Sudan University of Science and Technology

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Removal Efficiency of some Toxic Heavy Metals from Water by Adsorption by Using Graphite Activated Carbon (GAC)

كفاءة إزالة بعض الفلزات الثقيلة السامة من الماء عن طريق الادمصاص باستخدام الجرافيت المنشط بالكربون

A thesis submitted in partial fulfillment for the requirements of the degree of M. Sc. in Chemistry

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صدق الله العظيم

سورة الفاتحه الآية (1)

Dedication

To my parents, sisters and brothers

To all people whose health suffers from lack of
clean water

Acknowledgements

To the light, my god, for his guidance, to Dr. Mutasim Maknoon, for his great efforts of supervising and leading me to accomplish this fine work. My thanks extended to my friends and family for their great support and encouragement, I thank them all. To my mother and father, for their warm, kinds encourage and love, to every person for lighting some part of my pathway, I thank them for their trust in me.

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Abstract

Heavy metals are known to be toxic for living organisms even if they are present at low levels. The presence of heavy metals, organic dyes and microbial pollutants in water continue to be a major concern and the removal of such contaminants is considered to be a major problem in environmental remediation. In the present study, activated graphite was used for removal of some heavy metal ions from aqueous solutions by batch adsorption method. The adsorption efficiency of removal of heavy metal ions by activated graphite was studied and the concentration of some heavy metals namely, Cu, Zn, Pb and Cd was determined using the Atomic Adsorption Spectrophotometer (AAS).The experimental data were calculated and the results revealed that the removal percentage decreased as the concentration of heavy metal increased. Therefore, the increase of solution concentration leads to decrease in the adsorption capacity of heavy metal ions by adsorbent. The results revealed that the activated graphite is an effective adsorbent for removal of zinc, lead, cadmium, and copper ions from aqueous solutions.

الملخص

من المعروف ان الفلزات الثقيله تكون سامه للكائنات الحيه حتي لو كانت موجوده في مستويات منخفضه. وجود المعادن الثقيله و الاصباغ العضويه والملوثات الميكروبيه في المياه هي الشاغل الرئيسي لكثير من المهتمين وازالتها تعتبر مشكله في المعالجه البيئيه. في هذه الدراسه تم استخدام الجرافيت االمنشط لازالة بعض ايونات المعادن الثقيله (النحاس‘ الرصاص، الزنك، والكادميوم) من محاليلها المائيه بطريقة الادمصاص(الامتزاز). وتم حساب البيانات التجريبيه واظهرت النتائج والتي استخدم فيها جهاز الامتصاص الذري ان نسبة الازالة انخفضت كلما زاد تركيز المعادن الثقيله، ولذلك فان زيادة تركيز المحلول يؤدي الي انخفاض في قدرة ادمصاص ايونات المعادن الثقيله بواسطة الجرافيت النشط. كما اوضحت النتائج ان الجرافيت النشط فعال لازالة ايونات الرصاص، النحاس، الزنك والكادميوم من محاليلها المائيه.

CHAPTER ONE

INTRODUCTION

Introduction

1.1 Background

Ensuring the availability of clean, abundant fresh water for human use is among the most pressing issues facing the world (Gleick, 1998).

In some parts of the world a source of water of any kind may be attractive and the need is great. Pure water is never found in nature and its increasingly rare to encounter a source of water that can be used without treatment. In our civilized society potable water of an acceptable and reliable quality is demanded as a right. Water characteristics or quality are widely used expressions which reflect the constituents present in water if they have adverse effect or not. From the consumer's view the water shall be clear, off odor, of taste and aesthetically acceptable (AWWA, 1971). The desirable characteristics of water vary with its intended use. Water for drinking and food purposes must be free from chemical contaminants and microorganisms causing diseases or adverse physiological effects. Other uses of water such as industry and agriculture require special qualities of water. Water quality depends largely on the source of water. The type of pollutants differs with the source of water. Some sources of water, particulary the ground water may be suitable for direct consumption, but the majority of surface waters require treatment before consumption (Lewis, 1980).The evaluation of industrial and chemical societies, organizations and great advances in science have resulted in many questions being raised about potability or safety of drinking water. To protect people against the effects of the long-term chronic exposure of many heavy metals the world health organization (WHO), United States

Environmental Protection Agency (USEPA).and other organizations proposed maximum concentration limits for all heavy metals in water (Alan and Kenneth, 2003). This put more pressure on chemists and water treatment specialists to solve problems associated with heavy metal pollution and any other kind of pollutant in water to reduce their concentrations to the allowed level of drinking as stated by WHO or USEPA.

Water pollution is of great concern since water is the prime necessity of life and extremely essential for the survival of all living organisms. Moreover, water pollution is considered to be a major environmental problem worldwide, and among the various water pollutants, heavy metal require special attention because of their toxic effect on humans and the environment(Tuzzen, 2009). Heavy metals are considered to be the most pollutant in source and treated water. The increased use of heavy metals industrially resulted in an increase in the availability of metallic substances in natural source water (Tangjuank et al., 2009). Moreover, heavy metals form a very dangerous category due to their toxic and carcinogenic nature, non-biodegradable and hence, tend to accumulate in the environment for long time. Some of these toxic elements are: cadmium, lead, zinc, copper, mercury, chromium and nickel (Fu and Wang, 2011).

