



Heavy metal- Wastewater Treatment from Galvanization Industry Using Nanoadsorbent

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Submitted to the College of Engineering
In partial fulfillment of the requirements for the
Bachelor degree in Environmental Technology Engineering

Palestine Polytechnic University

May, 2016

Abstract

Galvanization industry generates wastewater that is mainly contaminated with heavy metals including (Fe, Cu, Mn, Pb, Cd, Zn, Co, Cr, Mg, Ni). In Palestine the wastewater from this industry is usually discharged into the empty land or sewer system without any treatment. This study aim at investigating the use of magnetic nanoadsorbent for the removal of heavy metals particularly Zn from the wastewater. Samples of wastewater were collected from different rinsing tanks in galvanization process at different time intervals, and their properties including PH, E.C, TDS, Turbidity, and concentration of elements were measured. The result showed that the wastewater is highly contaminant with heavy metals. The characteristic test of wastewater were varied according to the sequence of galvanization process; samples collected from the rinsing tank after acidic treatment has the lowest pH and highest turbidity, whereas samples collected from rinsing tank after fluxing tank has the highest pH and Zn concentration. Batch adsorption experiments were performed for Zn removal from real samples and model solutions ($ZnCl_2$, ICP standard solution, and $Zn(NO_3)_2$) by using iron oxide magnetic nanoparticles as adsorbent. Effects of initial concentration and pH on the adsorption were investigated using Inductively Coupled Plasma device (ICP). The result was obtained using model solutions ($ZnCl_2$ and $Zn(NO_3)_2$) were not reproducible to the metal solution instability. Where the results obtained from the adsorption on real samples were highly reproducible and a Zn removed up to 93% was achieved in less than ten minutes of adsorption. The adsorption process of wastewater favorable at high pH value and the optimum value was 10. The main conclusion of the present study is that galvanization wastewater industry should be property treatment before being discharge and adsorption method with nanoparticles could be effectively used for removal of heavy metals for wastewater.

الإهداء

فلسطين نها القُها الأ

داها ب ه هيدا

ها بسنين عُ سيرا

طين على تراها الطاه .

ه ه

وحيدة ب بودية ف طيع ر هم ينا

" "

حياتي كلها, لك
....

لى من وقف على المنابر و أعطى من حصيلة فكره لئنبير ذربنا ...

...

...

لزميلاتنا و زملائنا مهندسي و مهندسات المستقبل

إليكم جميعاً تُهدي فاتحة العطاء على أمل .

الشكر

سُبْحَانَهُ ، عَلَيْنَا فَضْلُهُ

وَ أَنْتُمْ عَلَيْنَا نِعْمِهِ وَ أَعْطَانَا مِنْ كَرَمِهِ ، وَ عَلَّمَنَا مِنْ عِلْمِهِ..

ثُمَّ نَتَقَدَّمُ بِخَالصِ الشُّكْرِ وَالْعِرْفَانِ لِلسَّيِّدَةِ هُنَا مِنْ جَامِعَةِ "بِيرزيت" عَلَى مَجْهُودِهَا الْكَبِيرِ

وَ عَلَى كُلِّ مَا قَدَّمْتَهُ مِنْ أَجْلِنَا...

وَ كُلِّ الشُّكْرِ لِتَسْمِ هَنْدَسَةِ تِكْنُولُوجِيَا الْبِيئَةِ مُمْتَلَّةً بِكُوَادِرِهَا إِدَارِيَّةٍ وَ أَكَادِيمِيَّةٍ

أُعْلِمِي مَا لَيْسَ تَكْفِيكَ حُرُوفٍ أَوْ جُمَلٍ فَلَقَدْ تَعَبْتَ مِثْلَنَا وَاللَّهِ يَجْزِي بِالْعَمَلِ

كَمَا وَ نَتَوَجَّهُ بِالشُّكْرِ لِلْأَسْتَاذِ الْفَاضِلِ وَ الْمَخْلُصِ وَائِلِ عَوْضِ اللَّهِ..

وَ نَتَقَدَّمُ بِالشُّكْرِ لِلدُّكْتُورِ إِبْرَاهِيمِ الْمَصْرِيِّ الْمُحْتَرَمِ..

كَمَا وَ نَشْكُرُ رَامِي التَّمِيمِي، فَضْلَ مُحَمَّدٍ، وَ هَيْبَةَ شَاهِيْنِ...

خَوْتِنَا وَأَخَوَاتِنَا جَمِيعًا، وَكُلِّ مَنْ لَمْ يَبْخُلْ عَلَيْنَا بِمَدِّ يَدِ الْمَسَاعِدَةِ وَالِدَعَاءِ

وَ إِلَى زَمِيلَاتِنَا رَفِيقَاتِ الرُّوحِ مُهَنْدِسَاتِ تِكْنُولُوجِيَا الْبِيئَةِ كُلِّ الشُّكْرِ...

إِنْ لَمْ نَقُلْ شُكْرًا لَكُمْ سَيَقُولُهَا قَلْبِي لِمَنْ ؟

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Chapter One

Proposal

1.1 Introduction

Everyday, nearly in every facet of life, we use products created by iron mining industry. The iron formed industry, which is one of the most important fundamental sectors of the national economy, is one of the significant indicators of the economic power and comprehensive national strength of a country. The iron formed industry is the most widely used as structural materials and the most important functional materials in the modern era[1], the proportion of iron production is 95% of the global production of metals. The wide range of application of the industry's products do not dispense the iron formed industry including construction, machinery, automobiles, household appliances, shipbuilding, light industry, energy and transportation[1], because of this importance, we should be noted that one of the basic problems faced by the iron formed is rust and corrosion, when the steel is exposed to the weather (air) or water. So the corrosion prevention is an essential factor in the economic utilization of steel, and the electrolytic methods used to prevent steel from this problem. When the iron structures are protected by completely covering their surface with zinc; a process known as galvanizing.

In Palestine the metal industry has a wide variety of products, ranging from construction related industries to production of mechanical and electrical machines. The sector is the second largest industry exported products after stone and marble industries. More specifically, it exported about 72 million dollars in the year 2007. The aggregated data are summarized in the Table (1.1), and the galvanization factories are estimated 22.6% of industries as Palestinian Central Bureau of Statistics (PCBS). The galvanization process can be divided into main categories, in Palestine the cold galvanization only used[2].

Table 1.1: The exports of the metal industry in Palestine[2].

	Items	\$
1	Iron or steel	40919000
2	Aluminum	14430000
3	Electrical machinery	10089000
4	Auto and parts	6971000
	Total	72409000

The galvanization industry which is the process of applying protective steel by using zinc coating despite its importance for depend on it other industry (iron formed industry), but it has a serious problems effect on our environment generally and our health due to wastes out from this industry especially wastewater[1].

1.2 Scientific Background

The term of heavy metals refers to any metallic chemical elements that has a relatively high density greater than 5 g/cm^3 and atomic number above 20, and is toxic or poisonous at low concentrations, not biodegradable and accumulate in living organisms. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), zinc (Zn) and lead (Pb)[3].

Heavy metals are the most hazardous pollutants present in industrial wastewater, the different treatment technologies were proposed includes chemical precipitation, ion exchange, electrochemical removal, adsorption with varies adsorbents, and membrane filtration which has different types such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) techniques are used in a wide range[4, 5]. Chemical precipitation is the most widely used for heavy metals removal from inorganic effluent with lime or limestone as precipitant agents due to their availability and low-cost, but these technologies have significant disadvantages such as incomplete removal, high-energy requirements, production of toxic sludge and large amount of it that requires further treatment, and they are often expensive, especially when the heavy metals concentrations are very low (e.g., 10–100 mg/L) and ineffective in meeting stringent effluent standards. These processes as known physicochemical methods. Other methods called Biological methods which used biomass of several microorganisms and microalgae as adsorbents[6, 7].

Nanotechnology has indeed taken a central place in the industrial wastewater treatment, for many important reasons: nanoparticles relatively low cost, unique properties such as large surface area, short adsorption equilibrium time, so that it can be used to remove high amount of pollutant in shorter time, high reactivity, high specificity, self-assembly and dispersibility. In addition, it should generate a minimum amount of sludge. Nanoadsorbents could be employed most effectively not only in a very low concentration range ($\sim 1\text{ppm}$) of pollutant, but also in a very high concentration range ($\sim 1000\text{ppm}$)[7].

Nanoparticles used to remove olive mill wastewater (OMW) effluent[6]. The aim is the effectiveness of the magnetic iron oxide nanoparticles in adsorption process to remove large organic contaminants from (OMW). Batch and continuous mode processes were applied to determine the effect of contact time, solution pH, coexisting contaminants and the adsorption isotherm. The results showed that the adsorption was fast[6].

Iron oxide (Fe_3O_4) nanoadsorbents have been employed for the removal of Pb (II) ions from aqueous solutions by a batch-adsorption technique. Iron nanoadsorbents effectiveness, the effect of solution pH, coexisting cations, and initial Pb (II) concentration on the adsorption was studied. The outcomes of this study are, Pb (II) adsorption was fast, and maximum removal was observed at pH 5.5[7].

In 2013, the aim in this study was to investigate the treatment efficiency of the wastewater from rinsing after copper plating by zerovalent iron nanoparticles (nZVI). Removal of copper and nickel was observed in this study. Concentration of metals in raw wastewater was 22.4 mg/L for copper and 1.3 mg/L for nickel. 99 % of copper was removed by nZVI dose 3 g/L in 73 hours, likewise the highest removal efficiency of nickel was up to 80 % for the same nZVI dose in 6 hours. The removal efficiency 80 % for nickel was sufficient. The reaction seems to be relatively fast, high removal efficiencies were observed after 30 minutes. Further time of exposure was beneficial only for copper removal, nickel concentration become stable after 2 hours. Reaction conditions were monitored only but no effect of pH, temperature or conductivity was investigated[8].

Application of iron oxide based nanomaterial is more attractive for removal of heavy metals contamination from the water because of their important features like small size, high surface area, and magnetic property. Magnetic property of iron oxide nanoparticles enables easy separation of adsorbents from the system and could be reused for further application. Reusability of iron oxide based nanomaterial leads to a decrease in the economic burden. Iron oxide nanoparticles are synthesized by three important methods are: physical, chemical, and biological[9].

Iron oxides nanoparticles have prominent result for decontamination of arsenic from the water. They showed excellent adsorption capacity to remove As (III) and As (V). Heavy metals in the

solution easily diffuse on the active surface of Fe₃O₄ nanoparticles. Surface area of magnetic nanoparticles plays a significant role in the adsorption process; high surface nanoparticles can easily undergo aggregation in the solution which could decrease their efficiency[9].

Also, due to wide range of application of copper can be accumulated in the environment which makes water more pollute. Nanoadsorbent is useful for removal of Cu (II) from aqueous system. Magnetic nanoparticles bearing amine group on their surface were able to remove 98% copper from polluted river and tap water. The maximum adsorption capacity was 25.77 mg/g at pH 6 and 298 K. Magnetic nanoparticles having amine functionality on the surface lead to an increase in adsorption capacity which increases with pH. At lower pH, amine group undergoes protonation which decreases adsorption efficiency; however, at higher pH strong complexation takes place between Cu (II) and free amine group. The adsorption rate is so fast and equilibrium was achieved within 2 min. It showed that chemical adsorption takes place and strong complexation between Cu (II) and amine group of arabic gum. The effect of pH on adsorption is also investigated at pH < 2 no adsorption took place. At pH (2–6), adsorption increases with increase in pH. The maximum capacity of Cu (II) removal were 96.15 mg/g[9].

Fe₃O₄ nanoadsorbents have been demonstrated for the removal of other heavy metals such as Pb (II) ions from aqueous solution using a batch-adsorption technique. The effect of temperature, pH, and coexisting ions on the adsorption of Pb (II) has been studied in detail. Adsorption equilibrium was achieved within 30 min. The amount of Pb (II) adsorbed increases with increasing temperature as well as there is no effect of coexisting cation on the adsorption. The maximum adsorption capacity of Pb is 36 mg/g. The adsorption of Pb (II) increases with increase in the pH[9].

It was used as nanoadsorbent to detoxify heavy metals such as Cu (II), Zn (II), and Pb (II). The maximum adsorption capacities of tubular maghemite adsorbents towards Cu (II), Pb (II), and Zn (II) were 111.11, 71.42, and 84.95 mg/g, respectively[9].

Unmodified nanoparticles are able to remove 43.47% of 50 ng/mL of Hg(II) from polluted water while modification with MBT improved the removal efficiency up to 98.6% in the same concentration within 4 min. There is no considerable effect on adsorption efficiency by

variation of pH and electrolyte NaCl concentration. All heavy metals were removed over to 85% [9].

