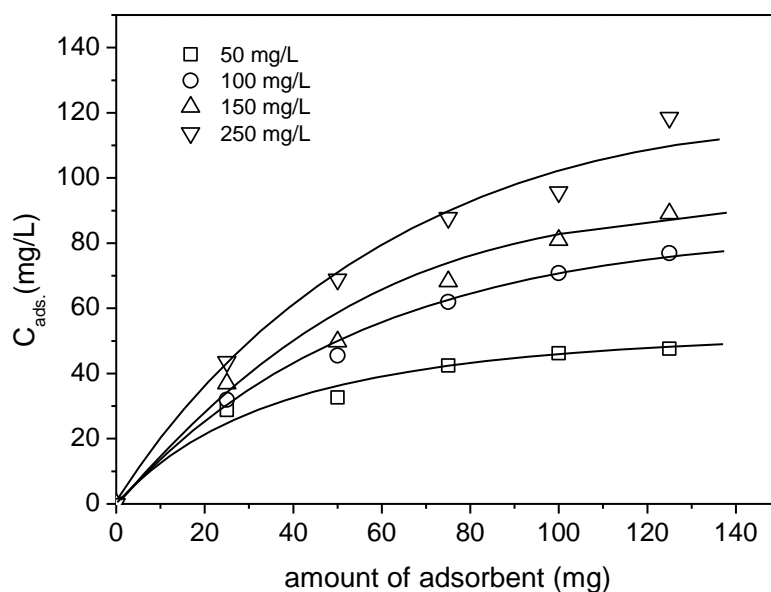


Figure 3.3. Concentration of the adsorbed Cd (II) with different initial concentration depending on the amount of adsorbent.

Concentration of the adsorbed Cr(III) depending on the amount of adsorbent is given on Fig.3.4 with different initial metal concentrations. If the amount of adsorbent is 50 mg, 31% of the initial Cr(III) of 100 mg/L, 29% of the initial Cr(III) of 150 mg/L and only 20% of the initial Cr(III) 250 mg/L can be removed. If the amount of adsorbent is 75 mg, 40%, 35% and 22% of the initial Cr(III) concentration of 100, 150 and 250 mg/L was removed, respectively. If the amount of adsorbent is increased to the 125 mg, then the Cr (III) removal increases to 75%, 48% and 30% of the initial Cr(III) for the concentration of 100, 150 and 250 mg/L, respectively. Based on the experimental results, it can be concluded that the Cr(III) removal by the activated sludge as an adsorbent material was less effective than the other heavy metals, Pb(II) and Cd(II) and also no remarkable change occurred with different initial concentration of Cr (III) metal.

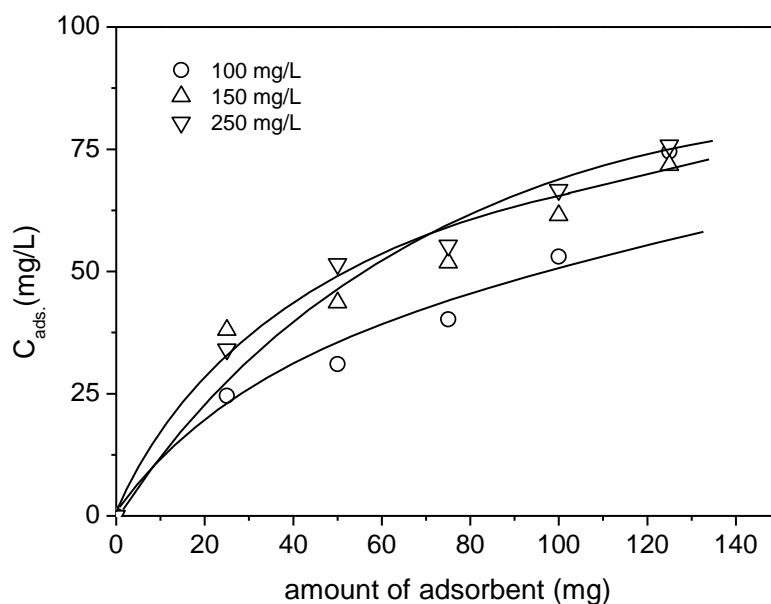


Figure 3.4. Concentration of the adsorbed Cr (III) with different initial concentration depending on the amount of adsorbent.

3.4. ADSORPTION ISOTHERMS

The relation between the amount of adsorbate on a solid adsorbent and the pressure (in case of gases) or the solution concentration (in case of liquids) is known as the adsorption isotherm. Adsorption equilibrium data are typically plotted in the form of an adsorption isotherm with the mass adsorbed on the y-axis and the mass in the fluid on the x-axis at a constant temperature.

The experimental results corresponding to the adsorption of Pb (II) with different initial concentration onto 50 and 100 mg of activated sludge are shown in Figs. 3.5 and 3.6, the adsorption of Cd (II) with different initial concentration onto 50, 75 and 100 mg of activated sludge are shown in Figs. 3.7, 3.8, 3.9 and the adsorption of Cr (III) with different initial concentration onto 50 and 100 mg of activated sludge are shown in Figs. 3.10 and 3.11, respectively.

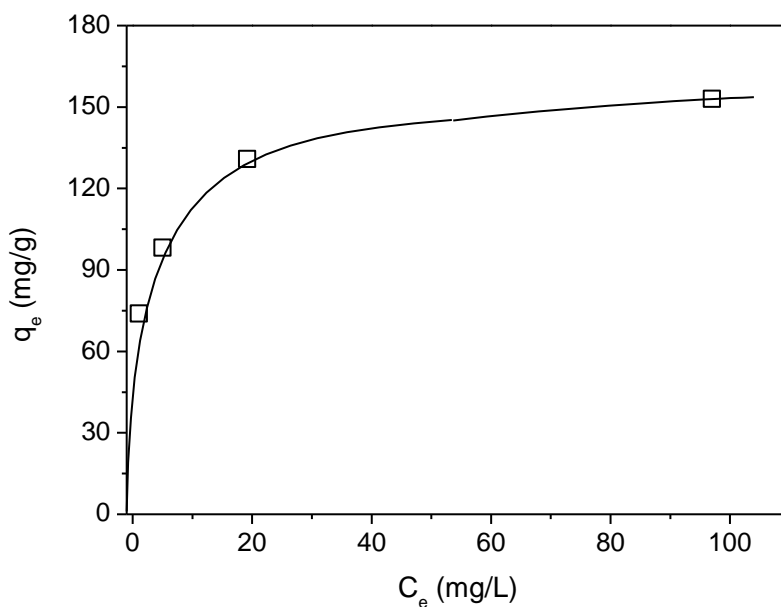


Figure 3.5. Equilibrium isotherm of Pb (II) onto the 50 mg of sludge.

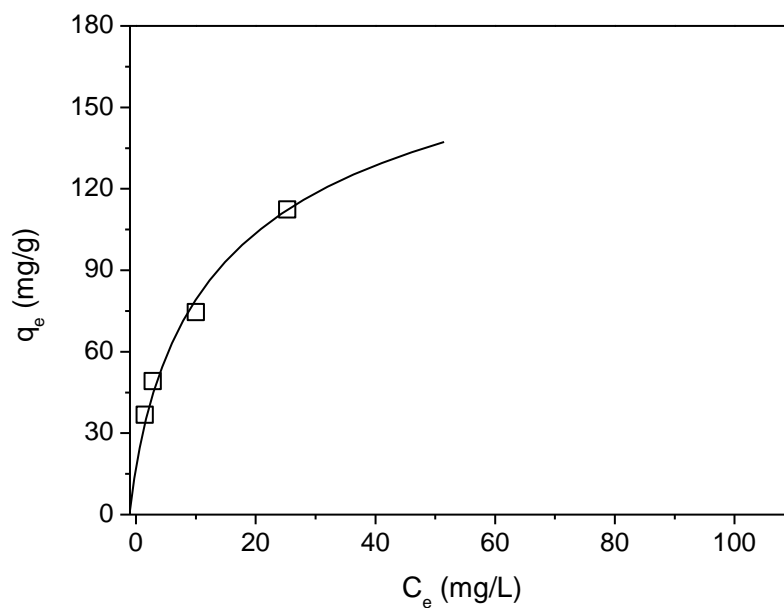


Figure 3.6. Equilibrium isotherm of Pb (II) onto the 100 mg of sludge.

For Pb (II) adsorption onto 50 mg adsorbent, as it can be seen in Fig. 3.5, q_e (mg/g) increased with initial metal concentration, but kept nearly same for 150 and 250 mg/L initial metal concentration where q_e reached its maximum value, 153 mg/g.

However, for Pb (II) adsorption onto 100 mg adsorbent, q_e increases gradually but not kept constant as shown in Fig. 3.6 and it only reached to 112 mg/g at 250 mg/L initial Pb (II) concentration. Hence, low weight of adsorbent shows higher affinity than high amount of adsorbent on adsorption of Pb (II).