Nanomaterials have a wide range of applications, as in the technological and environmental challenges in the areas of the solar energy conversion, catalysis, medicine, and water treatments (Shannon et al., 2008). Several studies have addressed nanoparticles, mainly metal oxides, as effective and efficient adsorbent in the cleanup of environmental contaminants, mainly because nanoparticles can penetrate into the contamination zone where microparticles cannot (Geo et al., 2011). Conventional techniques for removing heavy metal from water and wastewater include electroplating, evaporating membrane filtration, oxidation, reduction, ion exchange and adsorption (Chingombe et al., 2005). Among these methods, adsorption is the most effective technique, various adsorbents such as activated carbon, silica gel, and graphite oxide can be used in the purification of water (Tangjuank et al., 2009). Historically graphite oxide and other carbon based nanomaterials have been used as adsorbent for environmental purification and water treatment application for the removal of inorganic and organic pollutants (Gao et al., 2011).

Graphite oxide and its composites offer utility in several applications due to its unique two-dimensional nature and associated band structure (Rao et al., 2010). Feature like large surface area and presence of surface functional groups make single sheets of carbon and their composites an attractive adsorbent candidate for water purification. The present study aimed to test the effect of graphite oxide in the removal of heavy metal ions, using batch adsorption methods.

1.2 Scope of study

Many universities, research centers and academic institutes are conducting research programs in water treatment. They all try to find the optimal conditions, low cost and most effective methodology by which maximum contaminants can be eliminated from water to make it safe for drinking.

The objective of this research is:-

* To study the removal of four heavy metals, namely copper, lead, cadmium and zinc from water by using graphite granules collected from dry batteries, and evaluation of its capacity for removing heavy metals.

* To study the optimal conditions: pH, concentration and the equilibrium time for effective adsorption.

CHAPTER TWO
LITERATURE REVIEW

2.1 Water resources

2.1.1 Introduction

Water resources are under major stress around the world. Rivers, lakes, and underground aquifers supply fresh water for irrigation, drinking, and sanitation, while the oceans provide habitat for a large share of the planets food supply. Today, however, expansion of agriculture, damming, diversion, over-use, and pollution threaten these irreplaceable resources in many parts of the globe.

Providing safe drinking water for the more than 1 billion people who currently lack it is one of the greatest public health challenges facing national governments today. In many developing countries, safe water, free of pathogens and other contaminants, is unavailable to much of the population, and water contamination remains a concern even for developed countries with good water supplies and advanced treatment systems. And over-development, especially in coastal regions and areas with strained water supplies, is leading many regions to seek water from more and more distant sources.

Water covers about three-quarters of earth surface and is a necessary element for life. During their constant cycling between land, the oceans, and the atmosphere, water molecules pass repeatedly through solid, liquid, and gaseous phases (ice, liquid water, and water vapor), but the total supply remain fairly constant. A water molecule can travel to many parts of the globe as it cycles.

There are three basic steps in the global water cycle: water precipitates from the atmosphere, travels on the surface and through ground water to the oceans, an evaporates back to the atmosphere from land or oceans.

Significant salt content exit because precipitation is greater than evaporation on land. Most of the precipitation that is not transpired by plants or evaporated infiltrates through soils and becomes ground water, which flows through rocks and sediments and discharges into rivers. (Bridget et al., 2007)

2.1.2 Natural water sources

Fresh water represents 6% of the world's water supply, but is essential for human uses such as drinking, agriculture, manufacturing, and sanitation. Two-thirds of the global fresh water is found underground.

If you dig deeply enough anywhere on earth, you will hit water. Millions of people worldwide depend on ground water stocks, which they draw from aquifers-permeable geologic formations through which water flows easily. Very transmissive geologic formations are desirable because water levels in wells decline little even when pumping rates are high, so the wells do not need to be drilled as deeply as in less transmissive formations and the energy costs of lifting water to the surface are not excessive (Peter. 2006).

2.2 Water pollution

2.2.1 Classification and categories of water pollution

In general, pollutants can be released into the environment as gases, dissolved substances or in the particulate form.

Pollution may result from point sources or diffuse sources (non-point sources). There is no clear-cut distinction between the tow, because a diffuse source on regional or even local scale may result from a large number of individual point sources, such as automobile exhausts. An important difference between a point and a diffuse source is that a point source may be collected (diffuse sources consisting of many point sources, it may also be controlled and all point sources can be identified). The major point sources of pollution to fresh waters originate from the collection and discharge of domestic wastewaters, industrial wastes or certain agricultural activities, such as animal husbandry. Most other agricultural activities, such as pesticide spraying or fertilizer application, are considered as diffuse sources. The atmospheric fall-out of pollutants also leads to diffuse pollution of the aquatic environment.

By definition a point source is a pollution input that can be related to a single outlet. Untreated, or inadequately treated, sewage disposal is probably still the major point source of pollution to the world's waters. Other important point sources include mines and industrial effluents.