1.3 Problem Statement

This research project was answered the following questions:

- **Main problem**

Can nanoparticles used to remove heavy metals, mainly Zn from galvanization wastewater?

- **Sub problem**

1- What are the physiochemical characteristics of galvanization wastewater industry?

2- What is the efficiency of traditional adsorbents (i.e lime and activated carbon) to remove heavy metals from galvanization wastewater industry?

3- What is the efficiency of nanoparticles to remove heavy metals (i.e Zn) from galvanization wastewater industry?

1.4 Goals and Objectives

- **Main goal**

The main goal of this study was investigated the use of nanoadsorbent (nanoparticle) for treatment of galvanization wastewater industry, particularly heavy metals removal, via batch adsorption process in order to cooperate in reducing the environmental negative impacts.

- **Specific objectives (purposes)**

- To analyze the wastewater that generated from different galvanization Processes tank to perform adsorption experiments.

- Use traditional adsorbents such as lime and activated carbon to remove Zn from galvanization wastewater industry and noted its efficiency.

- To identify kinetic and equilibrium characteristics of the adsorption process.

- To study multi component (heavy metals) adsorptions uses nanoparticles, and test the selectivity of the nanoadsorbent to certain types of heavy metals.

1.5 Research Importance

قال تعالى "وَجَعَلْنَا مِنَ الْمَاءِ كُلَّ شَيْءٍ حَيٍّ أَفَلَا يُؤْمِنُونَ(الأنبياء:30)
 Allah says "and made from water every living thing then will they not believe"
 These words are enough to indicate the importance of water in our life, and as it a very important source for people, environment and everything in our life even industry where there are a lot of products depends on water to be produced especially galvanization industry when in this industry use water in all its steps. So the importance of this study comes from the large amount of wastewater having heavy metal outflow that thrown into the sewer system or into the empty land and how to treat this amount of wastewater. For this we'll solve this problem by using nanoparticles[10].

1.6 Research Methodology

- Collection of water samples from each tank of galvanization process at a different time, and prepared several model solution of Zn.
- Identify all the physiochemical characteristics of all samples at a different time.
- Measuring the concentration of heavy metals in the samples.
- Conductly adsorption experiments using different types of adsorbents.
- Studying the adsorption.
- Compare the heavy metals removal efficiency of natural and nanoparticles adsorption.

1.7 Budget

The estimated cost for the implementation our project is around as shown in Table (1.2) below.

Table 1.2: The estimated cost for implementing the project.

Description	Quantity	Cost (\$)
Transportation	-	450
Sulfuric acid reagent	100 g	30
Paper filter	1 box	5
Flask	1	5
Gloves	1 box	3
Digestion solution	50 mL	20
Acid reagent	50 mL	20
Titrimetric FAS	200 g	40
Zinc chloride (ZnCl ₂)	100 g	50
ICP Multi Element Standard Solution IV 1.11355.0100 (40ppm)	500 mL	70
Inductively coupled plasma device (ICP) test	100 samples	3700
Rotary shaker	1	300
Zinc nitrate (Zn (NO ₃) ₂)	50 g	30
Electrical conductivity meter EE002	-	225

1.8 Action Plan

Chapter Two

Galvanization Industry and its Environmental Impact

2.1 Galvanization Industry

Galvanization industry is one of the biggest industries in the world, but at the same time it is the main environmental problems causes environmental pollution, especially its contaminants that out come from wastewater. Therefore we need to manage these wastes through many ways like recycle and reuse, the way of waste disposal, use cleaner fuels, and find specific solutions. There are several applications and techniques used to reduce wastes (In all its forms), so it is possible to solve environmental problems through the fast development of the scientific environmental applications to points that was hopeless[11].

The galvanization was invented in India, where Pillar constructed in Delhi during 4th century. It was named in English electric shocks, in the 19th century also termed Faradism. This sense is the origin of the meaning of the metaphorical use of the verb galvanize, as in galvanize into action[12].

The history of galvanization industry was beginning in 1742 when a French chemist named P.J. Malouin, in a presentation to the French Royal Academy, described a method of coating iron by dipping it in molten Zn. In 1836, Stanilaus Tranquille Modeste Sorel, another French chemist, obtained a patent for a means of coating iron with Zn. A British patent for a similar process was granted in 1837[11]. With industrial revolution and development, the iron formed process can be found in almost every major application and industry. The utilities, construction, machinery, automobiles, household appliances, shipbuilding, light industry, energy and transportation, to name just a few[12], because of this importance they noted that one of the basic problems faced by the iron formed is rust and corrosion, although there are different methods to prevent corrosion by coated metals with something which does not allow moisture and oxygen to react with it, Coating of metals with paint, oil, grease or varnish and Coating of corrosive metals with non-corrosive metals also prevents corrosion such as Tinning, Electroplating, Anodizing, Alloying, but galvanization industry was a perfect solution method of corrosion protection, because It can be applied on wide range of products, it use in myriad applications worldwide, low cost, ease of application and comparatively long maintenance-free service life. The coating normally lasts at least 20 to 40 years in industrial environments and 50 to 100 years in less aggressive atmosphere[13], in which the substrate is coated with Zn and completely covers the steel surface of it, the term galvanization has largely come to be associated with Zn coatings, to

the exclusion of other metals . Metallic zinc is strongly resistant to the corrosive action of normal environments[14]. This proven corrosion resistance is a result of zinc's ability to form a dense, adherent corrosion byproducts, which leads to a rate of corrosion considerably lower than ferrous materials – 10 to 100 times slower, depending on the environment.

2.1.1 Galvanization process

Galvanization processes around the world have two mainly types: hot-dip galvanized (hot dip zinc or hot galvanizing) and cold (electric galvanized), and the main differences between these types include, in their manner of operation ,where in hot dip galvanized is in 450-480 degrees of molten liquid Zn in Zn plating, in cold at room temperature by electroplating of Zn plating, hot dip galvanized thickness is much larger than cold galvanizing, cold galvanized can only side plating, but hot dip galvanized can for all sides plating(in/out), and for fee standards, hot dip according to the thickness of the material fee, while cold most of the plating charge according to square meters. Although, the hot dip galvanized is dozens of times of cold galvanizing for anticorrosive, and adhesion of cold galvanizing is inferior to hot dip galvanized, developed countries in the world use it, but developing country used cold process due to price[15].

Contrast development in galvanizing industry, developing countries didn't take into account of this sector, except in late time, so it didn't reach progress and spread as the world that they done. Palestine is one of these developing countries, and it has 15 factories of galvanization industry.

Because Palestine is one of developing countries, the type of galvanization industry that use is cold galvanizing. So we will talk about this type in details.

We will start talking about factory materials required as world specification in the Table (2.1).

The most important point in the process of this type is the solution (ENTHOBRITE DIMENSION) in galvanizing tank is Non Cyanide Zinc (NCz), some of features , easy to use additive system, low stress ductile deposit, highly corrosion resistant coating, excellent plating speed, coverage and distribution, increased production efficiency, and no blistering or adhesion failures.

Table 2.1: The material that required in galvanization processes[6,8].

Material	Description
Arachidonic acid (AA)	It's an acid solution, use to prevent corrosion, reduce acid's odor and as a detergents for grease and oil.
NCz ENTHOBRITE DIMENSION	It produces glossy power leveling, very good penetrating and with extremely uniform thickness distribution, and it can be passivated in order to produce layers of chrome with much improved corrosion resistance.
ENTHOBRITE NCz DIMENSION A	Used for the preparation and completion is most important component. It's a silky sheen throughout the Current densities. Also, this component is due the exceptional power bath and internal tensions run small spraycoating(base sol.)
ENTHOBRITE NCz CONDITIONER	This additive additions above supports the operation and improves both the the synthesis of fine-grained crystalline structure, adherence, submission, also panned the effect of water's element on coating Zn.
NCz ENTHOBRITE DIMENSION B	Polishing agent used for the preparation and completion. This component is a polishing agent and it only works in combination with NCz DIMENSION A.
ENTHOBRITE NCz C	Gloss agent who along with ENTHOBRITE NCz DIMENSION B. The partially remove the effect of impurities organic. It is used both for cooking and for completion.

Material	Description
ENTHOBRITE NCz AS	Splash (if necessary). Highly active, produce a layer of foam even small dosing quantities.
Zinc metallic	Use balls or pieces of pure Zn (99.99%) in steel baskets.
Caustic soda	Sodium hydroxide or Potassium hydroxide.
Sodium dichromate (trivalent chrome)	Use to coat the plate's surface after Zn fluxing, it made three inch of chrome on the surface to panned metal oxidation and save the color.

2.1.2 Galvanization steps

Cold galvanization industry has three mainly steps and these steps are: surface preparation, galvanizing, and Post-Treatment or Inspection. After all of these steps have a three rinsing tanks; the first and the second tanks containing water only, while the last one has an activated carbon, anion, and cation to remove pollutants from water. So it will not be disposed, but in Palestine after each step has one rinsing tank contains water, and this water will be disposed into empty lands and sewer system which causing a water pollution.

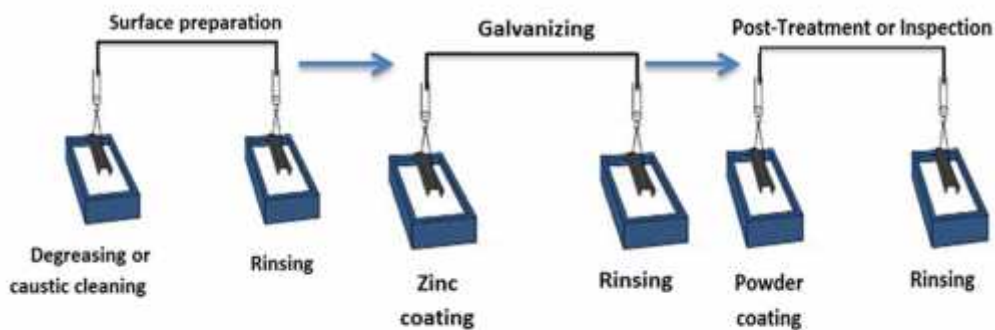


Figure 2.1: The three main steps in galvanization industry processes which include surface preparation, galvanizing, and post treatment respectively.

1- Surface preparation

Because the cleaning ability of all Zn alkaline solutions without cyanide is relatively weak and Zn will not react with the steel surface unless it is perfectly clean, Parts preparation contains Degreasing and pickling solutions should be examined regularly to maintain concentrations and temperatures Optimal, so the purpose of surface preparation is obtain the cleanest possible steel surface by removing all of the oxides and other contaminating residues.

- Degreasing or Caustic Cleaning: First the steel is immersed in an acid degreasing or caustic solution to remove organic contaminants such as dirt, oil, and grease from the surface of the steel. In this factory use nitric acid HNO_3 with AA acid (Arachidonic acid) to mitigate odor of acid, and a certain percentage of water.
- Washing or Rinsing tank: After degreasing the steel is rinsed with water to dilute acid.

2. Galvanization

The goal of this stage is Zn coating on the steel, and there are several methods to Zn coating and the most commonly types of Zn coatings are; Zn electroplatin, Mechanical plating, Sherardising, Continuously galvanized sheet, Continuously galvanized wire, Galvanized pipe and tube, Zn metal spraying, but in the factory that we chose, is used Zn electroplatin method.

- Zn coating or Fluxing tank: In this tank the steel was immersed with Zn balls ,sodium hydroxide(NaOH) ,enthobrite NC_Z conditioner , and enthobrite NC_Z 5001(A,B,C) plus. Where all of this materials were mixed in the tank and applying an electric current to uniformly coat the surface. Fluxing removes oxides that form on the very active steel surface produced from the pickling operation and prevents further oxides from forming on the surface of the metal prior to galvanizing and promotes bonding of the Zn to steel surface.
- Washing or Rinsing tank: After galvanizing the steel is rinsed with water to dilute alkaline.

3. Post-treatment or Inspection:

- Powder coating tank: in a mild solution of sodium dichromate. This solution is designed to provide a thin Zn chromate layer for the initial protection of Zn surface. The last step is post treatment and its purpose is paint steel by using PERMAPASS material.
- Washing or Rinsing tank: After powder coating the steel is rinsed with water[16,18].

2.1.3 Factory conditions

The tanks made from Steel lined preferably with PVC (Polyvinylchloride) or other approved material (in order to prevent stray current) like (PP and PE), and the volume of each tank is 10 m³. For plating the sodium hydroxide to zinc metal ratio should be at least 10:1, operating condition of cold galvanizing illustrated in Table (2.2), also the typical temperature is 26C°.

Table 2.2: The amount of material which required in the process[6,8].