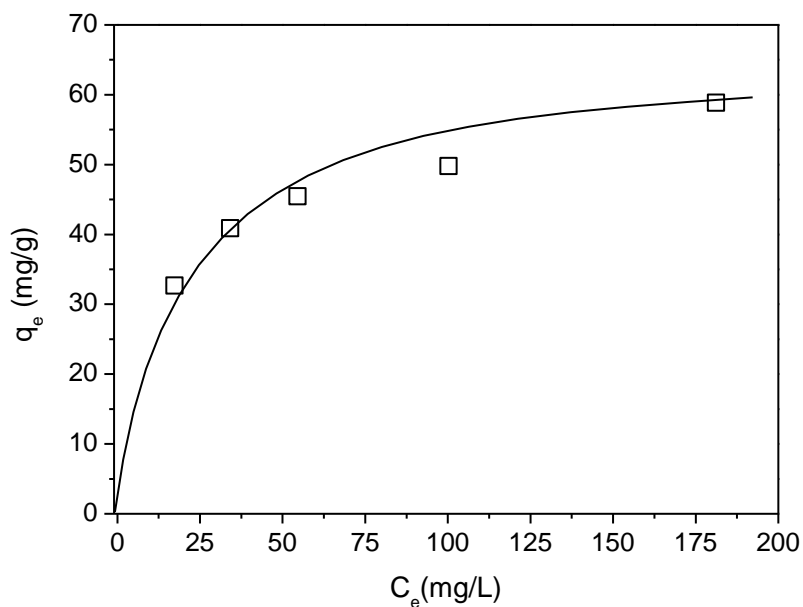


Figure 3.7. Equilibrium isotherm of Cd (II) onto the 50 mg of sludge.

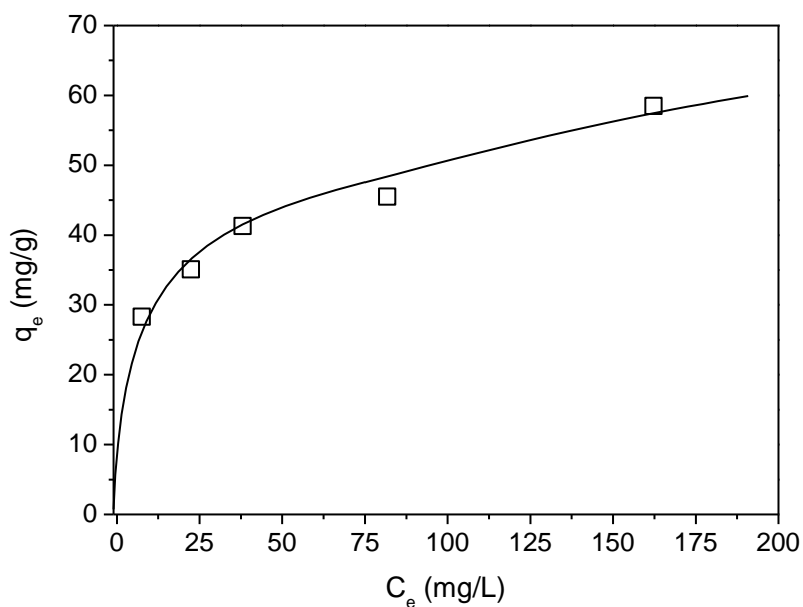


Figure 3.8. Equilibrium isotherm of Cd (II) onto the 75 mg of sludge.

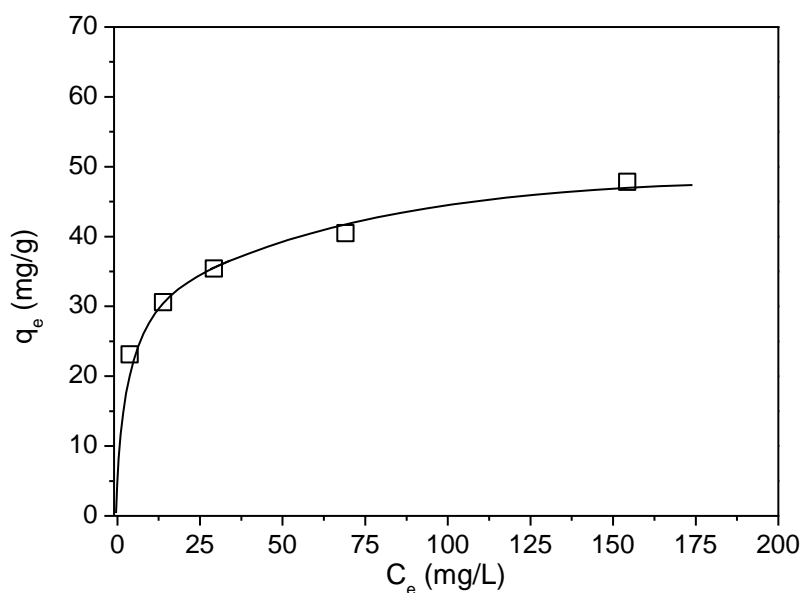


Figure 3.9. Equilibrium isotherm of Cd (II) onto the 100 mg of sludge.

For the Cd (II) adsorption onto 50 mg adsorbent, as it can be seen in Fig. 3.7, q_e (mg/g) increased with initial metal concentration, reached its maximum value, 69 mg/g, at 250 mg/L initial Cd (II) concentration. However, for Cd (II) adsorption onto 75 mg adsorbent, q_e decreases to 59 mg/g and onto 100 mg adsorbent q_e decreases to 48 mg/g at 250 mg/L initial Cd (II) concentration, shown in Figs. 3.8 and 3.9, respectively. As the weight of the adsorbent increases, q_e (mg/g) decreases while the initial Cd (II) concentrations are equal. It can be seen from all three figures that Cd (II) adsorption onto the different adsorbent weight increases gradually with increase in initial Cd (II) concentration.

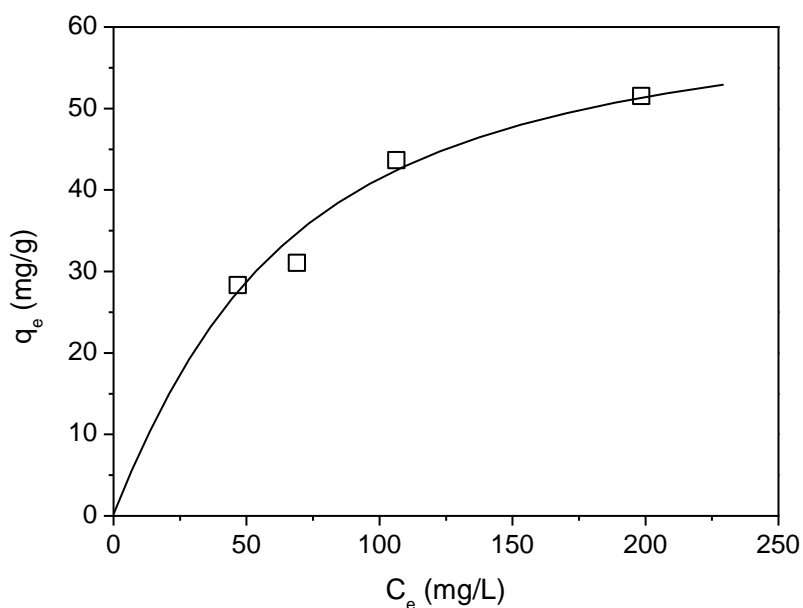


Figure 3.10. Equilibrium isotherm of Cr (III) onto the 50 mg of sludge.

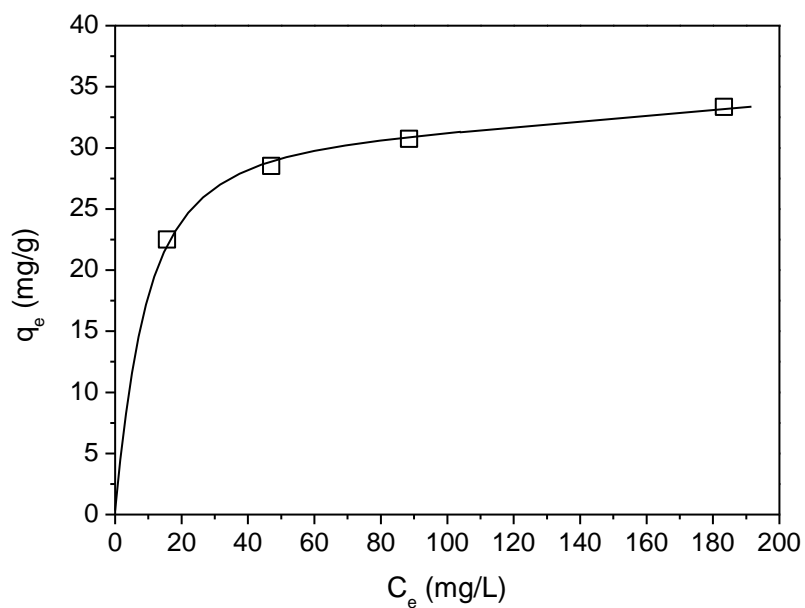


Figure 3.11. Equilibrium isotherm of Cr (III) onto the 100 mg of sludge.