As point sources are localized, spatial profiles of the quality of the aquatic environment may be used to locate them. Some point sources are characterized by relatively constant discharge of the polluting substances over time, such as domestic sewers, whereas others are occasional or fluctuating discharges, such as leaks and accidental spillages. A sewage treatment plant serving a fixed population delivers a continuous load of nutrients to a receiving water body. Therefore, an increase in river discharge causes grater dilution and a characteristic decrease in river concentration. This contrast with atmospheric deposition and other diffuse sources where increased land run-off often causes increased pollutant concentrations in the receiving water system.

Diffuse sources cannot be ascribed to a single point or a single human activity although, as pointed out above, they may be due to many individual point sources to a water body over a large area. Typical examples are;

- Agricultural run-off, including soil erosion from surface and sub-soil drainage. These processes transfer organic and inorganic soil particles, nutrients, pesticides and herbicides to adjacent water bodies.
- Waste disposal sites which include municipal and industrial soil waste disposal facilities; liquid waste disposal (particularly if groundwater is impacted); degraded sediment disposal sites (both confined and open lake). Depending on the relative sizes of disposalsites and receiving water bodies, these sources of pollution can be considered as either diffuses or point sources.

The time variability of pollutants release into the aquatic environment falls into four main categories. Sources can be considered as permanent or continuous (e.g. domestic wastes from a major city and many industrial wastes), periodic(e.g. seasonal variation associated with influx of tourist populations, or food processing wastes), occasional (e.g. certain industrial waste releases), or accidental(e.g. tank failure, truck or train accidents, fires, etc.). the effects of these various types of pollutants on receiving water bodies are rather different. The continuous discharge of municipal sewage, for example, may be quite acceptable to a river during high discharge periods when dilution is high and biodegradation is sufficient to cope with the pollution load. During low discharges, however, pollution level and effects may exceed acceptable levels in downstream river stretches (Deborah, 1996).

2.2.2 Pollution management and control

There are many approaches that could be adopted in water pollution control and management. It could be through prevention, practice efforts or join a project/program; Regulation and monitoring or engaging in control measures by reducing or minimizing waste.

Pollution control means to control the emissions and effluents into the air, water and land or soil. Without pollution control, the waster products from consumptions, heating, agriculture, mining, manufacturing, transportation and other human activities, whether they accumulate or disperse, will degrade the environment. Pollution prevention and waste minimization are more desirable than pollution control. However, pollution could be minimizing by adopting these practices (i) by recycling (ii) by reusing (iii) waste minimization (iv) by mitigating (v) by preventing (vi) by compost. Apart from all these mentioned above, you can also use pollution control devices which include Dust collection system e.g. bag houses, cyclones, electrostatic precipitators, scrubbers e.g. baffle spray scrubber, ejector venture scrubber, mechanically aided scrubbers, spray tower, wet scrubber, sewage treatment e.g. sedimentation (primary treatment), activated sludge bio filters (secondary treatment, also used for industrial waste water), aerated lagoons, constructed wetlands (also used in urban runoff); industrial wastewater treatment e.g. ultra filtration, API oil-water separators, bio filters, dissolved air flotation (DAF), powdered activated carbon treatment; the last but not the least are vapor recovery system and phytoremediation.

2.2.3 Risk assessment of drinking water contaminants

Pollution poses a serious risk to life especially when the water is a source of drinking and for domestic purposes for humans polluted waters are potent agents of diseases such as cholera, typhoid and tuberculosis. A major water pollutants has been oil spilled in large quantities from tankers of broken oil pipes from oil industries which kills sea weeds, mollusks, marine birds, crustaceans, fishes and other sea organisms that serve as food for humans. This leads to calcium deficiencies in our diet. Some insecticides like DDT are particularly dangerous when allowed into bodies of water because its concentration increases along the food chain. Oysters for an example can accumulate DDT to a concentration. 70,000 times that of DDT in sea water. The effects of water pollution in some areas has been to an extent of irreversibly changing aquatic ecosystems. This is dangerous to plants and animals including humans. Since water pollution has direct consequences on human well beings, an effective teaching strategy in the formal education sector is essential for a better understanding so as to develop the right attitude towards water. This is why the guided discovery approach is a teaching strategy which when adequately utilized and combined with other methods of science teaching will leave lasting impression on the learner as well as help him solve the problems of his immediate environment (Owa, 2013).

2.2.4 Heavy metals contamination

Heavy metals are elements of high density, and they are toxic at even low concentrations. They can also be defined as the elements in the d-block in the periodic table such as cadmium (Cd), lead (Pb), copper (Cu), and mercury (Hg). Heavy metals are natural compounds of the earth crust. Some heavy metals are vital to maintain the metabolism in our bodies at certain concentration such as zinc. However the excess of these heavy metals can lead to poisoning via drinking water contamination, high ambient air concentrations, or eating contaminated food. It is well known also that the specific gravity of heavy metal elements is more than five times the specific gravity of water where the specific gravity of water is 1 at temperature 4^oC. for instance, the specific gravity of some toxic heavy metals is: lead, 11.34; cadmium, 8.65 copper, 8.93; and mercury, 13.546 .

Heavy metals are very dangerous due to the fact that they can bioaccumulate in our bodies resulting in increasing the concentration of chemicals in the biological organism compared to the chemicals concentration in the environment.