Tank's name	Material	Typical	Range
Degreasing or caustic cleaning	Arachidonic acid (AA)	1% from tank's concentration	-
	Nitric acid (HNO ₃)	15% from tank's concentration	-
Zn coating or fluxing	Zinc metal	12 g/L	10-14 g/L
	Sodium hydroxide	120 g/L	110-140 g/L
	ENTHOBRITE NCz DIMENSION A	14 ml/L	12-16 ml/L
	NCz ENTHOBRITE DIMENSION B	3 ml/L	2-4 ml/L
	ENTHOBRITE NCz C	3 ml/L	2-4 ml/L
	ENTHOBRITE NCz CONDITIONER	20 ml/L	15-30 ml/L
Powder coating	Sodium dichromate	15 ml/L	14-16 ml/L

2.2 Galvanization Industry Effluent and its Effects

Despite its important, the galvanization industry as any industry in the world has many risks and has range of negative effects on the environment and human health as well as animals that come from chemical substances that used particularly Zn. "It is unfortunate that Zn is almost always mentioned in conjunction with those other 'heavy metals' of ill environmental repute, cadmium and lead".

When we talk about the environmental risks that we found in this factory we must take in our concerns the effects of the environmental elements that includes air, water, and soil, as well as human health.

2.2.1 Air pollution

The contaminants which are discharged whenever the fresh flux and new chemical substances are added to the basins, also during the immersion of steel into the galvanizing basins these chemicals would be fly into the air in a very high concentrations particularly Caustic soda, Acid and particulate matter (PM₁₀), so they make the odor in the place very troublesome and no one can stay in this place near to these basins. And these emissions especially acid vapor harm the respiratory system of the workers and cardiovascular systems, also may lead to cancer disease in the long term exposure. Also effects on animal or plant life, damage to materials of economic value to society and damage to the environment (e.g., climatic modifications).

2.2.2 Solid waste

A solid waste comes only from chemical plastic tanks, cartons and Zn residue. They disposed in waste containers without thinking about re-use or recycle it.

2.2.3 Water pollution

The mainly pollution comes from the wastewater that out from all basins in factory, that's include large amounts of contaminants such as heavy metals (Zn), acids (Nitric acid), fat, grease oil, alkaline solutions and suspended solids. This wastewater disposed as it into the sewer system or to the empty land without any remediation, so there are many problems here. When wastewater goes in to the sewer system, it would be destroying the network because metals

accumulate in it, and when it is thrown in to the near land it would be leachate in to the soil and harm it, the color of land was black and trees was died, and it may leachate and arrive to the groundwater so water would pollute with acidic, bases components and heavy metals especially Zn due to the presence of large quantities of it in the wastewater of Galvanization plant as we said. Large quantities of Zn can be found in soils, so animals will be die and human health destroy; this is because of some plants can absorb Zn. As a result this would effect on food chain, habitat and biodiversity.

The factory should dispose wastewater every 10 days from rinsing tanks, so about 30m³ of wastewater thrown without any treatment which means 90 m³ every month generate wastewater.

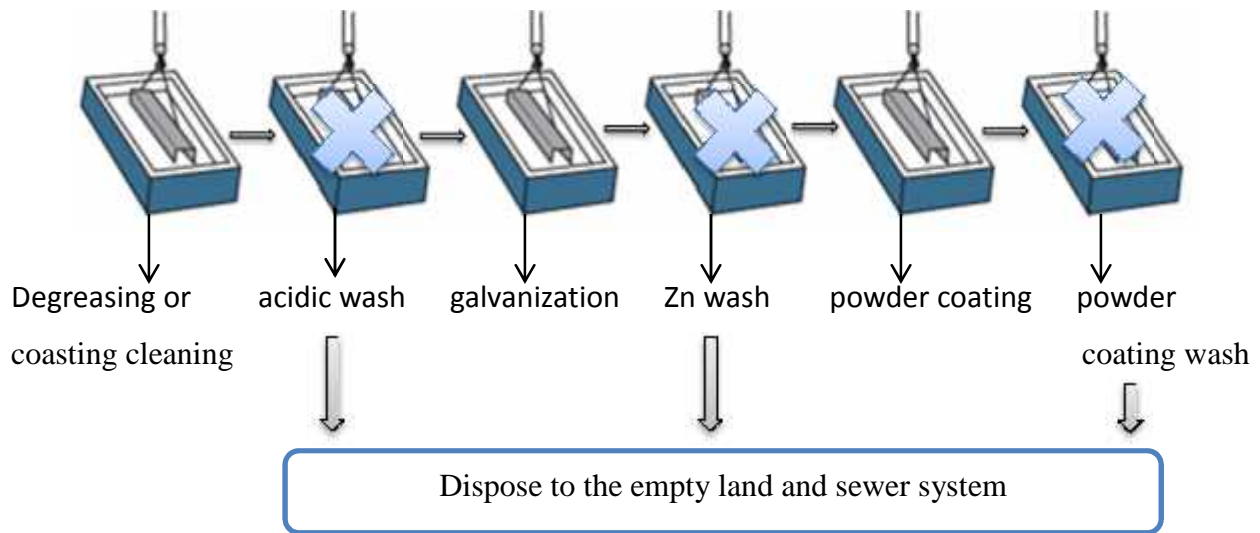


Figure 2.2: The rinsing tanks which dispose their wastewater every 10 days.

2.3 Waste Treatment of Galvanization Industry

Treatment plants in Palestine as any treatment plant in the world, include five stages, are preliminary, primary, secondary, tertiary and sludge treatment, where physical, chemical, and biological treatment for pollutants will be done, but industrial wastewater in Palestine especially galvanization industry are throughout in the wadi, empty lands, and sewer system as it without any treatment. So we can remediate some of contaminants like inorganic pollutants (heavy metals) through chemical treatment, this treatment called pre-treatment, where it is treated in the factory [19].

2.3.1 Gas effluents treatment

For the air pollution control approach shown in Table (2.3), attempts to protect the environment have especially relied on isolating contaminants from the environment and using end-of-pipe filters and scrubbers.

The dust and odour cleaner is part of a complex system consisting of, ductwork, fans, and cleaners. It should be noted that system efficiency varies widely for each type of cleaner, depending on its design, energy input and the characteristics of the out stream and the contaminant[19].

Table 2.3: The air pollution control approach[9].

Control method	Example	Description	Efficiency
Condensation	Contact condensers surface condensers	The vapour is cooled and condensed to a liquid. This is inefficient and is used as a preconditioner to other methods.	80+% when concentration >2,000 ppm.
Absorption	Wet scrubbers (packed or plate absorbers)	The gas or vapour is collected in a liquid.	82–95% when concentration <100 ppm 95–99% when concentration >100 ppm
Adsorption	Carbon, Alumina Silica gel, Molecular sieve	The gas or vapour is collected on a solid.	90+% when concentration <1,000 ppm 95+% when concentration >1,000 ppm

Control method	Example	Description	Efficiency
Incineration	Flares, Incinerator Catalytic incinerator	An organic gas or vapour is oxidized by heating it to a high temperature and holding it at that temp. for a sufficient time period.	Not recommended when concentration <2,000 ppm 80+% when concentration >2,000 ppm
Wet scrubbers	Venturi, Wetted filter Tray or sieve scrubber	Liquid droplets (water) collect the particles by impaction, interception and diffusion. The droplets and their particles are then separated from the gas stream.	For 5 μm particles, 98.5% at 6.8 w.g.; 99.99+% at 50 w.g. For 1 μm particles, 45% at 6.8 w.g.; 99.95 at 50 w.g.
Electrostatic precipitators	Plate-wire, Flat-plate Tubular Wet	Electrical forces are used to move the particles out of the gas stream onto collection plates	95–99.5% for 0.2 μm particles 99.25–99.9+% for 10 μm particles
Filters	Baghouse	A porous fabric removes particulates from the gas stream. The porous dust cake that forms on the fabric then actually does the filtration.	99.9% for 0.2 μm particles 99.5% for 10 μm particles

2.3.2 Soil contamination

There are several technologies or techniques used to treat soil contamination from heavy metals. For example, use of phytoremediation and biochar technologies in soil remediation from heavy

metals. Fellet et al. (2011) tried to use biochar to remediate a multicontaminated mine soil. Biochar addition didn't result in the decrease of the total heavy metal content of the soil, however, biochar addition reduced the bioavailability of Cd, Pb and Zn and the mobility (measured using a leaching experiment) of Cd, Cr and Pb[20].

All ready when we applied the technology of wastewater treatment, soil contamination will be in safe site.

2.3.3 Water effluents treatment

Water pollution is the main problem that we faced in galvanization industry, because it has a large amount of Zn. It is one of the metallic chemical elements (called heavy metals) which may be considered as a “contaminant” if it occurs where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect[21].

The most important technique that is used to remove heavy metals from industrial wastewater effluent is adsorption, and we will talk about it later. Now the most popular techniques are used including:

- **Chemical precipitation:** Chemical precipitation is a conventional technology for removing dissolved metals from wastewater containing toxic metals, which involve the addition of chemical reagents to the mixture (wastewater) for convert the dissolved metals into solid particle form ,so a chemical reaction, triggered by the reagent, causes the dissolved metals to form solid particles[22]. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriated discharged or reused [23]. The process works is dependent upon the kind of metal present, the concentration of the metal, and the kind of reagent used. Precipitation can be induced by the addition of an alkali, sulfide, coagulant, or other reagent that will bond with dissolved metal ions [22]. The process usually uses pH adjustment, addition of a chemical precipitant, and flocculation [24].
- **Ion exchange:** Ion-exchange processes have been widely used to remove heavy metals from wastewater[23]. Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from a wastewater solution is exchanged for a similarly charged ion attached to an immobile solid

particle. It means that the ions in solutions are replaced by different ions originally present in the solid[22].

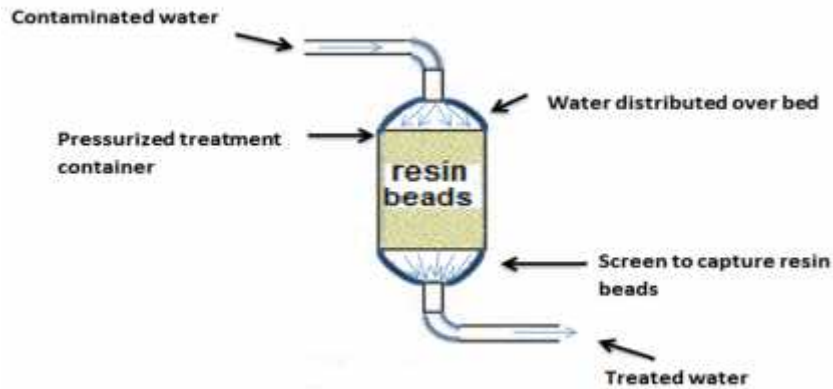


Figure 2.3: Ion exchange is a reaction wherein an ion from a wastewater solution is exchanged for a similarly charged ion attached to an immobile solid particle[25].

- Membrane filtration: Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency[23]. Membranes provide physical barriers that permit the passage of materials only up to a certain size, shape or character. There are four cross flow, pressure-driven membrane separation processes currently employed for liquid/liquid and liquid/solid separation: ultrafiltration (UF), reverse osmosis (RO), nanofiltration (NF), and microfiltration (MF). Membranes are manufactured in a variety of configurations including hollow fiber, spiral, and tubular shapes. Each configuration offers varying degrees of separation[26].

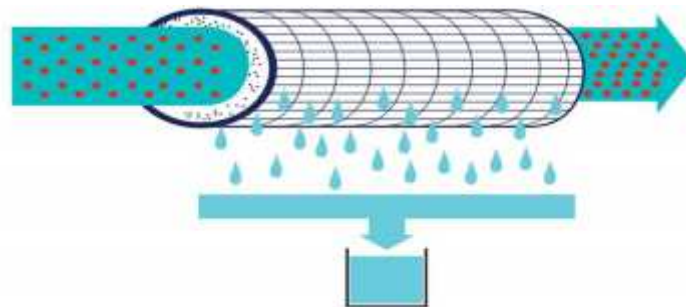


Figure 2.4: Membrane Filtration has a porous act as a barrier that prevent or allow contaminants pass according to membrane type[27].

- Coagulation and flocculation: Coagulation and flocculation followed by sedimentation and filtration is also employed to remove heavy metal from wastewaters as used to increase particle size through aggregation[23]. The precipitation process can generate very fine particles that are held in suspension by electrostatic surface charges. These charges cause clouds of counter-ions to form around the particles, giving rise to repulsive forces that prevent aggregation and reduce the effectiveness of subsequent solid-liquid separation processes. Therefore, chemical coagulants are often added to overcome the repulsive forces of the particles. The three main types of coagulants are inorganic electrolytes (such as alum, lime, ferric chloride, and ferrous sulfate), organic polymers, and synthetic polyelectrolytes with anionic or cationic functional groups. The addition of coagulants is followed by low-shear mixing in a flocculator to promote contact between the particles, allowing particle growth through the sedimentation phenomenon called flocculant settling[24].