For Cr (III) adsorption onto 50 mg adsorbent, as it can be seen in Fig. 3.10, q_e (mg/g) increased with initial Cr (III) concentration, reached its maximum value, 51 mg/g, at 250 mg/L initial Cr (III) concentration. However, for Cr (III) adsorption onto

100 mg adsorbent, q_e decreases to 33 mg/g at 250 mg/L initial Cr (III) concentration. As the weight of the adsorbent increases, q_e (mg/g) has decreased, nearly 64%, while the initial Cd (II) concentrations are equal.

It can be concluded from all figures from Fig. 3.5 to Fig. 3.11 that adsorbent has higher affinity for Pb (II) than for Cd (II) than for Cr (III) for both 50 and 100 mg of adsorbent, in this order.

3.4.1. Langmuir Isotherms

Langmuir model is the simplest theoretical model for monolayer adsorption onto a surface with finite number of identical sites. A plot of C/q versus C should produce a straight line with a slope of $1/q_m$ and an intercept of $1/K_A q_m$. The Langmuir formulation is theoretical rather than empirical [10]. Langmuir plots for the Pb (II), Cd (II) and Cr (III) adsorptions on the 100 mg of adsorbent are presented in Figs.3.12, 3.13 and 3.14, respectively. The Langmuir parameters are also given on Table 3.3.

A plot of C/q versus C showed a straight line with the correlation coefficient (r^2) of 0,9759 for Pb (II). The K_A and q_m values were determined by regression analysis to be 0,1974 L/g and 131,6 mg/g, respectively; that is Pb (II) saturation value for activated sludge would be 131,6 mg/g with monolayer adsorption.

A plot of C/q versus C yielded a straight line with correlation coefficient (r^2) of 0,9945 for Cd (II). The K_A and q_m values were determined by regression analysis to be 0,1063 L/g and 49,8 mg/g, respectively; that is Cd (II) saturation value for activated sludge would be 49,8 mg/g with monolayer adsorption.

A plot of C/q versus C exhibited a straight line with correlation coefficient (r^2) of 0,9995 for Cr (III). The K_A and q_m values were determined by regression analysis to be 0,100 L/g and 35,1 mg/g, respectively; that is Cr (III) saturation value for activated sludge would be 35,1 mg/g with monolayer adsorption.

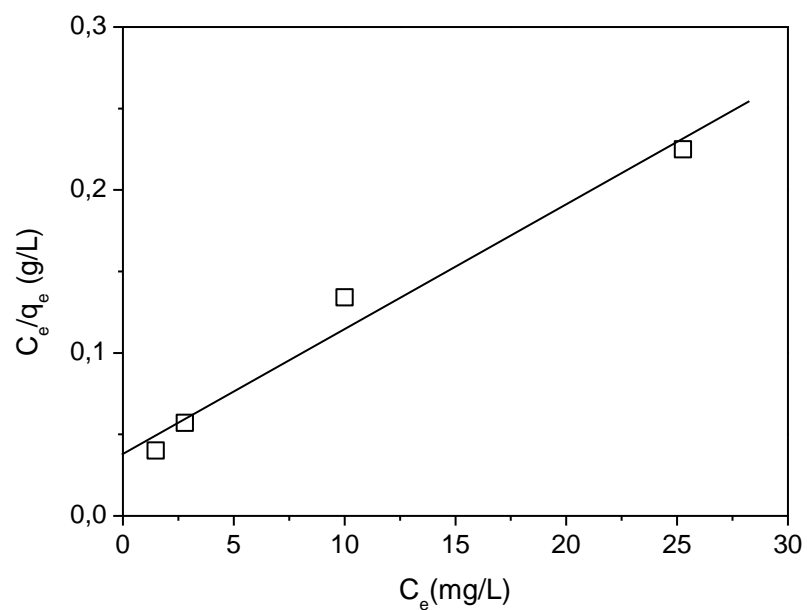


Figure 3.12. Langmuir isotherm for the adsorption of Pb (II) onto 100 mg of activated sludge.

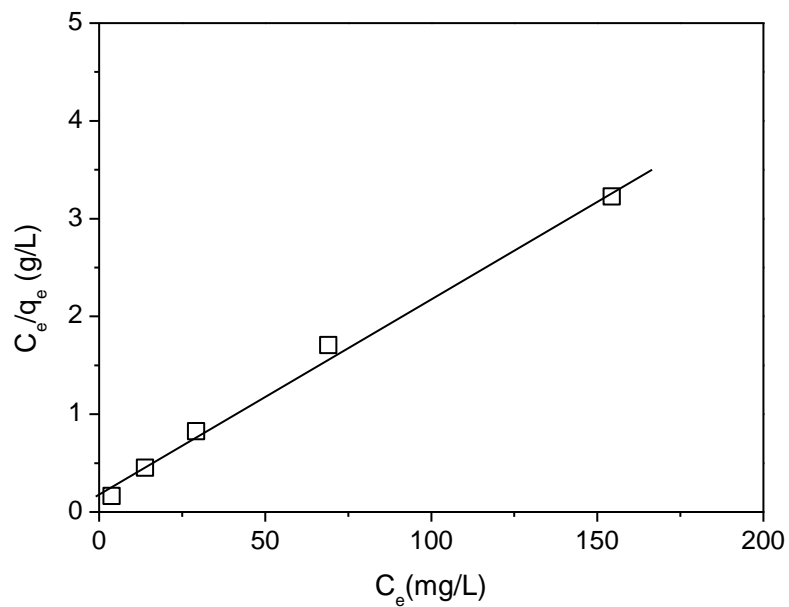


Figure 3.13. Langmuir isotherm for the adsorption of Cd (II) onto 100 mg of activated sludge.

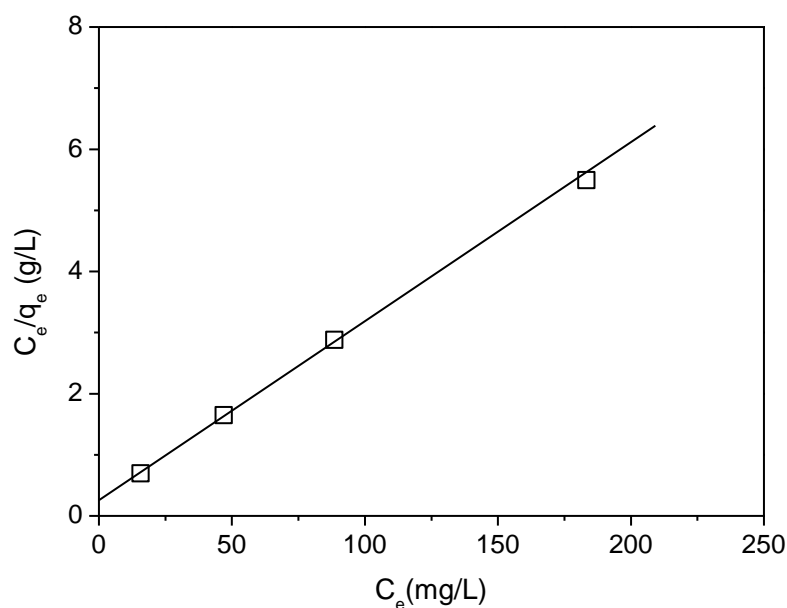


Figure 3.14. Langmuir isotherm for the adsorption of Cr (III) onto 100 mg of activated sludge.

Table 3.3. Langmuir parameters for the heavy metal adsorption onto the sludge.

Heavy metal	q_m (mg/g)	K_L (L/g) ($\times 10^{-3}$)	r^2
Cd	49.8	106.3	0.9945
Pb	131.6	197.4	0.9759
Cr	35.1	100.0	0.9995

Based on the Langmuir results, a characteristic dimensionless parameter, separation factor, R_L , which indicates whether the adsorption process on the studied adsorbent is favorable or not, can be defined as;

$$R_L = \frac{1}{1 + K_L C_0}$$

According to the theory, the case of $R_L = 0$ corresponds to irreversible adsorption, $0 < R_L < 1$ to favourable equilibrium, $R_L = 1$ to linear and $R_L > 1$ to unfavourable equilibrium [84]. The calculated R_L values for the C_0 of 100 mg/L are

0.05, 0.09 and 0.1 for the Pb(II), Cd(II) and Cr(III), respectively. These values imply that the adsorption of such metals is favourable on the adsorbent employed in the study.

3.4.2. Freundlich Isotherms

Freundlich expression is an empirical equation applicable to non-ideal sorption on a heterogeneous surface as well as multilayer sorption. Freundlich isotherms are often used to characterize adsorption phenomena in the liquid phase.

If the metals are adsorbed onto activated sludge, a plot of $\ln q_e$ versus $\ln C_e$ should give a straight line with a slope of $1/n$ and an intercept of $\ln K_F$ ($C = 1$). Equilibrium K_F and n values defined in Chapter 2 can be determined by regression analysis of the isotherm data [10]. Freundlich isotherm equilibrium curves of Pb (II), Cd (II) and Cr (III) adsorption onto 100 mg of adsorbent are presented in Figs.3.15, 3.16 and 3.17. The Freundlich parameters are also given on Table 3.4.