There are about 35 metal elements that may be considered harmful because of their residential exposure. Twenty five elements of those metals of those metals are considered as heavy metals such as arsenic, cadmium, copper, gold, iron, lead and zinc. The excess amount of these elements results in reducing the mental and nervous functions, damaging the blood compositions, lungs, kidneys, liver, and other essential organs. Furthermore, long term exposure to heavy metal may induce Alzheimer’s disease, Parkinson’s disease, muscular dystrophy,, and multiple sclerosis. It is also known that heavy metals cause cancer.

Heavy metals can reach surface water either through industrial and consumer wastewater discharged into water bodies or from acidic rain leached to the soils and releasing heavy metals into groundwater and surface water.

2.2.4.1 Zinc health effects

Zinc is an essential and beneficial element for human bodies and plants. Complete exclusion of Zn is not possible due to it is dual role, an essential microelement on the one hand and a toxic environmental factor on the other (refrence). However, Zn can cause nonfatal fume fever, pneumonitis, and is a potential hazard as an environmental pollutant. Zinc is an essential nutrient in humans and animals that is necessary for the function of a large number of metalloenzymes.

2.2.4.2 Cadmium health effects

Cadmium could be produced as a byproduct during the refining of some heavy metals, namely, zinc and lead; however, besides the detrimental impacts of cadmium, it has a significant use if it is recycled. Cadmium is commonly used in nickel/cadmium batteries for its high tolerance to physical and electrical stress. Furthermore, it can be used in coating for its high corrosion resistance, pigments, and electronic compounds such as batteries. Cadmium could reach our bodies through food if it has been added to agricultural soil or fertilizers in various ways, such as atmospheric deposition and discharging industrial wastewater into surface water. Long term exposure can lead to the severe lung diseases and lung cancer. Moreover, high concentration of cadmium cause bone defects, osteomalacia and osteoporosis. In addition to that, high exposure to cadmium may cause hypertension. The average daily intake for human is found to be 0.15micro gram from air and 1 micro gram from water, furthermore, smocking a packet of 20 cigarettes can lead to increase the inhaling cadmium up to 4 micro gram.

Satarug (2004) has stated the effects of chronic exposure to low-level cadmium in foods and cigarette smoke as a result of bioaccumulation in the human body. The levels of Cd in the organs such as liver and kidney increase with age. Cd persists in kidneys of humans for many years where the half life time could be estimated to be 30 years. This has been associated with occurrence of Cd toxicity, and mortality risk by 40-100%. Besides, an excess amount of Cd may tend to pathologies such as renal failure, diabetics, and osteoporosis.

2.2.4.3 Copper health effects

Copper can reach our bodies through drinking water in copper pipes. Although copper is a vital element that our body needs, high doses of copper can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Moreover people that have Wilson disease are at risk for health effects from overexposure to copper.

Since copper has many practical uses ranging from coils to electrical wires and pipes, it can easily accumulate in the environment. Although our bodies need copper for good health, an excess amount of copper exposure or accumulation into human bodies can cause adverse health effects; for example, vomiting, diarrhea, stomach cramps, nausea, liver damage and kidney disease. Unfortunately, children are more vulnerable to the toxic effect of copper much more than adults due to the fact that their bodies have not yet developed the mechanism needed to adapt to increased copper levels. The U.S. environmental protection agency (USEPA) introduced a law to reduce the exposure if the level of copper more than 10 percent of the collected tap water samples exceeds 1,300 micrograms per liter.

2.2.4.4 Lead health effects

Lead has a significant role in many industries because it is ductile and easily shaped. It has been used in many sectors and products: batteries, petrol additives, chemical compounds, pigments, and cabs. According, lead can find pathway human beings through drinking water, food, air, soil and dust. Overdoes of lead and term exposure can tend to serves impacts especially on infants. High concentrations of lead may cause problems in the synthesis of hemoglobin, effects of the kidney, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system. Lead mainly can be found in foods from depositions of dust and rain containing lead on crops and soil. It can also accumulate in the human body from point source emissions. For example, lead can exist in drinking water from old lead piping and from illegal discharging of industrial waste water of high concentration into surface fresh water.

2.2.4.5 Nickel health effects

Nickel is a naturally occurring element that exists in various mineral forms. It is used in a wide variety of applications including metallurgical processes and electrical components such as batteries. Nickel contamination of the environment occurs locally from emissions of metal mining, smelting, and refining operations; from combustion of fossil fuels; from industrial activities, such as nickel plating and alloy manufacturing; from land disposal of sludges, solids, and slags; and from disposal as effluents. Nickel toxicity reduces photosynthesis, growth, and nitrogenase activity of algae; fermentative activity of a mixed rumen microbiota; growth rate of marine bacteria; metabolism of soil bacteria; and mycelial growth, spore germination, and sporulation of fungi. Toxic effect of nickel to humans and laboratory mammals are documented for respiratory, cardiovascular, gastrointestinal, hematological, ocular, dermal, and reproductive systems.