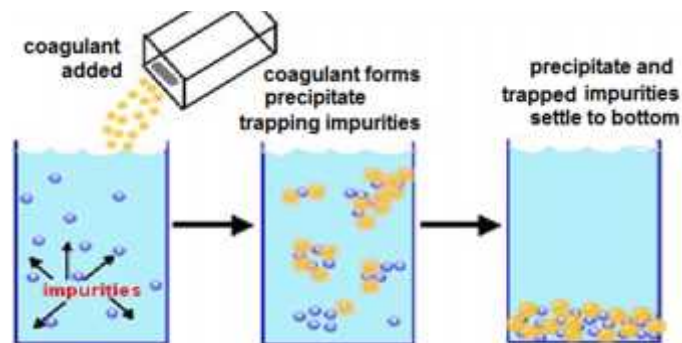


Figure 2.5: Coagulation and flocculation based on adding coagulants which allowing particles growth, then contaminants will be settling[28].

- Flotation: Flotation has nowadays found extensive use in wastewater treatment. Flotation has been employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing. Dissolved air flotation (DAF), ion flotation and precipitation flotation are the main flotation processes for the removal of metal ions from solution. DAF is to allow micro-bubbles of air to attach to the suspended particles in the water, developing agglomerates with lower density than water, causing the flocs to rise through the water and accumulating at the surface where they can be removed as sludge. Ion flotation has been shown a promising method for the removal of heavy metal ions from wastewaters[23].

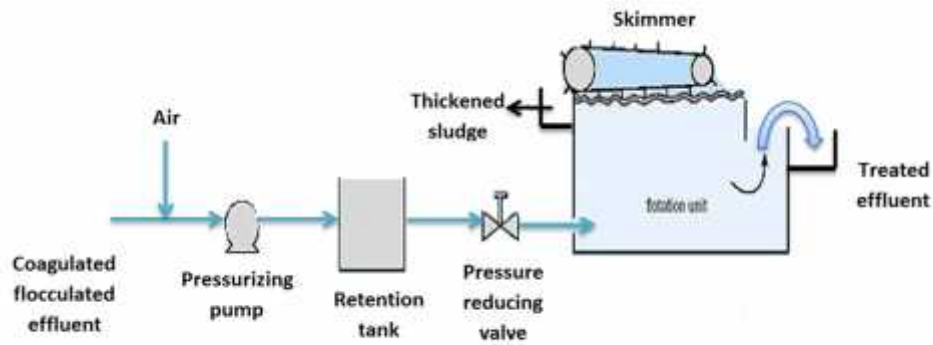


Figure 2.6: Flotation has been employed to separate heavy metal from a liquid phase using bubble of air to attach to the suspended particles in the water[29].

- Electrochemical treatment: Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state[23]. There are two types are:
 - Electrocoagulation (EC): has been used industrially and demonstrated its superior performance in treating effluents containing suspended solids, oil and grease, and even organic or inorganic pollutants that can be flocculated.
 - Electroflotation (EF): is widely used in the mining industries and is finding increasing applications in wastewater treatment[30]. EF is a solid/liquid separation process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis[23].

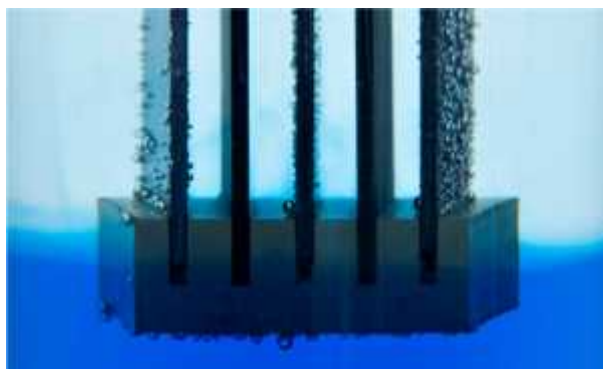


Figure 2.7: Electrochemical treatment involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state[31].

2.4 Heavy Metals

The term of heavy metals which classified from an inorganic contaminates, refer to any metallic chemical element that has a relatively high density greater than 5 g/cm³ and atomic number above 20, and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), zinc (Zn) and lead (Pb)[32].

Inorganic contamination of aquatic environments is caused by naturally occurring substances (fluoride, arsenic, and boron), industrial waste (zinc, mercury, cadmium, chromium, cyanide, and others), agriculture and domestic waste (nitrogen compounds), and systems for the distribution of drinking water (aluminum, copper, iron, lead, and zinc)[33].

In the Table (2.4), WHO guideline for drinking water quality recommended values for 18 inorganic substances.

Table 2.4: Values of inorganic substances in drinking water according WHO[33].

Compounds	Guideline Value(mg/L)
Antimony	0.018
Arsenic	0.011
Barium	0.700
Boron	0.010
Cadmium	0.003
Chromium	0.050
Copper	2.000
Cyanide	0.070
Fluoride	1.500
Lead	0.010
Manganese	0.500
Mercury	0.001
molybdenum	0.070
Nickel	0.020
Nitrate	50.00
Nitrite	3.000
Selenium	0.010
uranium	0.009

While the Environmental Protection Agency (EPA) according the maximum Concentration levels (MCL) for inorganic contaminates regulated as Table (2.5).

Table 2.5: The MCL for inorganic contaminates regulated in U.S. (EPA)[24].

Compounds	MCL(mg/L)
Antimony	0.006
Arsenic	0.000
Asbestos	7 Million fibers/Per Liter
Barium	2.0000
Beryllium	0.0040
Cadmium	0.0050
Chromium	0.1000
Copper	1.3000
Cyanide	0.2000
Fluoride	4.0000
Lead	0.0000
Mercury	0.0020
Nickel	0.1000
Nitrate	10 as Nitrogen
Nitrite	1 as Nitrogen
Selenium	0.0500
Thallium	0.0005

While the EPA has established National Secondary Drinking Water Regulations (NSDWRs) that set non-mandatory water quality standards for 15 contaminants in Table (2.6). These contaminants may cause aesthetic effects like taste, odor, or color in drinking water. EPA recommends secondary standards to water systems but does not require systems to comply. However, states may choose to adopt them as enforceable standards.

Tale 2.6: The national secondary drinking water regulations in EPA[34].

Contaminant	Secondary MCL	Noticeable Effects
Aluminum	0.05 to 0.20mg/L	colored water
Chloride	250.00 mg/L	salty taste
Color	15.00 color units	visible tint
Copper	1.00 mg/L	metallic taste; blue-green staining
Corrosivity	Non-corrosive	metallic taste; corroded pipes/ fixtures staining
Fluoride	2.00 mg/L	tooth discoloration
Foaming agents	0.50 mg/L	frothy, cloudy; bitter taste; odor
Iron	0.30 mg/L	rusty color; sediment; metallic taste; reddish or orange staining
Manganese	0.05 mg/L	black to brown color; black staining; bitter metallic taste
Odor	3 TON (threshold odor number)	"rotten-egg", musty or chemical smell
pH	6.50 - 8.50	low pH: bitter metallic taste; corrosion high pH: slippery feel; soda taste; deposits
Silver	0.10 mg/L	skin discoloration; graying of the white part of the eye
Sulfate	250.00 mg/L	salty taste
Total Dissolved Solids (TDS)	500.00 mg/L	hardness; deposits; colored water; staining; salty taste
Zinc	5.00 mg/L	metallic taste

Zn is a natural component of the earth's crust and an inherent part of our environment. It is present in rock, soil, air, and water. Plants, animals and humans also contain Zn. The average natural level of Zn in the earth's crust is 70 mg/kg (dry weight), ranging between 10 and 300 mg/kg[35]. Zn is a transition metal that occurs in the center of the periodic table[36], and its atomic number 30, atomic mass is 65.38. It has a number of characteristics that make it a well-suited corrosion protective coating for iron and steel products. The first use of it in construction was in 79 AD. Zn is an excellent corrosion resistance in most environments accounts for its

successful use as a protective coating on a variety of products and in many exposure conditions[37]. Although Zn is essential micronutrient for most of industry, environment, even human, but it also main problem as heavy metal in wastewater.

2.5 Adsorption

2.5.1 Introduction

Over the last few decades adsorption has gained paramount importance in industry and environmental protection as a purification and separation process[30]. Adsorption is integral to a broad spectrum of physical, biological, and chemical processes and operations in the environmental field. Purification of gases by adsorption has played a major role in air pollution control, and adsorption of dissolved impurities from solution has been widely employed for water purification[38].

Now adsorption viewed as a superior method for wastewater treatment and water reclamation; as an effective and economic method especially in heavy metals treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process[23].

The most general definition describes adsorption as an enrichment of chemical species from a fluid phase on the surface of a liquid or a solid, when a liquid is brought in to contact with a solid, part of it is taken up by the solid. The solid that takes up the liquid or the solute is called the "adsorbent", and the liquid taken up on the surface is called "adsorbate"[39]. The term "absorption" is totally differing from "adsorption". Absorption is assimilation of molecular species throughout the bulk of the solid or liquid, so it's a bulk phenomenon, in which contaminants are dissolved in bulk. While adsorption is accumulation of the molecular species at the surface rather than in the bulk of the solid or liquid, so it's a surface phenomenon in which adsorbate trans to adsorbent as amass transfer[40].

2.5.2 Adsorption Process

Adsorption works on the principle of adhesion. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface to

another ,the adsorbing phase is the "adsorbent", and the material concentrated or adsorbed at the surface of adsorbing phase is the "adsorbate" .The process can take place in any of the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas. in focusing on wastewater treatment the system is solid-liquid[30]. Depending on the nature of attractive forces existing between the adsorbate and adsorbent, adsorption can be classified as: Physical adsorption or physisorption and Chemical adsorption or chemisorptions. In physical adsorption, the forces of attraction between the molecules of the adsorbate and the adsorbent are weak Van der Waals' type. Since the forces of attraction are weak, the process of physisorption can be easily reversed by heating or decreasing the concentration of the adsorbate. In contrast, the forces of attraction between the adsorbate and the adsorbent in chemisorption are very strong(covalent and ionic bonds), the molecules of adsorbate form chemical bonds with the molecules of the adsorbent present in the surface[41].

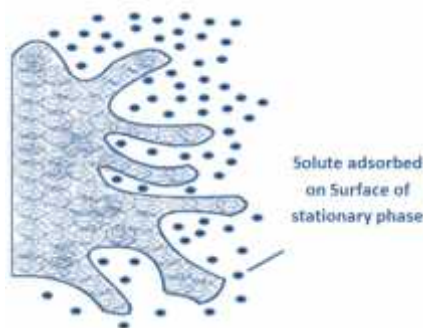


Figure 2.8: Adsorption process which involves separation of a substance from one phase accompanied by its accumulation at the surface to another ,the adsorbing phase is the "adsorbent", and the material adsorbed at the surface of adsorbing phase is the "adsorbate"[42].

More of the solid adsorbents process has a complex porous structure that consists of pores of different sizes and shapes. In terms of the science of adsorption, the total porosity is usually classified into three groups; micropores (smaller than 2 nm), mesopores (in the range of 2 to 50 nm), and macropores (larger than 50 nm). The adsorption in micropores is essentially a pore-filling process because sizes of micropores are comparable to those of adsorbate molecules. All atoms or molecules of the adsorbent can interact with the adsorbate species that is fundamental difference between adsorption in micropores and larger pores like meso- and

macrospores, thus the size of microspores determines the accessibility of adsorbate molecules to the internal adsorption surface[30].

Adsorption refers to the existence of a higher concentration of any particular component at the surface of a liquid or a solid phase. Adsorption is invariably accompanied by evolution of heat, i.e. it is an exothermic process. Its mean ΔH of adsorption is always negative, but at some cases it's an endotherm[43].

2.5.3 Factors Affecting Adsorption

Adsorption has many factors affect on its process, Table (2.7) show these factors.

Table 2.7: Factors affecting adsorption and there effect[44, 45].

Factors	There effects on adsorption process
Surface area of adsorbent	Larger surface area imply a greater adsorption capacity
Particle size of adsorbent	Smaller particle sizes reduce internal diffusion so it has short path to transfer inside solid pores structure of the small particle size and mass transfer limitation to penetrate of the adsorbate inside the adsorbent; which means it gives higher adsorption rates.
Contact time or residence time	The longer residence time means the more complete the adsorption will be. Therefore, the required contact time for sorption to be completed is important to give insight into a sorption process. This also provides information on the minimum time required for considerable adsorption to take place.
Solubility of adsorbent	The slightly soluble metal ions in water will be more easily removed from water (i.e.,adsorbed) than substances with high solubility.