The plots of $\ln(q_e)$ versus $\ln(C_e)$ at four Pb (II) concentrations resulted in excellent linearity with a correlation coefficient (r^2) of 0.9959 which clearly indicates that the Freundlich model fits well the adsorption of Pb (II) onto the activated sludge. The K_F and n values for Pb (II) were determined as 2575 mg/kg and 2.5. The n value can be used to evaluate the adsorption intensity. In case of $1 < n < 10$, adsorption is favourable. The lower n value implies the more favourable adsorption within this range [85]. The n value is between 1 and 10 for the adsorption of Pb (II) which indicates heterogeneity of the adsorbent and favourable adsorption [86].

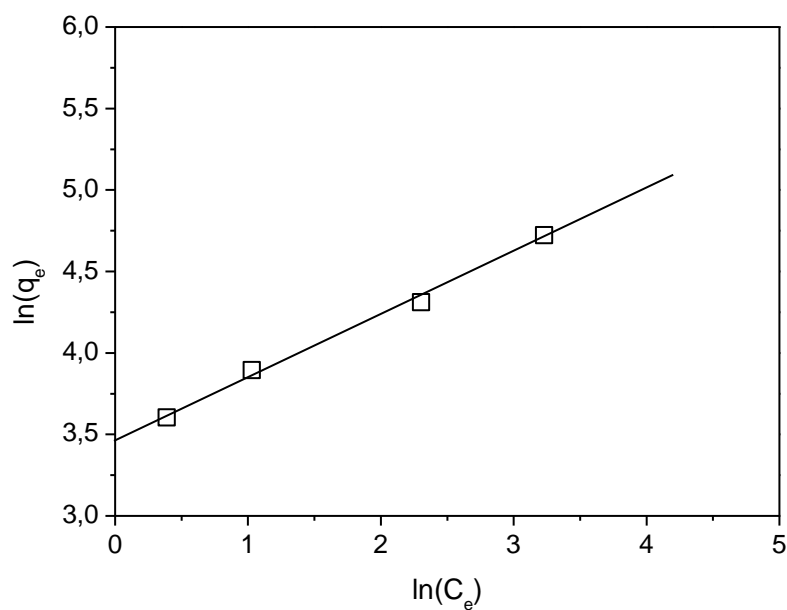


Figure 3.15. Freundlich isotherm for the adsorption of Pb (II) onto 100 mg of activated sludge.

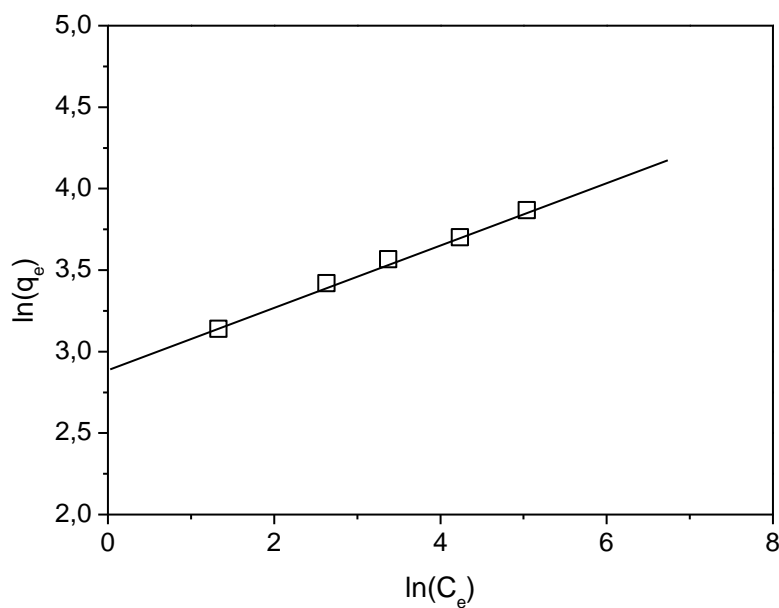


Figure 3.16. Freundlich isotherm for the adsorption of Cd (II) onto 100 mg of activated sludge.

The plots of $\ln(q_e)$ versus $\ln(C_e)$ at various Cd (II) concentrations also defined a good linearity with a correlation coefficient (r^2) of 0.9965 which evidently indicates that

the Cd (II) was adsorbed onto the activated sludge. The K_F and n values for the adsorption of Cd (II) were determined as 797 mg/kg and 5.2, respectively. The n value indicates heterogeneity of the adsorbent and favourable adsorption [86], similarly to the adsorption of Pb (II).

The plots of $\ln(q_e)$ versus $\ln(C_e)$ at four Cr (III) concentrations yielded a linear with a correlation coefficient (r^2) of 0.9697. The K_F and n values for the adsorption of Cr (III) onto the sludge were found to be 517 mg/kg and 6.5, respectively. The n value indicates heterogeneity of the adsorbent and favourable adsorption for the Cr (III) [86].

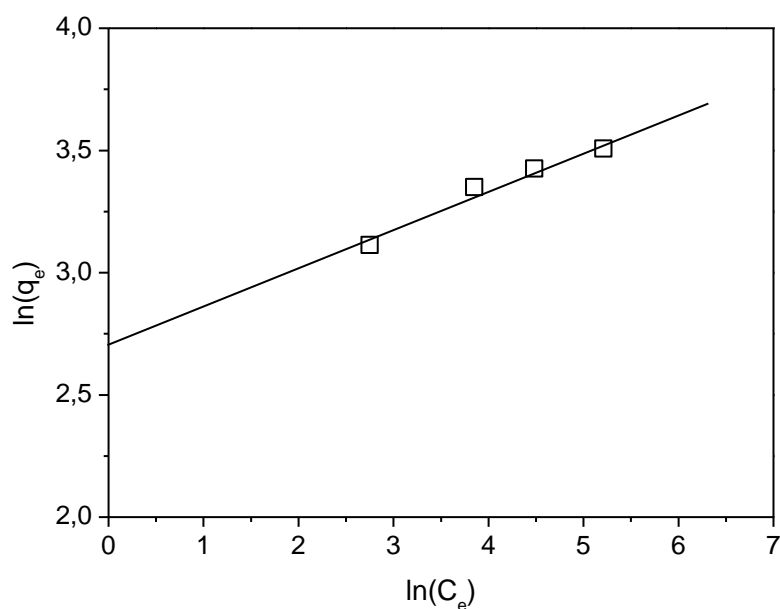


Figure 3.17. Freundlich isotherm for the adsorption of Cr (III) onto 100 mg of activated sludge.

Table 3.4. Freundlich parameters for the heavy metal adsorption onto the sludge

Heavy metal	n	K_F (mg/kg)	r^2
Cd	5.2	797	0.9965
Pb	2.5	2575	0.9959
Cr	6.5	517	0.9696

3.5. ADSORPTION KINETICS

The prediction of batch adsorption kinetics is necessary for the design of industrial adsorption columns. The nature of the adsorption process will depend on physical or chemical characteristics of the adsorbent and also on the system conditions [22]. The study of adsorption kinetics defines the solute uptake rank, evidently controlling the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Pb (II) and Cd(II) adsorption on the activated carbons were analysed using pseudo first-order, pseudo second-order and intraparticle diffusion kinetic models.

Contact time is an important parameter because this factor determines the adsorption kinetics of an adsorbate at a given initial concentration of the adsorbate. The effect of contact time on the heavy metal ions adsorption by treatment sludge was investigated for 5 to 90 minutes. In this study, the kinetic studies were carried out for the different initial metal concentrations [150, 200 and 250 mg/L for Pb(II) and 75, 100, 125 mg/L for Cd(II)] at room temperature.

Time variation of Pb (II) and Cd (II) adsorption on activated sludge at different initial metal concentrations are shown in Figs. 3.18 and 3.19, respectively.

The uptake amount of Pb (II) and Cd (II) ions on activated sludge increases rapidly with increasing of the contact time 0 to 90 minutes. On changing the initial concentration of Pb (II) solution from 150 to 250 mg/L, the amount adsorbed decreased from 59 mg/L (39% removal) to 45,7 mg/L (26,4 % removal) at room temperature at 90 minutes contact time. However, for two hours mixing mentioned in Chapter 2, 100 mg of adsorbent has adsorbed 99,41 % (149,11 mg/L) and 89,89 % (224, 73 mg/L) of Pb (II) metal with a 150 mg/L and 250 mg/L initial concentrations, respectively. So, it could be concluded from these results that 90 minutes is not enough for effective Pb (II) adsorption.

On changing the initial concentration of Cd (II) solution from 75 to 100 mg/L, the amount adsorbed increased from 58 mg/L (77 % removal) to 79,5 mg/L (80 % removal) at room temperature at 90 minutes contact time. When two hours mixing were carried out as mentioned in Chapter 2, 125 mg adsorbent has adsorbed 87,5 % (65,6 mg/L) and

77 % (76,9 mg/L) of Cd (II) metal with 75 and 100 mg/L initial concentrations, respectively. It is clearly seen from these results that even if there is no significant change on Cd(II) adsorption with a 100 mg/L initial concentration, there is a big difference on Cd(II) adsorption with a 75 mg/L initial concentration. Therefore, 90 minutes is not enough for effective Cd (II) adsorption.