2.2.4.6 Chromium health effects

Chromium (Cr) is one of the most important chemical contaminants of concern. It exist in a series oxidation states from -2 to +6 valence; the most important stable states are 0 (element metal), +3 (trivalent), and +6 (hexavalent). Cr^{3+} and Cr^{6+} are released to the environment primary from stationary point sources resulting from human activities. Acute and chronic adverse effects of chromium to warm blooded organisms are caused mainly by Cr^{6+} compounds. Most investigators agree that chromium in biological materials in probably always in the trivalent state, that greatest exposures of Cr^{3+} in the general human population are through the diet, and that no organic trivalent chromium complexes of toxilogical importance have been described. Hexavalent chromium is present in the effluents producing during electroplating, leather tanning, cement, mining, dyeing, and photography industries and causes severe environmental and public health problems. It is concentration in industrial wastewater range from 0.5 to 270 mg/L and the tolerance limit for Cr^{6+} for discharge into inland surface water is 0.1 mg /L and in potable water is 0.05mg/L.

2.3 Water chemistry

2.3.1 Introduction

Water is a chemical compound of hydrogen and oxygen. In the gaseous state, at least, it has the molecular formula H_2O. Although the same formula also represents the compositions of liquid water and ice. The molecules in these two states are associated structurally, and it's a good idea to think of the condensed phases in terms of these associations rather than as simple aggregates of molecules. Because three isotopes of hydrogen and three of oxygen exist in nature, 18 varieties of water molecules are possible.

The physical properties of water are unique in a number of respects, which are departure from what might be considered normal for such a compound, and are of great importance, with respect both to the development and continued existence of life forms and to the shape and composition of the Earth's surface. The boiling and freezing points of water are far higher than would be expected for a compound having such a low molecular weight, and the surface tension and dielectric constant of liquid water are also much greater than might be expected. When water freezes it is density decreases; in fact, the maximum density of water at 1 atmosphere pressure occurs near 4°C. Although this type of behavior is not unique in liquid-solid transitions, it is an attribute of water that is most fortunate for all life forms (John, 1985).

2.3.2 Water molecule

Water molecules have a simple structure: two hydrogen atoms bonded to one oxygen atom-H_2O. This simple structure is responsible for water unique properties. The bond between each hydrogen atom and the oxygen atom results from a pair of electrons shared between the two atoms. In water, the electrons in the shared paired are not shared equally between the hydrogen and oxygen atoms. The oxygen atom has a greater affinity for electrons than does the hydrogen atom, and the electrons in the O-H bond are more attracted to oxygen. Because electrons have a negative charge (sigma -) and hydrogen a partial positive charge (sigma+). The H-O-H bond angle in water is 104.5^o, which mean that the molecule has a bent shape. This bent geometry and the accumulation of electrons on the oxygen side of the molecule cause the water molecule to have a negative charge on one side, the oxygen side and the positive charge on the other side, the hydrogen side. Molecules with the negative regions and positive regions are called polar molecules. Water molecules are polar molecules.

Polar molecules are attracted to each other. The attraction results from the negative region of one molecule, the oxygen atom, being drawn to the positive region of another molecule, the hydrogen atom. The attraction between water molecules are partially strong.

The chemical makeup of water gives it specific characteristics, such as its density and its ability to dissolve substances.

Density is a measure of the weight of a certain volume of a substance. For instance, a gallon of water weighs about eight pounds. The temperature of water helps determine its density. Cold water is denser, and therefore heavier, than warm water. This relationship is responsible for seasonal changes in water quality in some lakes. In the fall, the water of the surface of a lake cools and becomes denser than the water below, causing the surface water to sink. The warmer, lighter water on the bottom of the lake responds by rising to the surface; causing an overturn of the lake. This overturn results in a mixing of the suspended solids, nutrients, and dissolved gases in the lake's water.

The way hydrogen and oxygen are held together are held together to form an individual water molecule, and the way each molecule is connected to the next, is called chemical bonding. The type of chemical bonding exhibited by water allows it to dissolve substances easily, making it a good solvent. Almost all solids, liquids, and gases placed in water will dissolve to some extent. Even solid copper and lead will dissolve slightly when placed in water or when water runs over rock or soil formations containing these elements.

Some of the substances that dissolve in water reduce its quality and some improve it. For example, when lead dissolved in water, it reduces its quality. When oxygen gas dissolves, it generally improves the water's quality and benefits the organisms living in it.

We often measure dissolved oxygen, temperature, and pH to characterize the quality of our water. These measurements tell us if the water is of sufficient quality for its intended uses. We also measure other substances to help characterize our water, including organic substances, inorganic substances, solids, nutrients, toxics, and microorganisms (Kenneth and Vigil, 2003).

2.3.3 Water as solvent

Water, which not only dissolves many compound but also dissolves substances than any other liquid, is considered the universal solvent. A polar molecule with partially-positive and negative charges, it readily dissolved ions and polar molecules. Water is therefore referred to as a solvent: a substance capable to dissolving other polar molecules and ionic compounds. The charges associated with these molecules from hydrogen bonds with water, surrounding the particle with water molecules. This is referred to as a sphere of hydration, or a hydration shell, and serves to keep the particles separated or dispersed in the water.

Water ionic compounds are added to water, individual ions interact with Polar Regions of the water molecules during the dissociation process, disrupting their ionic bonds. Dissociation occurs when atoms or groups of atoms break off from salt (NaCl, or sodium chloride): when NaCl crystals are added to water, the molecules of NaCl dissociate into Na^+ and Cl^- ions, and spheres from hydration around the ions. The positive-charged sodium ions is surrounded by the partially negative-charge of the water molecule’s oxygen; the negatively-charged chloride ion is surrounded by the partially-positive charge of the hydrogen in the water molecule.