Factors	Their effects on adsorption process
Affinity of the solute for the adsorbent	If the surface of adsorbent is slightly polar, the non-polar substances will be more easily picked up by the adsorbent than polar ones.
Size of the molecule with respect to size of the pores	Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes.
Degree of ionization of the adsorbate molecule	More highly ionized molecules are adsorbed to a smaller degree than neutral molecules.
pH	The removal efficiency increases with increasing initial pH.
Effect of initial concentration	At high-level concentrations, the available sites of adsorption become fewer. High concentration will create and activate some new activation sites and occupies the available binding sites faster causing the remaining solutes unable to bind on to the adsorbent.
Dosage effects	The removal efficiency is generally increased as the concentration dose increases over these temperature values
Temperature	Adsorption increases at low temperature conditions. Since adsorption is an exothermic process
Pressure	Adsorption increases with raising the pressure to a certain extent till saturation level is achieved. After saturation level is achieved no more adsorption takes place no matter how high the pressure is applied

2.5.4 Adsorption isotherms

Adsorption isotherms or known as equilibrium data are the fundamental requirements for adsorption systems design. The equilibrium is achieved when the capacity of the adsorbent materials is reached, and the rate of adsorption equals the rate of desorption. Theoretically adsorption capacity of an adsorbent can be calculated with an adsorption isotherm. There are basically four well established types of adsorption isotherm according type of bonding and No.of layers are: linear, Langmuir, BET , and the Freundlich adsorption isotherms[44].

The significance of adsorption isotherms comes from that they show the amount of material which is adsorbed on the surface at a particular temperature which depends upon the amount of that substance in the liquid phase (concentration) that is in contact with the surface. That mean, the amount of sorbed solute versus the amount of solute in solution at equilibrium[44].

The extent of adsorption is usually measured by coverage θ which is given by:

$$\theta = \frac{\text{Number of surface sites occupied}}{\text{Total number of surface sites}} \quad (2.1)$$

1- Linear adsorption isotherm

The simplest adsorption isotherm to fit to data because its assumes that linear partitioning, unlimited number of available sorption sites[46].

$$q_e = K.C_e \quad (2.2)$$

Where: q_e = amount of solute adsorbed per unit weight of solid at equilibrium(g/g), or (mg/g)
 C_e = Concentration of solute in equilibrium with mass of solute sorbed on solid (mg- solute/L),
 K = constant (kg/m^3) [47].

2- Langmuir adsorption isotherms

Langmuir adsorption isotherm describes quantitatively the formation of a monolayer (single layer) of adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place[44].The Langmuir adsorption is based on the view that every adsorption site is

identical and energetically equivalent (thermodynamically, each site can hold one adsorbate molecule)[44].

$$q_e = \frac{q_m c_e}{K + c_e} \quad (2.3)$$

3- Freundlich adsorption isotherms

Freundlich isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. It represents an initial surface adsorption followed by a condensation effect resulting from strong adsorbate-adsorbent interaction[44].

$$q_e = K \cdot C_e^n \quad (2.4)$$

4- Brunauer, Emmett and Teller (BET) isotherm

While the Langmuir isotherm provides a simple picture for looking at surface adsorption, but when more than one molecules can adsorb to each site on the adsorbent; a better approximation for this process is to use the BET Isotherm (named for its inventors, Brunauer, Emmett, and Teller) which allows for multilayered adsorption on isotherm. It assumes that a Langmuir isotherm applies to each layer and that no transmigration occurs between layers. It also assumes that there is equal energy of adsorption for each layer except for the first layer[48, 49].

$$q_e = \frac{K_b \cdot C_e \cdot Q^0}{C_s - C_e \{1 + K_b - 1 \frac{C_e}{C_s}\}} \quad (2.5)$$

K_b = a parameter related to the binding intensity for all layers.

C_s =saturation (solubility limit) concentration of the solute. (mg/L)

When $C_e \ll C_s$ and $K_b \gg 1$ and $K_{ad} = K_b / C_s$ BET isotherm approaches Langmuir isotherm[47].

2.5.5 Adsorbent types

1- Industrial adsorbents

- Carbon adsorbents: Are widely used in the removal of heavy metal contaminants it has a porous carbon structure, which contains small amounts of different heteroatoms such as oxygen and hydrogen. Also contain variable amounts of mineral matter (ash content) depending on the nature of the raw material used as precursor. There are many form of Carbon adsorbents as active carbons, active carbons fibers, molecular carbon sieves and carbon nano materials[50]. Its usefulness derives mainly from its large micropore and mesopore volumes and the resulting high surface area. Nowadays, the depleted source of commercial coal-based AC results in the increase of price[23]. It has a range of applications from gas, water, and metal purification to air filtration.
- Activated alumina: Is an adsorbent made of aluminum oxide (Al_2O_3). It is used as a desiccant for drying gases and air and as a fluoride filter for drinking water. It has specific use as a silica gel replacement in certain environments due to its thermal shock resistance and physical constancy when immersed in water.
- Silica gel or silicon dioxide: Is a common desiccant used in food preservation, humidity control, and various medical devices. It has a higher water absorption capacity than clay silicates, it is very inert, and it can be regenerated through heating.
- Organic polymers: Are chains of repeating carbon based molecules used as adsorbents in size-exclusion chromatography and gas separation processes with high retention power and selectivity. Most do not require disposal and the regeneration process is environmentally friendly.
- Molecular sieves or zeolites: Are naturally occurring adsorbents with uniform pore size that can be tuned to be highly selective. They are used as dehumidifiers and air purifiers due their high retention and adsorption capacities even at high temperatures. Zeolites are often combined with activated carbon for combined effectiveness.

2- Natural adsorbents

- Calcium sulfate: Is a natural mineral that is chemically stable, and readily retains its captured moisture. It costs little but also has a low adsorbency capacity and is best suited for small moisture capture operations or laboratory use.
- Calcium oxide: Is a slow but strong and high capacity desiccant also known as quicklime. It is caustic and expands as it adsorbs and does so over several days. It is most effective in high humidity environments
- Clay or clay silicates: Are natural mineral adsorbents that are used as spill cleaning agents, sealants, and packing materials because they are inexpensive, inert, and have a quick capture rate. However they begin to desorb at temperatures above 120°F[51].

And we have a Low-cost adsorbents has been investigated as a replacement for costly current methods[52]. Nearly 100 papers talk about low cost adsorbents have demonstrated outstanding removal capabilities for certain metal ions as compared to activated carbon. Adsorbents that stand out for high adsorption capacities are chitosan (Hg^{2+} , Cr^{6+} , and Cd^{2+}), zeolites (Pb^{2+} and Cd^{2+}), waste slurry (Pb^{2+} , Hg^{2+} , and Cr^{6+}), and lignin (Pb^{2+}). These adsorbents are suitable for inorganic effluent treatment containing the metal ions. It is important to note that the adsorption capacities of the adsorbents vary depending on the characteristics of the individual adsorbent, the extent of chemical modifications, and the concentration of adsorbate[53]. Other low cost adsorbents , adsorbents Agricultural and industrial waste by-products such as rice husk, peanut husk, charcoal, fly ash, biomass, and fly ash[54].

Moreover, during the few years new classes of mineral adsorbents have been developed[55], specifically Nanotechnology as adsorbents in all form; particles, tubes, rods, membrane, and fibers[56].

Nanoparticles have a wide range of applications, as in the technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatments. Many studies have addressed nanoparticles, mainly metal oxides, as effective and efficient adsorbents in the cleanup of environmental contaminants, mainly because nanoparticles can penetrate into the contamination zone where microparticles cannot.

In general, the term nanotechnology related to the preparation and application of materials at nanoscale (1–100 nm) has emerged as a fascinating area of interest for removal of various contaminants especially from wastewater effluents[6].

Nanoparticles in adsorption process are most importantly used as adsorbents for the removal of metal ions, and the commonly used are oxides of aluminum, iron, and titanium. Some workers have used nanoparticles of iron oxide for efficient removal of metal ions due to their high surface areas and ease of preparation[57].

Chapter Three

Experimental Work

3.1 Materials

Four real samples of galvanization wastewater were obtained from a local galvanization factory (Ghtasheh Company, Fawwar, Hebron, Palestine). These samples were collected from different tanks, sample 1 was collected from after acidic tank, while sample 2 was taken from galvanizing tank, after galvanizing tank where zinc wash sample 3 was taken, and sample 4 from wash of powder coating tank as shown as in figure (3.1), (Zinc Chloride ($ZnCl_2$), anhydrous, 98+%, AlfaAesar, Germany) as stock solution, ICP Multi Element Standard Solution at concentration 40mg/L, obtained from (MERK, Germany), Limestone was obtained locally from (caves) and it was sieved to very small size used as adsorbent,(Zinc Nitrate $Zn(NO_3)_2$ as stock solution, 98+% purity, sigma aldrich, Germany), Activated Carbon, and magnetic nanoparticles (Iron oxide powder (Fe_3O_4), 98+%, IoLiTec Ionic Liquids Technologies, Heilbronn, Germany).

3.2 Method

3.2.1 Wastewater characteristics

Wastewater characteristics of the real samples at different time intervals, these were analyzed before treatment including pH (PCE-228 pH-meter), chemical oxygen demand COD (COD Reactor CR25), electrical conductivity (EC) and total dissolved solid (TDS) (Electrical conductivity meter EE002), concentration of elements in galvanization process (ICP-Optical Emission Spectrometer (ICP-OES)), and turbidity (Waterproof Portable TN100 meter).

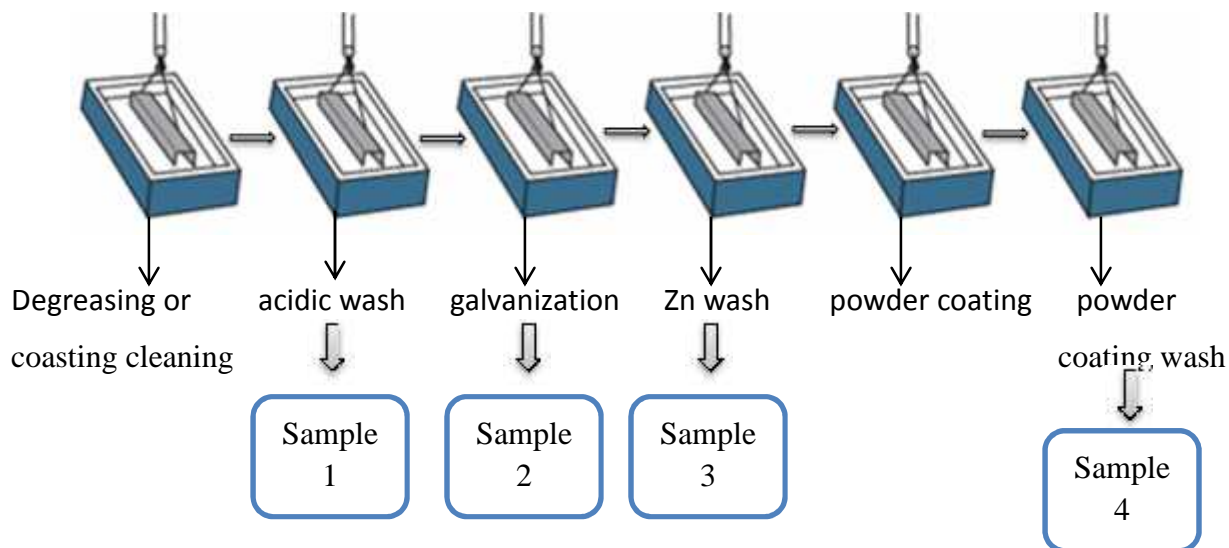


Figure 3.1: Real wastewater samples were collected from different tanks in galvanization process, these tanks are: acidic wash (sample 1), galvanization (sample 2), Zn wash (sample 3), and powder coating wash (sample 4).

3.2.2 Adsorption (Batch tests)

Adsorption experiments were carried out in a batch technique by using different types of adsorbents and solutions. According to the different adsorbents that were used; natural adsorbent, where 5 g of limestone was added to 100 ml of $ZnCl_2$ solution, and mixed on a stirrer at 100 rpm for 15, 30 minutes and 1 hour at constant pH 6. After that, the lime stone was separated by filtering from the aqueous solution, and E.C (Electrical conductivity meter EE002) was measured.