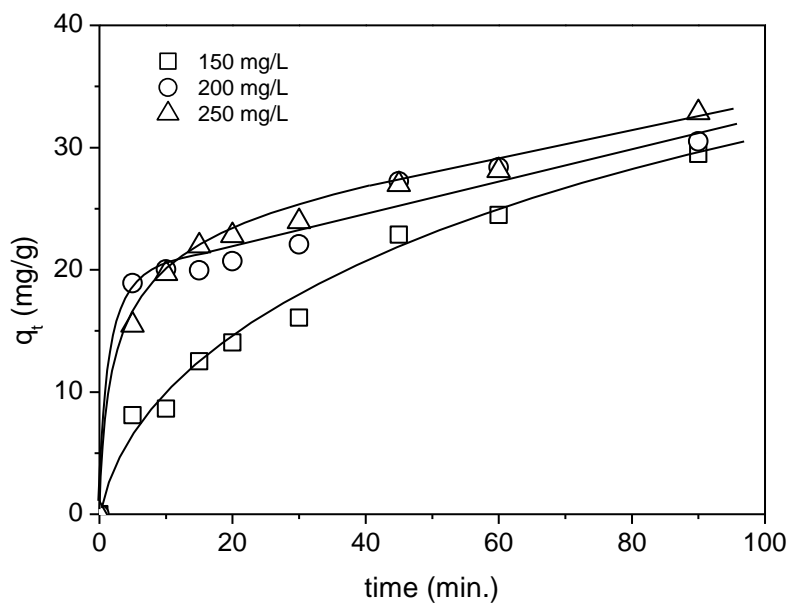


Figure 3.18. Time variation of Pb (II) adsorption on activated sludge at different initial metal concentrations.

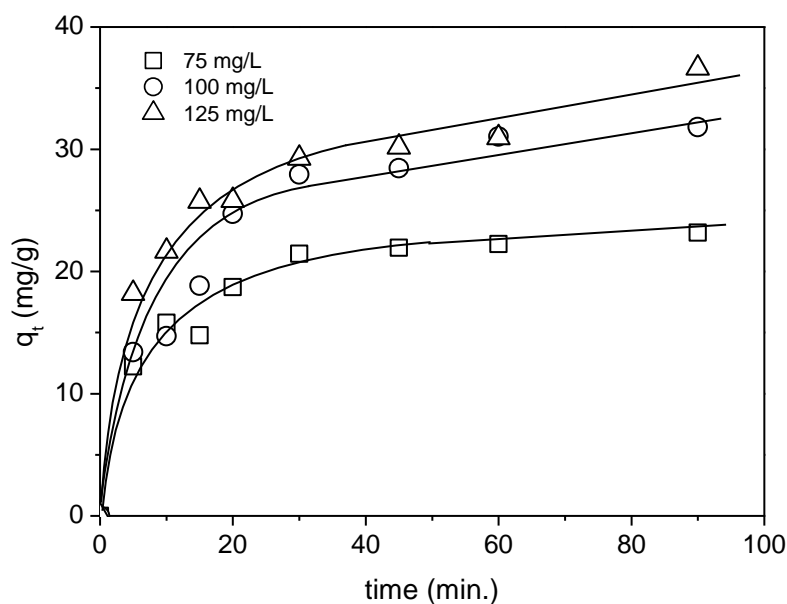


Figure 3.19. Time variation of Cd (II) adsorption on activated sludge at different initial metal concentrations.

The initial rapid phase is due to the presence of large number of vacant sites and, as a result there exist increased the concentration gradient between adsorbate in solution and adsorbate in the adsorbent surface. As time proceeds, this concentration is reduced due to the accumulation of Pb (II) and Cd (II) ions on the vacant sites, leading to decrease in gradient the adsorption rate after 45 minute.

In Figs. 3.18 and 3.19, it is clearly seen that the amount of adsorbate on the solid phase with lower initial concentration of metal was smaller than the amount when higher initial concentrations were used. It was also obvious that the removal of Cd (II) and Pb (II) was dependent on the concentration of Pb (II) and Cd (II) because the decrease in the initial Pb (II) or Cd (II) concentration increased the amount of Pb (II) or Cd (II) adsorbed. The data also showed that the adsorption capacity increased for the higher Pb (II) and Cd (II) ion concentrations.

The adsorption kinetic of Pb(II) and Cd(II) ions were modeled using the pseudo first order and pseudo second order equations. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (r^2 ,

values close or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of Pb (II) and Cd (II) adsorption.

3.5.1. Pseudo-Second Order Kinetics

The pseudo second order kinetic model which is discussed in Chapter 2 and linear form of this model is given by following equation:

$$\frac{t}{q} = \frac{1}{k_2 q e^2} + \frac{1}{q e} t \quad (3.1)$$

Pseudo-second order kinetic parameters for Pb and Cd are given on Table 3.5 and 3.6. The experimental points shown together with the theoretically generated curves (Figs. 3.20 and 3.21) reflect the extremely high correlation coefficients shown in Table 3.5 and 3.6 for Pb(II) and Cd(II), respectively. The data showed good compliance with the pseudo second-order kinetic model for both Pb (II) and Cd (II) adsorption.

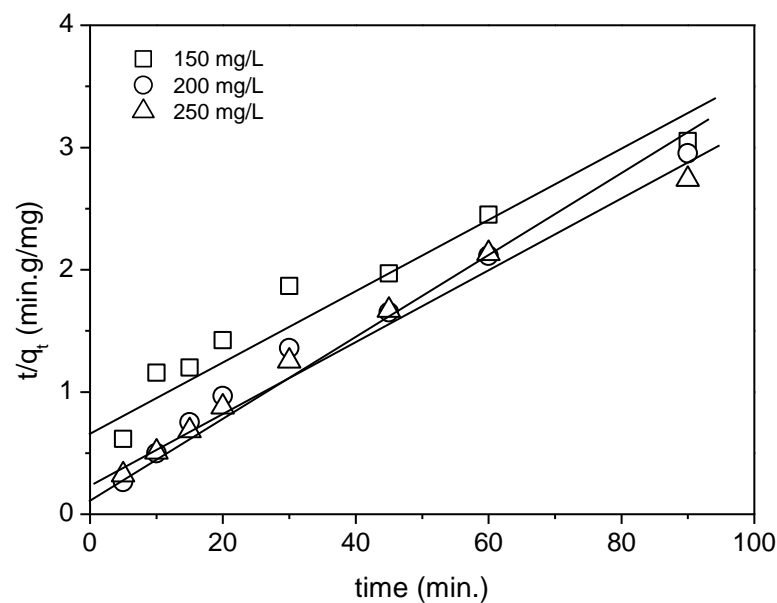


Figure 3.20. Pseudo-second order kinetic plots for the adsorption of Pb (II) onto the activated sludge at different initial metal concentrations.

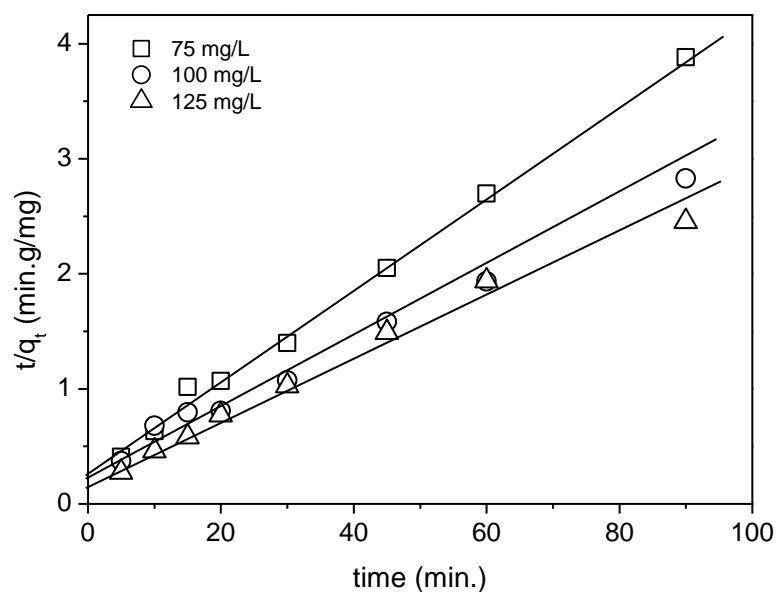


Figure 3.21. Pseudo-second order kinetic plots for the adsorption of Cd (II) onto the activated sludge at different initial metal concentrations.

Table 3.5. Pseudo-second order kinetic parameters for the Pb(II) adsorption.

C_0 (mg/L)	k_2 (g/mg.min.) ($\times 10^{-3}$)	q_e (mg/g)	r^2
150	0.84	38.2	0.9506
200	3.54	32.6	0.9870
250	3.03	34.5	0.9865

Table 3.6. Second-order kinetic parameters for the Cd(II) adsorption.