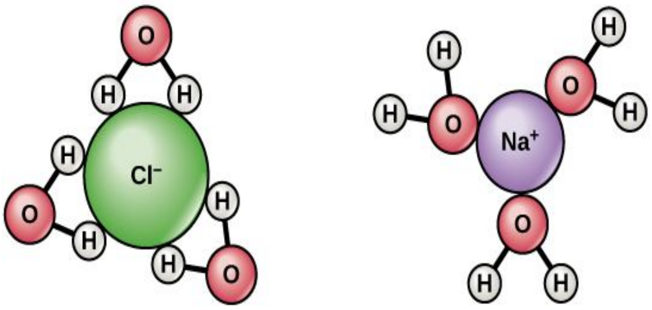

Fig 1: Dissociation of NaCl in water

Since many biomolecules are either polar or charged, water readily dissolves these hydrophilic compounds. Water is a poor solvent, however, for hydrophobic molecules such as lipids. Nonpolar molecules experience hydrophobic interactions in water: the water changes its hydrogen bonding patterns around the hydrophobic molecules to produce a cage-like structure called a clathrate. This change in the hydrogen-bonding pattern of the water solvent causes the systems's overall entropy to greatly decrease, as the molecules become more ordered than liquid water.

2.3.4 The three states of water

In a solid the particles (ions, atoms or molecules) are closely packed together. The forces between particles are strong so that the particles cannot move freely but can only vibrate. As a result, a solid has a stable, definite shape, and a definite volume. Solids can only change their shape by force, as when broken or cut.

In crystalline solids, the particles (atoms, molecules, or ions) are packed in a regularly ordered, repeating pattern. There are various different crystal structures, and the same substance can have more than one structure (or solid phase). For example, iron has a bodycentred cubic structure at temperatures below 912 °C, and a face-centred cubic structure between 912 and 1394 °C. Ice has fifteen known crystal structures, or fifteen solid phases, which exist at various temperatures and pressures (Wahab, 2005). Solids can be transformed into liquids by melting, and liquids can be transformed into solids by freezing. Solids can also change directly into gases through the process of sublimation, and gases can likewise change directly into solids through deposition.

A liquid is a nearly incompressible fluid that conforms to the shape of its container but retains a (nearly) constant volume independent of pressure. The volume is definite if the temperature and pressure are constant. When a solid is heated above its melting point, it becomes liquid, given that the pressure is higher than the triple point of the substance. Intermolecular (or interatomic or interionic) forces are still important, but the molecules have enough energy to move relative to each other and the structure is mobile. This means that the shape of a liquid is not definite but is determined by its container. The volume is usually greater than that of the corresponding solid, the best known exception being water, H_2O. The highest temperature at which a given liquid can exist is its critical temperature. A gas is a compressible fluid. Not only will a gas conform to the shape of its container but it will also expand to fill the container.

In the gas state, the molecules have enough kinetic energy so that the effect of intermolecular forces is small (or zero for an ideal gas), and the typical distance between neighboring molecules is much greater than the molecular size. A gas has no definite shape or volume, but occupies the entire container in which it is confined. A liquid may be converted to a gas by heating at constant pressure to the boiling point, or else by reducing the pressure at constant temperature.

At temperatures below its critical temperature, a gas is also called a vapor, and can be liquefied by compression alone without cooling. A vapor can exist in equilibrium with a liquid (or solid), in which case the gas pressure equals the vapor pressure of the liquid (or solid).

Water in the gas phase surrounds us in the atmosphere. The most simple weather determination includes a relatively humidity measure. On a large scale, water vapor blankets the earth and acts as a greenhouse gas, keeping heat from escaping into space. Pure water freezes at $32F^{O}$ ($0^{O}C$) and it boils at 212 F^{O} ($100^{o}C$) – at one atmosphere of pressure. Our temperature scales are set by these properties of water.

Water is an unique substance. Pure water in small portions is clear and colorless with no taste or odor. The properties of water make it both unusual chemically and critical biologically. The most basic of its interactions with other water molecules, and other materials, are associated with its electronic properties (Kim and Daniel, 1999).

2.3.5 Basic properties of water

2.3.5.1 The pH of water

pH is an abbreviation representing the activity or concentration of hydrogen ions in a solution. It describes the acidic or basic (also called alkaline) conditions of liquids on a scale that ranges from 0.0 to 14.0. Liquids having a pH of 7.0, such as distilled water is neutral, neither acidic nor basic. Liquids with a pH lower than 7.0 are acidic. Strongly acidic substances are called acids. Liquids with a pH greater than 7.0 are basic. Strongly basic substances are called bases. Acids and bases can be dangerous to humans and water environment. They cause irritations and burning and can be extremely toxic to aquatic organisms. Fortunately, acids and bases have the ability to neutralize the effect of each other. For instance, you can neutralize an acid with a low pH by adding a base to it to bring it to a pH of about 7.0. Many industries commonly use acids and bases in their production processes. The wastewaters generated from these processes are either acidic or basic and must be neutralized before being discharged in order to prevent water pollution. For instances, a company using acid in its production processes, such as a circuit board manufacturer, may generate an acidic wastewater with a pH of about 2.0. This industry would typically treat its wastewater by adding a base to neutralize the effect of the acid, obtaining pH of approximately 7.0 before discharging it back in to the environment.