The second adsorbent that was used is Activated carbon, which were used with different two solutions, the first solution where done by 0.5 g of activated carbon added to 100 ml of $ZnCl_2$ solution. and the second solution is $Zn(NO_3)_2$, where 0.1 g of activated carbon was added to 100 ml of $Zn(NO_3)_2$, and adsorption process was carried out at same conditions for these solutions, mixed on a stirrer at 100 rpm for 5, 10, 15, 20, 30 and 60 minutes, and pH 6. Then adsorbent separated by filtering from solution, and E.C and concentration of zinc were measured.

The final adsorbent that was used is Magnetic Iron Oxide nanoparticles, were used with different solutions, the first solution where done, 0.1 g of magnetic iron oxide nanoparticles were added to 50 ml of $ZnCl_2$ solution, mixed at 99 rpm on rotary shaker (Intelli-mixer), for 10, 20, 30, 60,

120, and 180 minutes. While 1 g of magnetic iron oxide nanoparticles were added to 50 ml of ICP standard solution mixed at 99 rpm on rotary shaker (Intelli-mixer), for 10, 20, 30 minutes. Also 0.5 g of magnetic iron oxide nanoparticles were added to 50 ml of $Zn(NO_3)_2$ solution mixed at 99 rpm on rotary shaker, for 10, 30, 60, 180, 300 minutes and overnight at pH 7. Finally 0.2 g of magnetic iron oxide nanoparticles were added to 100 ml of real sample (from tank 4) mixed on a stirrer at 100 rpm for 10, 30, 120 and 150 minutes, and this real sample was tested with nanoparticles mixed on a shaker at 99 rpm, for 10, 30, 60, 300 minutes and overnight. Then the magnetic nanoadsorbent was separated, and the aqueous concentrations were analyzed by ICP-Optical Emission Spectrometer (ICP-OES). And E.C (Electrical conductivity meter EE002). Various parameters were studied like initial concentration and pH, solution with different concentration were prepared (5.17, 2.59, 0.65, 0.32, and 0.16) at equilibrium time 3 hour and adsorbent dosage 0.1 g nano/50mL real sample, also various pH range (2, 5, 7, 10, 11, and 13) was studied at the same experimental condition. These experiments were conducted at room temperature.

Chapter Four

Results and Discussion

4.1 Wastewater Characteristics

The real wastewater samples characteristics, including pH, E.C, TDS, and turbidity were tested over a period of 60 days as shown in Table (4.1).

Table 4.1: pH, E.C, turbidity, and TDS characterization tests of real wastewater samples from local galvanization industry over 60 days.

Sample	device	Interval time	2	3	4	5	6
		1					
1	pH	0.22	0.44	0.29	1.35	3.22	2.72
	Turbidity(NTU)	7.51	9.20	17.54	6.28	21.3	3.56
	E.C(ms)	30.6	31.4	35.6	39.6	2.56	4.90
	TDS(ppm)*100	202	227	250	267	20.0	362
2	pH	13.80	14.40	14.03	14.83	14.78	14.68
	turbidity	30.00	56.4.0	36.70	41.00	65.30	309.0
	E.C	156.1	157.0	155.9	156.2	166.9	178.9
	TDS*100	1071	1035	1107	1083	1260	1191
3	pH	13.0	12.88	13.01	12.64	7.440	11.43
	turbidity	7.96	8.260	11.29	2.590	2.650	6.180
	E.C	7.20	7.980	8.270	9.200	1.164	1.708
	TDS*10	483	489.0	573.0	596.0	76.10	118.5
4	pH	8.72	7.61	9.82	8.00	7.45	6.93
	turbidity	2.59	0.68	2.75	0.58	6.99	2.18
	E.C	1.15	1.1237	1.182	1.267	1.02	1.051
	TDS	752	748	785	794	680	700

Table (4.1) shows the characteristics of wastewater samples collected over six time intervals. Sample 2 which was obtained from fluxing or galvanization solution tank showed the highest values of all tested properties since its tank contained zinc balls and alkaline solutions. Samples (1, 3, and 4) were collected from the rinsing tanks and the properties of wastewater varies according to their sequence in the galvanization process. For instance, sample 1 has the lowest pH values as this sample was obtained from the rinsing tank after acidic treatment of metals, and

it has the highest turbidity values because this tank is contaminated with fats and oils, where sample 3 has the highest pH values as this sample was obtained from the rinsing tank after fluxing tank which is highly alkaline, and sample 4 which was obtained from the rinsing tank after powder coating tank, has the lowest values of all tests; because this sample was obtained from the last tank which has a little amount of dissolved solids. In general wastewater samples have low COD values, so they have a little magnitude of organic matters.

When comparing the values of the tested properties over time intervals (60 days), sample 2 water characteristics have a stable range because the water in this tank wasn't change, only the substances were added at different times to preserve substance's concentration, about rinsing tanks, that a major change was occurred after time interval 4 which indicates that water in these tanks were recharged for example TDS that shown in figure (4.1).

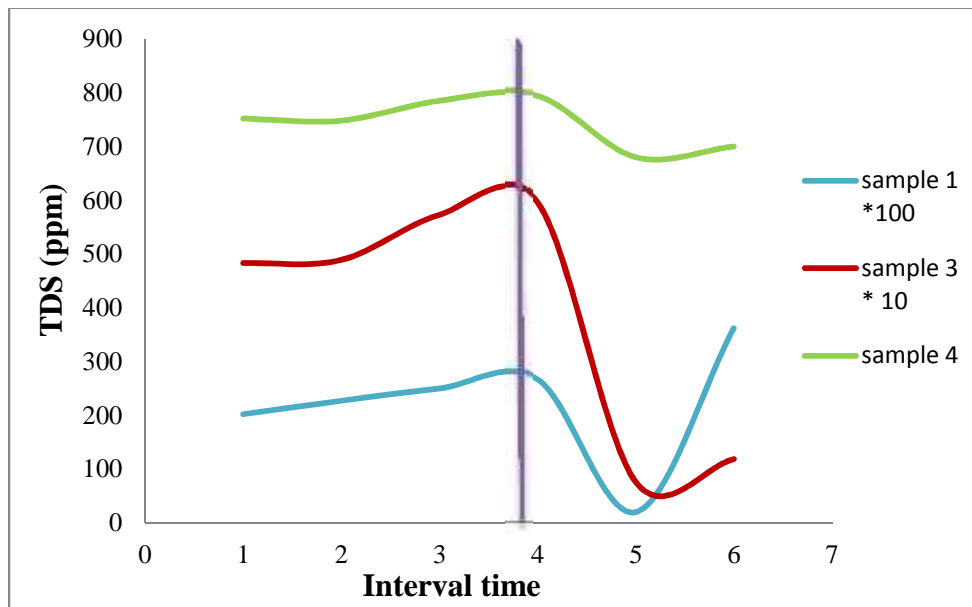


Figure 4.1: Several values of TDS in rinsing tanks with different time intervals along sixty days.

Real samples which obtained from rinsing tanks (1, 3, and 4) in the galvanization process, had these elements (Fe, Al, Cu, Mn, Pb, Cd, Zn, Co, Cr, B, Na, K, Mg, Ca, Ni), were analyzed to find their concentration as shown in Table (4.2), and the concentration of Zn in sample 2 was 1494 mg/L.

The concentration of elements in galvanization industry indicate that the wastewater for this industry is highly contaminated with toxic elements which requires proper treatment process before discharged to empty land or sewer system. The next section presents the results on applying adsorption technique for treat of wastewater contain toxic metals.

Table 4.2: Concentration of elements from rinsing tanks in galvanization industry.

Sample	Fe	Al	Cu	Mn	Pb	Cd	Ni
1	0.267	1.095	0.044	0.002	0.000	0.008	0.000
3	297.2	0.927	0.295	5.158	0.729	0.000	0.405
4	6.935	0.012	0.002	0.145	0.000	0.000	0.022

Sample	Zn	Co	Cr	B	Na	Ca	K	Mg
1	3.707	0.003	0.062	0.000	1626	7.261	12.32	0.173
3	16.72	0.063	0.441	0.000	57.79	111.2	8.503	39.66
4	0.843	0.006	20.79	0.000	108.6	93.63	8.066	45.51

4.2 Adsorption Tests

Adsorption tests were performed on model solutions and real wastewater samples that were collected from local galvanization factory.

4.2.1 Adsorption test on several model solutions

Various model solutions like ($ZnCl_2$, ICP standard, and $Zn(NO_3)_2$) were tested to determine the feasibility of the adsorption process on these solutions.

The result of adsorption process on $ZnCl_2$ solution by using limestone as adsorbent was conducted by E.C as shown in figure (4.2). On the other hand, figure (4.3) demonstrated the adsorption for ICP standard solution with magnetic nanoadsorbent was carried by ICP device, the elements concentrations decrease with time, and this relationship can be described by an exponential regression.

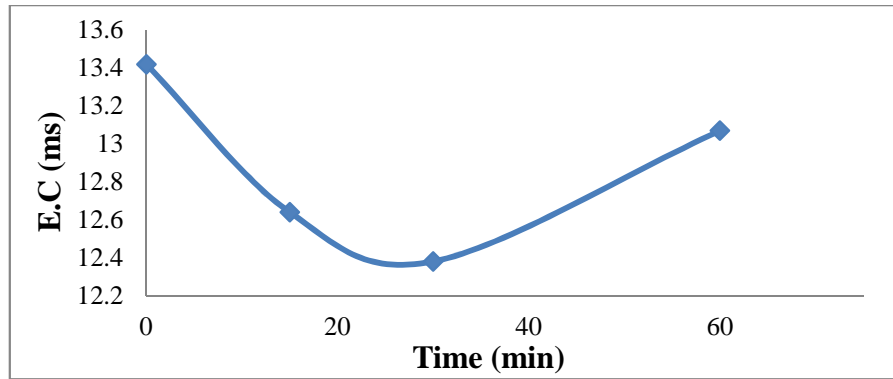


Figure 4.2: E.C value of $ZnCl_2$ as a function of contact time for adsorption experiments with a lime dose of 5 g/100 mL on a stirrer (100 rpm) at room temperature, and pH 6.

Lime stone adsorbent for $ZnCl_2$ solution didn't give an effective result, it just show a very weak adsorption that couldn't be taken into consideration, this result was due to the alkaline nature of lime stone where it's have the capability to buffer the solution, so it will increase the pH of the solution, this variation of the pH can affect the adsorption process, or it was due to the instability of the $ZnCl_2$ solution.

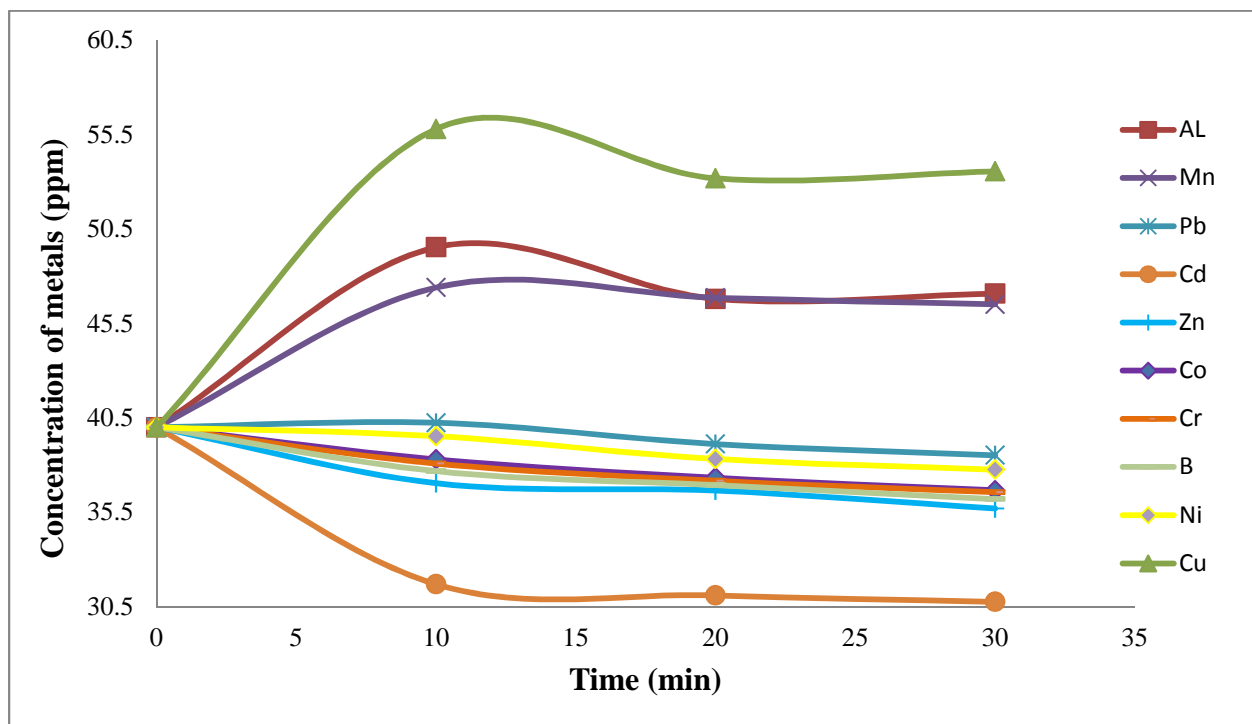


Figure 4.3: Concentration of different elements as a function of contact time for adsorption experiments on rotary shaker (99rpm) with iron nanoparticles 1g/50 mL.