C_0 (mg/L)	k_2 (g/mg.min.) ($\times 10^{-3}$)	q_e (mg/g)	r^2
75	6.18	24.9	0.9966
100	2.53	36.0	0.9936
125	3.13	38.0	0.9872

3.5.2. Pseudo-First Order Kinetics

Lagergren, the first order rate equation, is one of the most widely used for the adsorption of solute from a liquid solution. It is defined in Chapter 2. It is represented as:

$$\ln\left(\frac{q_e}{q_e - q}\right) = k_1 T \quad (3.2)$$

Pseudo-first order kinetics for the adsorption of Pb (II) onto the activated sludge with initial metal concentrations of 150, 200 and 250 mg/L is given in Fig. 3.22, 3.23 and 3.24, respectively. Pseudo-first order kinetic parameters for Pb (II) adsorption that are determined from the study are given in Table 3.7.

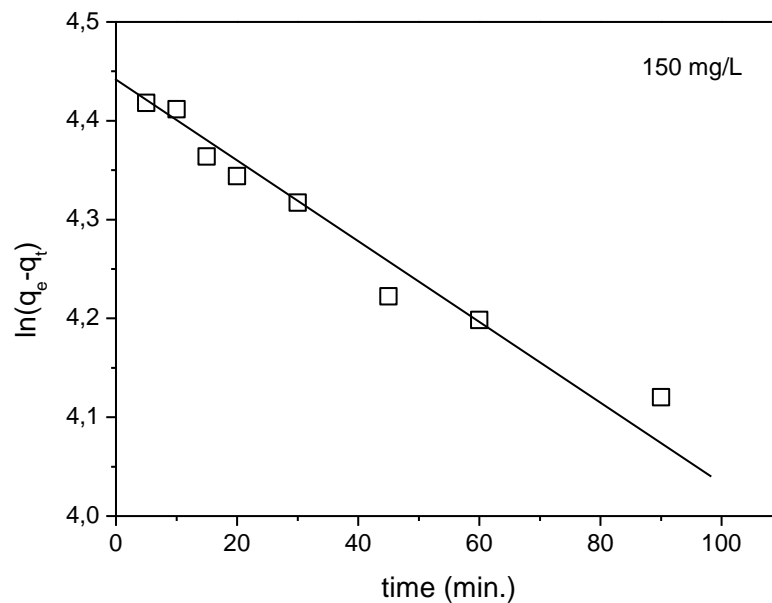


Figure 3.22. Pseudo-first order kinetic plots for the adsorption of Pb (II) (initial metal concentration of 150 mg/L) onto the activated sludge.

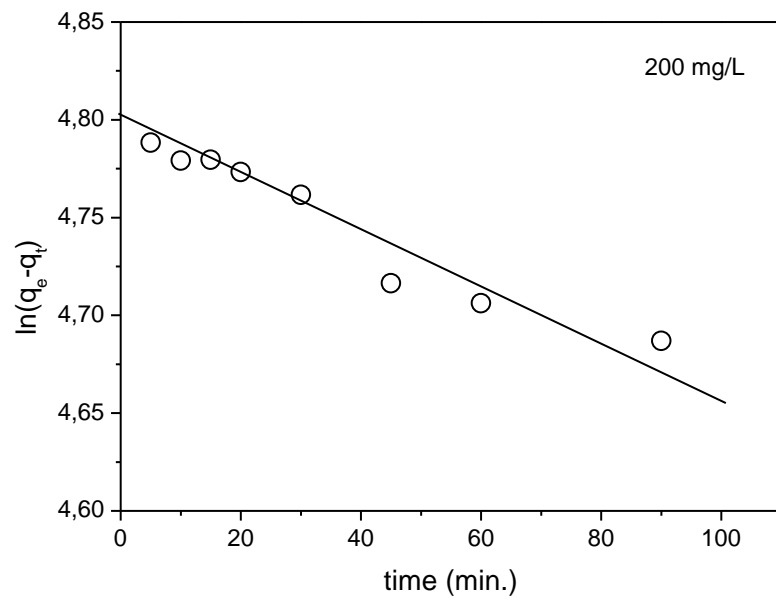


Figure 3.23. Pseudo-first order kinetic plots for the adsorption of Pb (II) (initial metal concentration of 200 mg/L) onto the activated sludge.

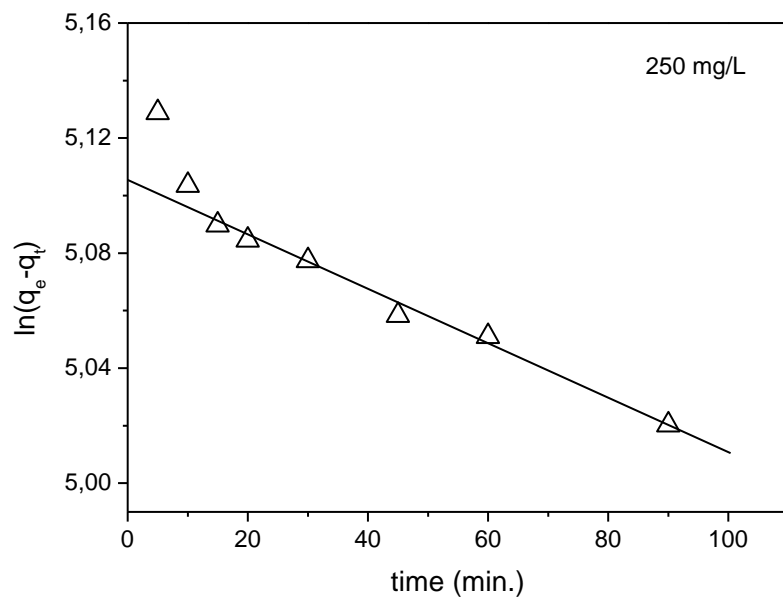


Figure 3.24. Pseudo-first order kinetic plots for the adsorption of Pb (II) (initial metal concentration of 250 mg/L) onto the activated sludge.

Table 3.7. First-order kinetic parameters for the Pb(II) adsorption.

C_0 (mg/L)	k_2 (g/mg.min.) ($\times 10^{-3}$)	q_e (mg/g)	r^2
150	2.3	123.9	0.9646
200	1.4	120.8	0.9396
250	1.7	113.8	0.9258

Pseudo-first order kinetics for the adsorption of Cd (II) onto the activated sludge with initial metal concentrations of 75, 100 and 125 mg/L is given in Fig. 3.25, 3.26 and 3.27, respectively. As seen in these figures, Cd (II) did not yield linear plots which indicates the adsorption rate of Cd (II) onto the adsorbent cannot be explained with the pseudo-first order model.

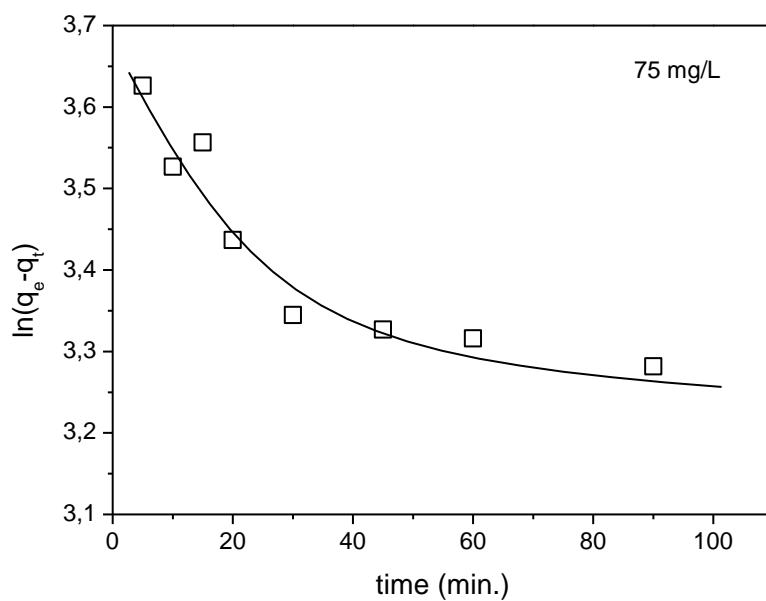


Figure 3.25. Pseudo-first order kinetic plots for the adsorption of Cd (II) (initial metal concentration of 75 mg/L) onto the activated sludge.

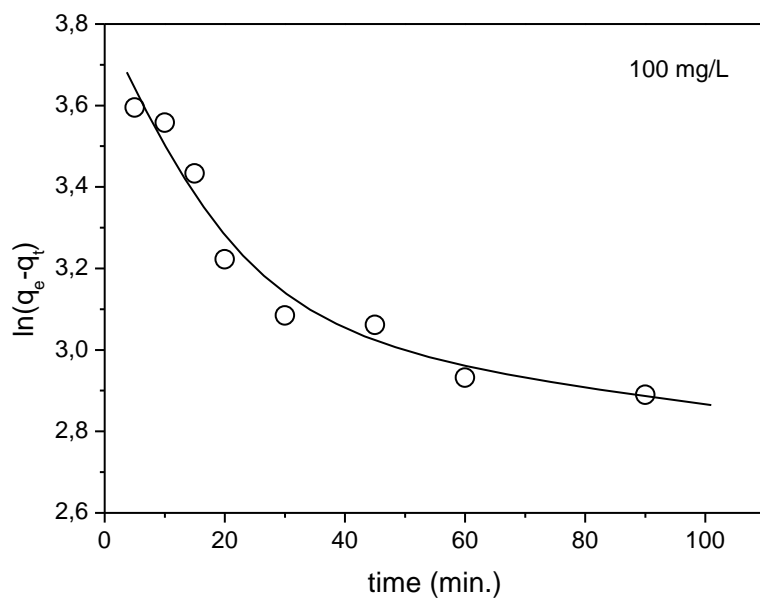


Figure 3.26. Pseudo-first order kinetic plots for the adsorption of Cd (II) (initial metal concentration of 100 mg/L) onto the activated sludge.