Most rivers, lakes, and other natural water bodies have a pH ranging from about 6.0 to 8.5. The type and amount of dissolved minerals, gases and aquatic organisms in the water determine the pH of water in nature. Most aquatic organisms cannot live the pH of the water gets much outside of this natural range (Kenneth and Vigil, 2003).

2.3.5.2 Alkalinity

Alkalinity is a chemical measurement of a water ability to neutralize acids. changes in pH upon the addition of acids or bases. Alkalinity of natural waters is due primarily to the presence of weak acid salts although strong base may also contribute(i. e OH^-) in extreme environments. Bicarbonates represent the major form of alkalinity in natural waters; its source being the partitioning of CO_2 from the atmosphere and the weathering of carbonate minerals in rock and soil. Other salts of weak acids, such as borate, silicates, ammonia, phosphates, and organic bases from natural organic matter, may be present in small amounts. Alkalinity, by convention, is reported as mg/L $CaCO_3$ since most alkalinity is derived from the weathering of carbonate minerals.

Neither alkalinity nor acidity, have any known adverse health effects. Nonetheless, high acidic and alkaline waters are considered unpalatable.

As mentioned previously, alkalinity in natural waters is primarily due to carbonate species and the following set of chemical equilibria is established in waters

$CO_2 + H_2O \leftrightarrow H_2CO_{3*}$

$H_2CO_3 \leftrightarrow HCO_3^- + H^+$

$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

Where $H_2CO_3^*$ represents the total concentration of dissolved CO_2 and H_2CO_3. The first chemical equation represents the equilibrium of CO_2 in the water (Snoeyink and Jenkins, 1980).

2.3.5.3 Ionic strength of water

The ionic strength of a solution is a measure of concentration of ions in that solution. Ionic compounds, when dissolved in water, dissociate into ions. The total electrolyte concentration in solution will affect important properties such as the dissociation or the solubility of different salts. One of the main characteristics of a solution with dissolved ions is the ionic strength.

The ionic strength**,** I, of a solution is a function of the concentration of all ions present in that solution.

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$$

Where c_i is the molar concentration of ion I (M, mol/L), z_i is the charge number of that ion, and the sum is taken over all ions in the solution. For a 1:1 electrolyte such as sodium chloride, the ionic strength is equal to the concentration, but for $MgSO_4$ the ionic strength is four times higher. Generally multivalent ions contribute strongly to the ionic strength (IUPAC, 2006).

2.3.5.4 Total dissolved solids (TDS)

Total dissolved solids (TDS) are the term used to describe the inorganic salts and small amount of organic matter present in solution in water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, hydrogen carbonate, chloride, sulfate, and nitrate anions.

The presence of dissolved solid in water may affect its taste. The potability of drinking water has been rated by panels of taster in relation to its TDS level as follows: excellent, less than 300 mg/liter; good, between 300-600 mg/liter; fair, between 600 and 900 mg/liter; poor, between 900and 1200 mg/liter; and unacceptable, greater than 1200 mg/liter. Water with extremely low concentration of TDS may also be unacceptable because of its flat, insipid taste (Bruvold and Ongerth, 1969).

Is a major of combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal sol) suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a filter with two micrometer (nominal freshwater systems, as salinity includes some of the ions constituting the definition of TDS. The principle application of TDS is in the study of water quality for streams, rivers, and lakes, although TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects) it is used as an indication of aesthetic characteristics of drinking water and an aggregate indicator of the presence of a broad array of chemical contaminants.

Primary source of TDS in receiving waters are agricultural and residential runoff, leaching of soil contamination and point source water pollution discharge from industrial or sewage treatment plants. The most common chemical constituents are calcium, phosphates, sodium, potassium, chloride, ,nitrates, which are found in nutrient runoff, general storm water runoff and runoff from snowy climates where road de-icing salts are applied. The chemicals may be cations, anions of one thousand of fewer molecules, so long as soluble micro granule is formed. The united state has established a secondary water quality standard of 500 mg/l to provide potability of drinking water (Dezuane, 1997).

2.3.5.5 Conductivity

Conductivity is a measure of the ability of water to pass an electrical current. Conductivity of water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate anions or sodium, magnesium, calcium, iron, and aluminum cations. Organic compound like oil, phenol, alcohol, and sugar do not conduct electrical current very well and therefore have a low conductivity when in water, the higher the conductivity. For this reason, conductivity is reported as conductivity at 25 degree Celsius (25^{o} C).

Conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows. Streams that run through areas with granite bedrock tend to have lower conductivity because granite is composed of more inert materials that do not ionize (dissolve into ionic components) when washed into the water. On the other hands streams that run through areas with clay soils tend to have higher conductivity because of the presence of materials that ionize when washed into water. Ground water inflows can have the same effects depending on the bedrock they flow through.

The basic measure unit of conductivity is mho or Siemens. Conductivity is measured in microhn per centimeter (microhn/cm) or microsiemens per centimeter (microsiemens/cm) (APHA, 1992).