For using iron oxide nanoadsorbent with ICP standard solution, it was noticed that Zn concentration was decreasing according to the time factor of adsorption process, but with little change. According to the other elements, Cd concentration had an effective decrease, while for B, Cr, Co, Ni, and Pb they had the same concentration approach of zinc in decrease.

But some elements had an increase in their concentrations which included Cu, Al, and Mn as shown in figure (4.3). The interpret of this results; increased could be attributed that some of the nanoparticles escaped to the supernatant which was detected in the samples. Beside the nanoparticles seem to be contaminated with Al and Mn; which resulted in an increase in their concentrations.

The expression of results that obtained depending on the relationship between percentage removal which calculate according Equ.(4.1) and time factor of adsorption process as shown in Figure (4.4), that indicate the total percentage removal was reached 70%, also the percentage removal of Cd, Zn, B, Cr, Co, Ni and Pb was increased respectively.

$$\text{Percentage Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (4.1)$$

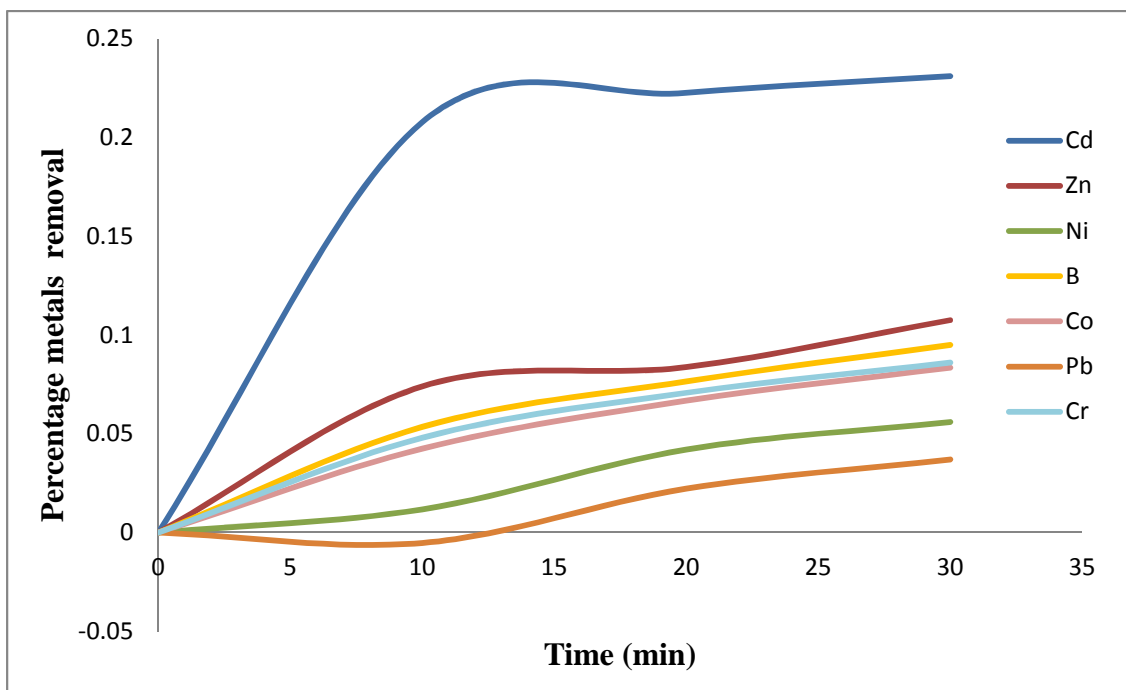


Figure 4.4: Percentage removal of elements as a function of contact time for adsorption experiments with iron oxide nanoparticles 1g/50 mL.

The difference in the percentage removal of elements maybe explained that the nanoparticles is more selective to certain heavy metals than others, and the low percentage removal was due to the fact related to the active sites. Adsorption's results of $ZnCl_2$ and $Zn(NO_3)_2$ solutions were not reproducible, so it was not efficient, and this is might be attributed to the Zn ions instability.

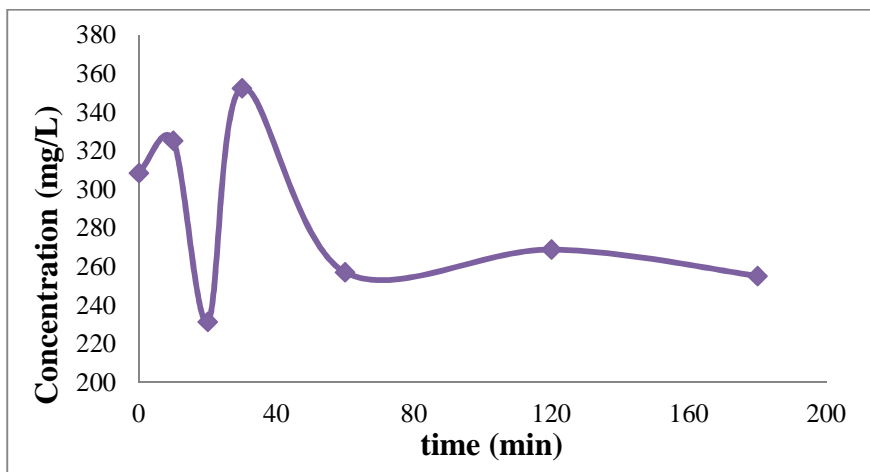


Figure 4.5: The concentration of $ZnCl_2$ as a function of contact time for adsorption experiment on rotary shaker at 99 rpm, iron nanoparticles dose of .1 g/50 mL, at room temperature, and pH6.

Figure (4.5) illustrate the results of $ZnCl_2$ solution that were obtained from ICP device which are not stable, so there is no adsorption occurs with nanoparticles here. Then activated carbon was used as adsorbent for the same solution, and the results that were obtained from E.C device showed in figure (4.6).

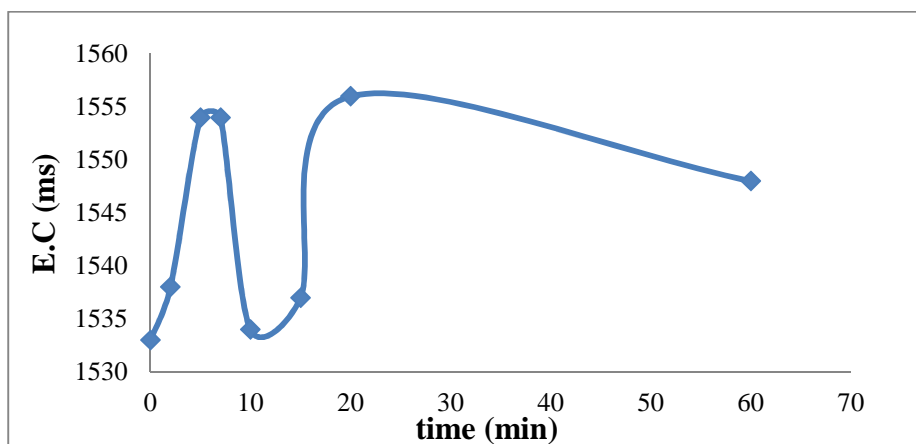


Figure 4.6: E.C value of $ZnCl_2$ as function of contact time for adsorption experiment on a stirring rate 100 rpm, activated carbon dose of .5 g/50 mL, at room temperature, and pH 6. The results obtained from E.C device are approximately having the same behavior of ICP device

results. This indicates that E.C can be used as an element's concentration indicator. As seen from figures (4.5, 4.6) the solution ($ZnCl_2$) is instable.

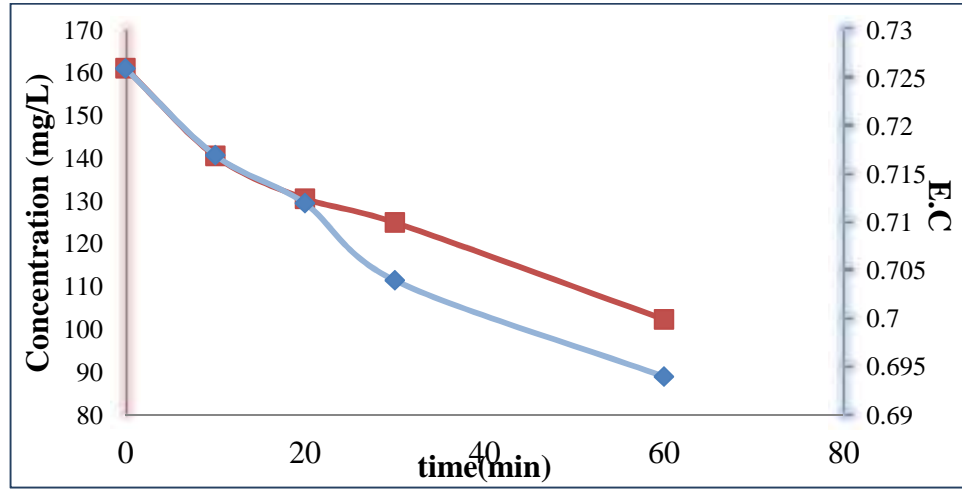


Figure 4.7: E.C, and Zn concentration values of $Zn(NO_3)_2$ as function of contact time for adsorption experiment, on a stirring rate 100 rpm, activated carbon dose of .1 g/100 mL, at room temperature, and pH 6.

According to the two curves that shown in figure (4.7), the adsorption process of $Zn(NO_3)_2$ solution occur through one hour and the concentration decreases nearly from 160 to 100 mg/L. the same test was repeated at the same conditions but over 24 hour, and the results appearing in figure (4.8).

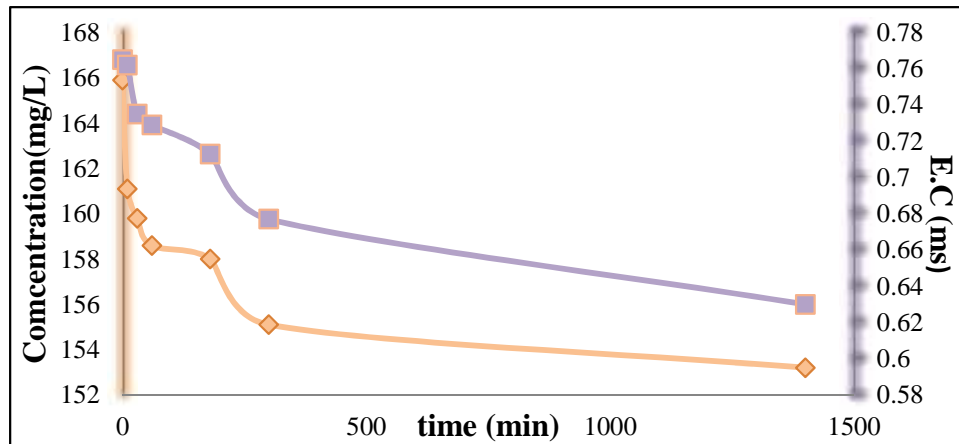


Figure 4.8: E.C, and Zn concentration values of $Zn(NO_3)_2$ as function of contact time for adsorption experiment, on a stirring rate 100 rpm, activated carbon dose of .1 g/100 mL, at room temperature, and pH 6.

The results that were obtained from figure (4.8) detect that adsorption process was done, but without the effectiveness that occur in the first test, the concentration was decreased from 166 to 153mg/L through 24 hour in this test, while it was decreased from 160 to 100 mg/L through one hour in the first test. Also the same solution ($Zn(NO_3)_2$) was used with iron nanoadsorbent at the same parameters, but with differ pH (pH7), and the results appearing in figure (4.9).