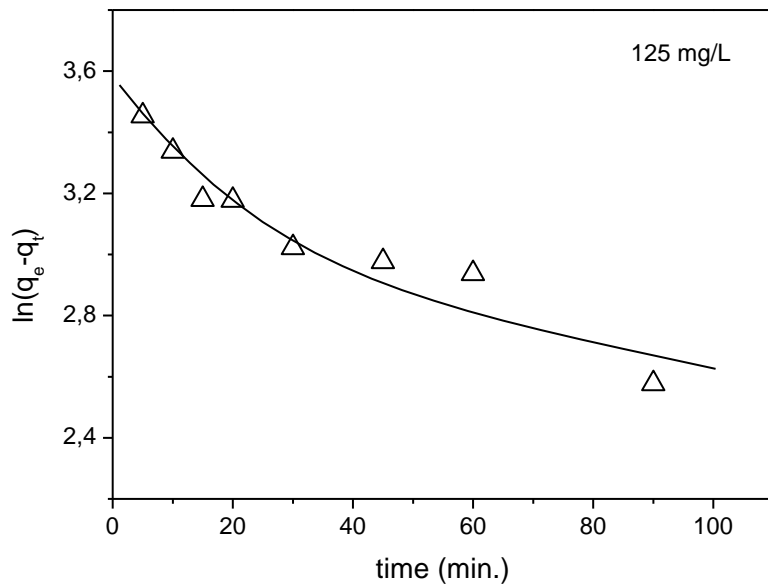


Figure 3.27. Pseudo-first order kinetic plots for the adsorption of Cd (II) (initial metal concentration of 125 mg/L) onto the activated sludge.

3.5.3. Intraparticle Diffusion

An intraparticle diffusion rate parameter has been defined characteristic of the rate of diffusion after the early stages of the adsorption. The rate parameter has been determined for a number of variables including adsorbent mass, initial concentration, and particle size [87].

Intra-particle diffusion model of Weber and Morris is expressed as [88];

$$q_t = k_p t^{1/2} + C \quad (3.3)$$

where q_t represents the amount of solute adsorbate per unit adsorbent (mg/g) at time t and k_p is the intraparticle diffusion rate constant (mg/g.min^{1/2}) and C is the intercept. If the plots of q_t versus $t^{1/2}$ is linear and passes through the origin, then the rate of adsorption is controlled by intraparticle diffusion for the entire adsorption period. If the plot of q_t versus $t^{1/2}$ represents multi-linearity, two or more steps are involved in the adsorption process [89].

Intraparticle diffusion or the adsorption of Pb (II) with an initial metal concentrations 150, 200, and 250 mg/L onto activated sludge are given in Fig.3.28, 3.29 and 3.30, respectively.

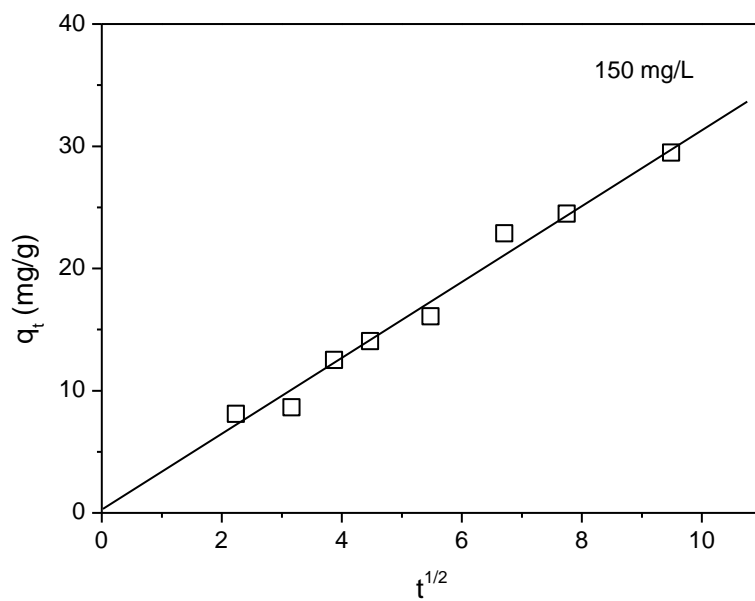


Figure 3.28. Intraparticle diffusion plots for the adsorption of Pb (II) (initial metal concentration of 150 mg/L) onto the activated sludge.

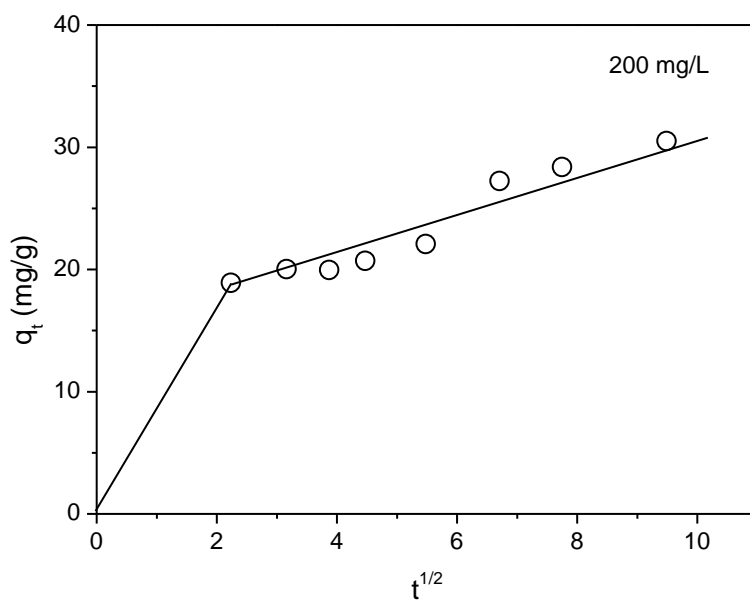


Figure 3.29. Intraparticle diffusion plots for the adsorption of Pb (II) (initial metal concentration of 200 mg/L) onto the activated sludge.

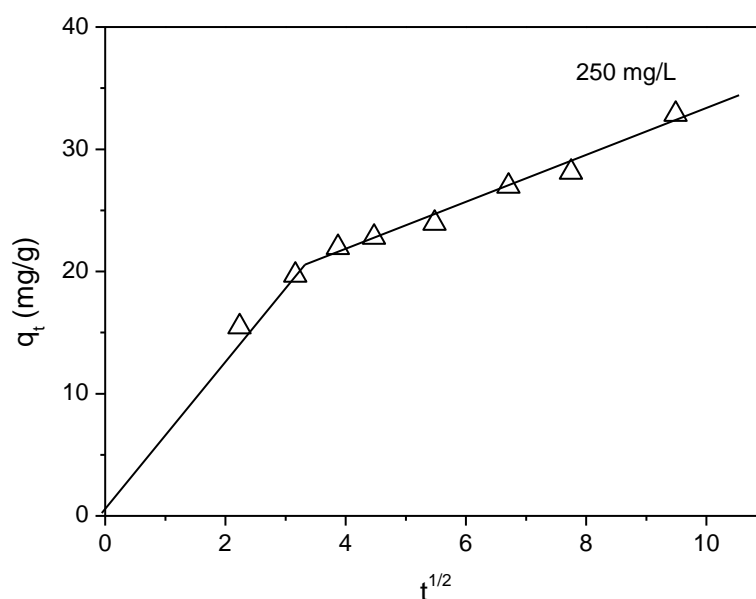


Figure 3.30. Intraparticle diffusion plots for the adsorption of Pb (II) (initial metal concentration of 250 mg/L) onto the activated sludge.

As seen in these figures, Pb(II) adsorption is controlled by intraparticle diffusion for the entire process for the initial metal concentration of 150 mg/L. But, the characteristic of the adsorption process varies with the increasing of initial metal concentration. Plots of q_t versus $t^{1/2}$ showed two parts of linearity. The first part can be attributed to bulk diffusion and the second part to intraparticle diffusion. A third part, a plateau, which represents equilibrium did not observed for the adsorption of Pb (II). This can be originated from the fact that time for the kinetic study (90 minutes) was probably not enough to approach to equilibrium.

Plots of intraparticle diffusion model for the adsorption study with the Cd (II) solutions of 75, 100, and 125 mg/L onto the activated sludge are given in Fig. 3.31, 3.32 and 3.33, respectively.