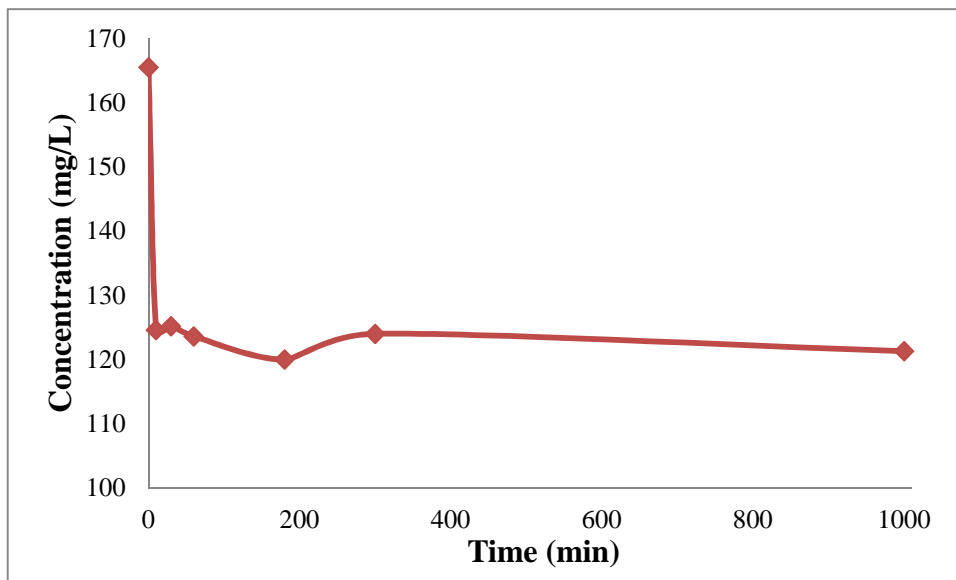


Figure 4.9: E.C, and Zn concentration values of $Zn(NO_3)_2$ as function of contact time for adsorption experiment, on rotary shaker at rate 99 rpm, iron nanoparticles dose of .5 g/50 mL, at room temperature, and pH 7.

Figure (4.9) illustrate that the concentration of $Zn(NO_3)_2$ decreases from 165 to 125 mg/L at the first ten minutes, but according to 24 hour the solution's concentration was decrease too little nearly in stable manner. These results that were obtained from tests on $Zn(NO_3)_2$ were detect that this solution was instable.

4.2.2 Adsorption test on real wastewater samples

The wastewater real samples test was done in order to check the possibility of using iron oxide magnetic nanoparticles to treat the contaminated wastewater with heavy metals especially Zn. The first test of adsorption was implemented on real sample for 150 minutes as shown in figure (4.10).

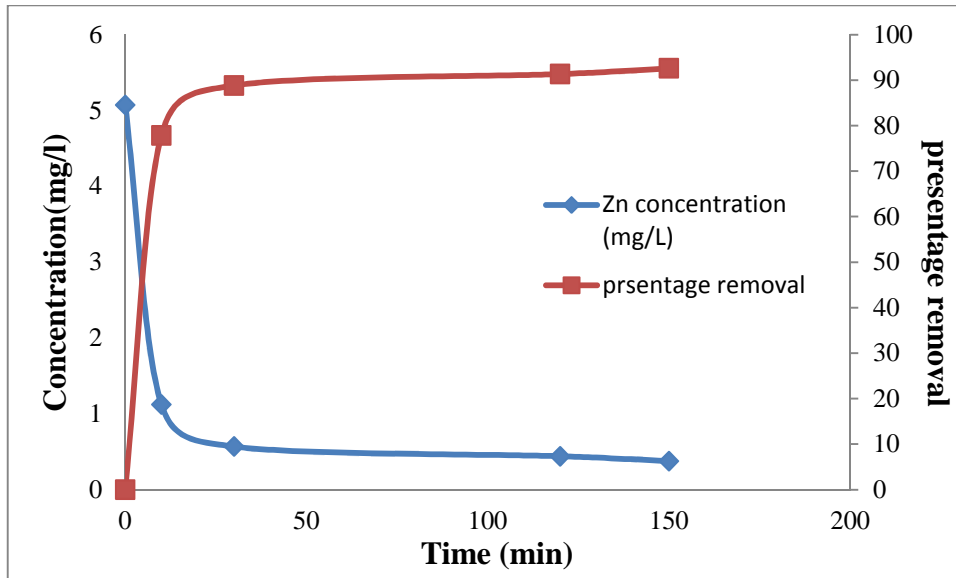


Figure 4.10: The concentration and the percentage of removal of Zn as a function of contact time for adsorption experiments at stirring rate 100 rpm, iron nanoparticles dose of .2 g/100 mL, at room temperature and pH13.

Figure (4.10) shows change in concentration of Zn along 150 minutes, where Zn concentration was decreased from 5 to 1 mg/L at the first 10 minutes. After this time period, the concentration of Zn was decreasing slightly, and the percentage of removal after 150 minutes reached 92.6%. The second test of adsorption was left for 24 hours and the obtained results were shown in figure (4.11).

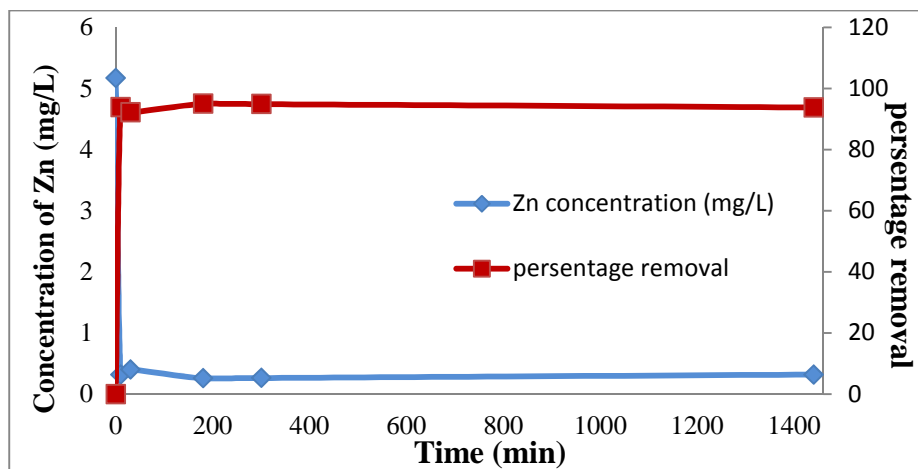


Figure 4.11: The concentration and the percentage of removal of Zn as a function of contact time for adsorption experiments at stirring rate 100 rpm, iron nanoparticles dose of .2 g/100 mL, at room temperature and pH13.

Figure (4.11) illustrate the adsorption test for the real sample left in contact with the adsorbent for 24 hours. At this time removal percentage reached its maximum value of 95% .Equilibrium in this case was reached after 3h, so to get more accurate results the solution was left overnight, and from the equilibrium data the adsorption capacity was calculated in order to determine the adsorption isotherm as shown in figure (4.12). Tests were implemented for real sample with different operating conditions to study the efficiency from PH and initial concentration effects.

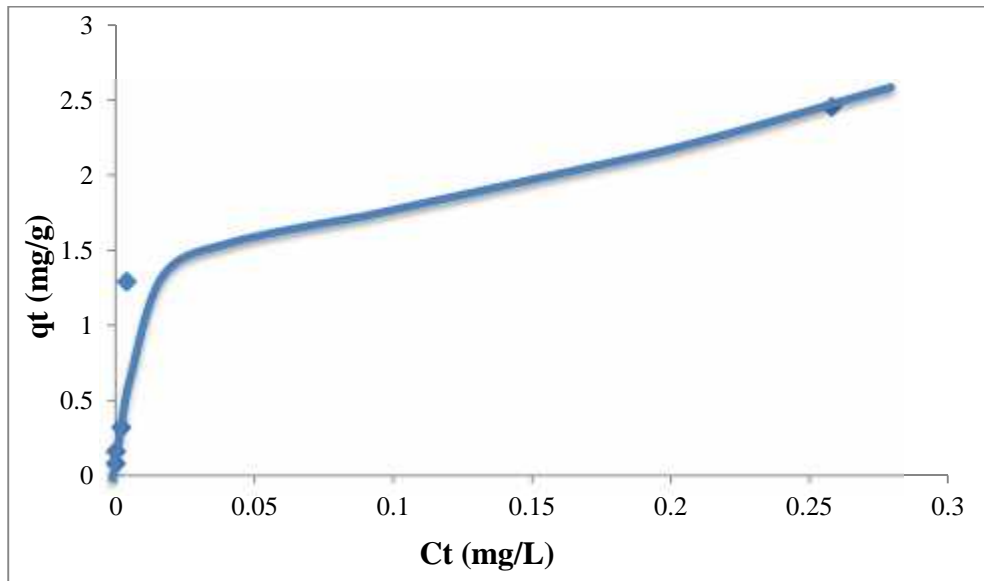


Figure 4.12: Adsorption capacity for various final concentrations as function of equilibrium of concentration on rotary shaker rate 99 rpm at 3 hours, iron nanoparticles dose of .1 g/50 mL, at room temperature and pH 13.

The concentrations (C_o and C_e) were calculated in order to find the adsorption capacity of iron nanoparticle at equilibrium (q_e) according to the mass balance at Equ (4.2). Figure (4.14) shows the adsorption capacity in (mg/g) as function of equilibrium concentration in (mg/L). This adsorption capacity was used to acquire the equilibrium adsorption isotherm, under the experimental condition obeyed frindlich isotherm.

$$qt = (C_o - C_e) * \frac{v}{m} \quad (4.2)$$

Where C_o and C_e are the initial and equilibrium concentrations of Zn (mg/L), respectively, q_t is the removal capacity of Zn at equilibrium (mg/g); V is the volume of the solution (mL), and m is the weight of adsorbents (mg).

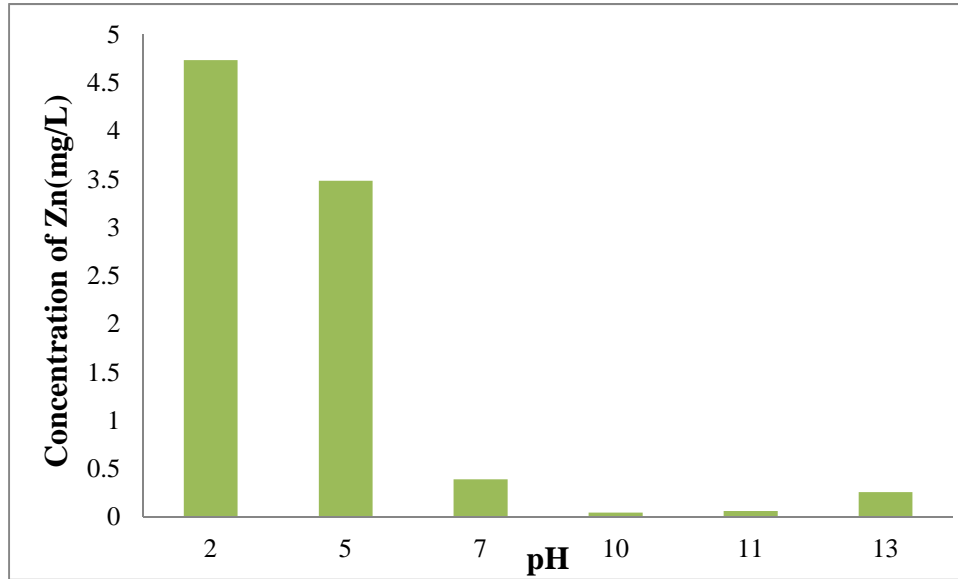


Figure 4.13: The effect of pH value on adsorption process of Zn element in real sample

Adsorption is rather favorable at high pH, and keeping in mind the real sample is highly alkaline, which indicates that the reduction in Zn concentration is due to adsorption rather than precipitation.

Recommendations

- 1- Other element like Sodium was observed as the high concentration in galvanization wastewater industry, which requires further treatment in order to protect our environment from this pollution.
- 2- Iron oxide magnetic nanoparticle considered as an effective adsorbent for the treatment of several heavy metals not only zinc element.
- 3- Some rinsing tanks were found highly acidic, others were highly alkaline depend on there sequence in the process. One should consider neutralizing these tanks together which will effectively treat their wastewater contaminant.
- 4- Safety measured should be taken into account workers while deal with galvanization wastewater and researcher.
- 5- Insitu treatment by adsorption is strongly recommended to implement of the galvanization plant in Palestine.

Conclusion

Galvanization wastewater from local galvanization plant was characterized and the wastewater in this industry was found high concentration with heavy metal, the PH, E.C, TDS, and turbidity were varied according to the sequence of the galvanization process. Adsorption with magnetic nanoparticle was found highly effective for the removal of Zn. The results were obtained showed removal efficiency as high as 93% could be achieved in less than ten minutes, and the optimum value of pH was 10. So this study is present that galvanization wastewater industry should be property treatment before being discharge and adsorption method with nanoparticles could be effectively used for removal of heavy metals for wastewater.

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