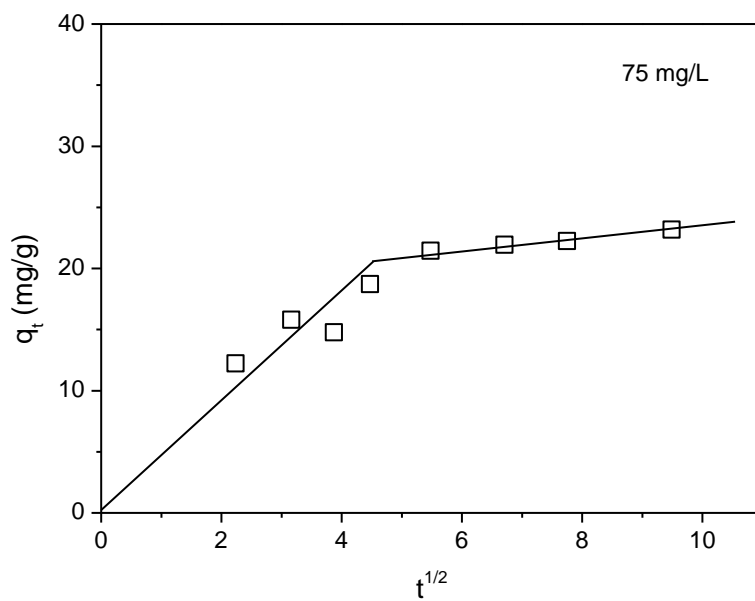


Figure 3.31. Intraparticle diffusion plots for the adsorption of Cd (II) (initial metal concentration of 75 mg/L) onto the activated sludge.

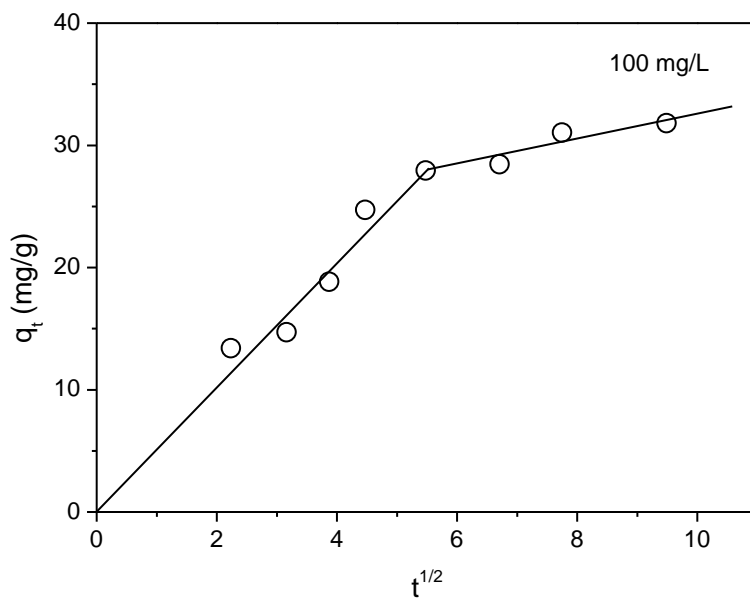


Figure 3.32. Intraparticle diffusion plots for the adsorption of Cd (II) (initial metal concentration of 100 mg/L) onto the activated sludge.

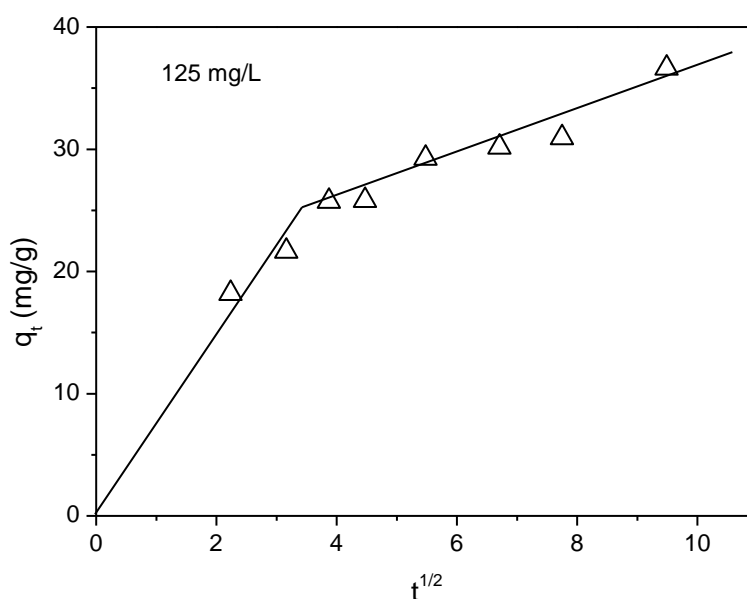


Figure 3.33. Intraparticle diffusion plots for the adsorption of Cd (II) (initial metal concentration of 125 mg/L) onto the activated sludge.

Similar to the adsorption of Pb (II), it can be concluded that the adsorption of Cd (II) involved bulk and intraparticle diffusion steps. For the both heavy metals, it is also difficult to speculate something about the degree of boundary layer control which is somewhat indicated by passing of the first part of the plots through the origin.

The calculated kinetic parameters for the intraparticle diffusion model are listed in Table 3.8.

Table 3.8. The kinetic parameters of intraparticle diffusion model for the removal of Pb(II) and Cd(II) from aqueous solution.

Heavy metal	C_0 (mg/L)	k_p (mg/g.min. ^{-1/2})	C (mg/g)	r^2
Pb (II)	150	3.147	0.04	0.9793
	200	1.784	13.85	0.9314
	250	1.912	14.08	0.9762
Cd (II)	75	0.427	19.06	0.9793
	100	1.055	22.05	0.8322
	125	1.846	18.15	0.9245

Considering the k_p values for the various initial concentrations of the Pb (II) and Cd (II) solutions, intraparticle diffusion rate parameter increases with the increasing of metal concentration, except the case of C_0 of 150 mg/L for the Pb (II). These results show that driving force for the adsorption process was enhanced with the increasing of initial heavy metal concentration, as expected.

CHAPTER 4

CONCLUSION

In this study, potential usage of the activated, waste-water treatment sludge as an adsorbent material was investigated, in detail, for the heavy metal removal from aqueous solutions, the Pb (II), Cd (II) and Cr (III) removal. Activated sludge was obtained from textile industry wastewater treatment plant. The pH of the sludge at the beginning of the study was adjusted to 7.0. Synthetic heavy metal solutions (Pb (II), Cd (II), Cu (III)) were prepared with using salts of these metals. In the experiments, the effects of adsorbent dosage, contact (agitation) time, and initial concentration of Pb (II), Cd (II) and Cu (III) on their removal were investigated separately.

According to the adsorption studies depending on the amount of adsorbent for different initial concentrations of metal, it is found that an effective Pb (II) removal from the aqueous metal solution was successfully performed by the activated sludge for the studied experimental conditions. Also, 50 mg of adsorbent has been enough for 99 % of initial Pb (II) concentration of 100 mg/L. As the initial concentration of the metal solution increases, adsorbent weight should also be increased in order to get effective adsorption.

According to the adsorption studies depending on the amount of adsorbent for different initial concentrations of metal, it is found that small percentage of Cd (II) removal from the aqueous metal solution was achieved by the activated sludge for the studied experimental conditions. 125 mg of adsorbent has removed 76 % of initial Cd (II) concentration of 100 mg/L, but 95 % of Cd (II) has removed. Like in the Pb (II), as the initial concentration of the metal solution increases, adsorbent weight should also be increased in order to get good adsorption.

When the maximum adsorbent weight (125 mg) and minimum initial metal concentration (100 mg/L) were used for adsorption, only 75 % of initial Cr (III) has removed. Based on the experimental results, Cr (III) removal by the activated sludge as an adsorbent material was less effective than the other heavy metals, Pb (II) and Cd (II) and also no remarkable change occurred with different initial concentration of Cr (III) metal.

Equilibrium data were analyzed by the Langmuir and Freundlich isotherms. According to the Langmuir isotherms, adsorption capacity (q_m) of the activated sludge were found to be decreased in the order of Pb(II)>Cd(II)>Cr(III) and the same order for K_L , Langmuir constant. According to the Freundlich isotherms, n values indicating the heterogeneity and favourable adsorption have indicated the same order as in Langmuir isotherm.

The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to determine kinetics parameters of adsorption of Pb(II) and Cd(II). It was found that the pseudo-first-order model fitted the adsorption process of lead while the pseudo-second-order model fitted well the adsorption of cadmium. It is also concluded from the pseudo-first and second order studies and moreover from intraparticle diffusion models that 90 minutes could not be enough for both Pb (II) and Cd (II) adsorption onto activated sludge. Intraparticle diffusion rate parameter increases with the increasing of metal concentration showing that driving force for the adsorption process was enhanced with the increasing of initial heavy metal concentration, as expected.

Consequently, it was concluded that the wastewater treatment sludge can be used as a high performance adsorbent for the heavy metal removal from aqueous solutions.

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