2.3.5.6 Hardness

Hard water is water that has high mineral content (in contrast with soft water). Hard water is formed when water percolates through deposits of calcium and magnesium-containing minerals such as limestone, chalk and dolomite (WHO, 2003).

Waters hardness is determined by the concentration of multivalent cations in the water. Multivalent cations are contain (positively charged metal complexes) with a charge greater than 1+. Usually, the cations have the charge of 2+. Common cations found in hard water include Ca^{2+} and Mg^{2+}. These ions enter a water supply by leaching from minerals within an aquifer. Common calcium-containing minerals are calcite and gypsum. A common magnesium mineral is dolomite (which also contains calcium) Rainwater and distilled water are soft, because they contain few ions (Hermann, 2006).

The following equilibrium reaction describes the dissolving and formation of calcium carbonate:

$$CaCO_3\ (s) + CO_2\ (aq) + H_2O\ (l) \leftrightharpoons Ca^{2+}\ (aq) + 2HCO_3^{-}\ (aq)$$

The reaction can go in either direction. Rain containing dissolved carbon dioxide can react with calcium carbonate and carry calcium ions away with it. The calcium carbonate may be re-deposited as calcite as the carbon dioxide is lost to atmosphere, sometimes forming stalactites and stalagmites.

Calcium and magnesium ions can sometimes be removed by water softeners (Nitsch, et al., 2005).

Temporary hardness is a type of water hardness caused by the presence of dissolved bicarbonate minerals (calcium bicarbonate and magnesium bicarbonate). When dissolved, these minerals yield calcium and magnesium cations (Ca^{2+}, Mg^{2+}) and carbonate and bicarbonate anions (CO_3^{2-}, HCO_3^-). The presence of the metal cations makes the water hard. However, unlike the permanent hardness caused by sulfateand chloride compounds, this "temporary" hardness can be reduced either by boiling the water, or by the addition of lime (calcium hydroxide) through the softening process of lime softening.() Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. When this is the case, it is usually caused by the presence of calcium sulfate and/or magnesium sulfates in the water, which do not precipitate out as the temperature increases. Ions causing permanent hardness of water can be removed using a water softener, or ion exchange column.

Total Permanent Hardness = Calcium Hardness + Magnesium Hardness

The calcium and magnesium hardness is the concentration of calcium and magnesium ions expressed as equivalent of calcium carbonate.

Total permanent water hardness expressed as equivalent of $CaCO_3$ can be calculated with the following formula: Total Permanent Hardness ($CaCO_3$) = 2.5(Ca^{2+}) + 4.1(Mg^{2+}).

With hard water, soap solutions form a white precipitate (soap scum) instead of producing lather, because the 2+ ions destroy the surfactant properties of the soap by forming a solid precipitate (the soap scum). A major component of such scum is calcium stearate, which arises from sodium stearate, the main component of soap:

$2\ C_{17}H_{35}COO^{-}\ (aq) + Ca^{2+}\ (aq) \rightarrow (C_{17}H_{35}COO)_2Ca\ (s)$

Hardness can thus be defined as the soap-consuming capacity of a water sample, or the capacity of precipitation of soap as a characteristic property of water that prevents the lathering of soap. Synthetic detergents do not form such scums.

Hard water also forms deposits that clog plumbing. These deposits, called "scale", are composed mainly of calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$), and calcium sulfate ($CaSO_4$) (Hermann, 2006).

The presence of ions in an electrolyte, in this case, hard water, can also lead to galvanic corrosion, in which one metal will preferentially corrode when in contact with another type of metal, when both are in contact with an electrolyte. The softening of hard water by ion exchange does not increase its corrosivity *per se*. Similarly, where lead plumbing is in use, softened water does not substantially increase plumbo-solvency (Sorg et al., 1999).

The World Health Organization says that "there does not appear to be any convincing evidence that water hardness causes adverse health effects in humans". (WHO, 2003). In fact, the United States National Research Council has found that hard water can actually serve as a dietary supplement for calcium and magnesium.

Some studies have shown a weak inverse relationship between water hardness and cardiovascular disease in men, up to a level of 170 mg calcium carbonate per litre of water. The World Health Organization has reviewed the evidence and concluded the data was inadequate to allow for a recommendation for a level of hardness (WHO, 2003). Recommendations have been made for the maximum and minimum levels of calcium (40–80 ppm) and magnesium (20–30 ppm) in drinking water, and a total hardness expressed as the sum of the calcium and magnesium concentrations of 2–4 mmol/L (Kožíšek, 2003).

2.3.5.7 Dissolved gasses

Carbon dioxide

Dissolved carbon dioxide (CO_2) associates with water molecules to form carbonic acid (H_2CO_3), reducing the pH and contributing to corrosion in water lines, especially steam and condensate lines. Carbonic acid, in turn, dissociated to bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}), depending on pH. Most of the CO_2 found in water comes not from the atmosphere but from carbonate that the water has dissolved from rock formations.

Oxygen

Dissolved oxygen (O_2) can corrode water lines, boilers and heat exchangers, but is only soluble to about 14ppm at atmospheric pressure.

Hydrogen sulfide

The infamous''rotten egg''odor, hydrogen sulfide (H_2S) can contribute to corrosion. It is found primarily in well water supplies or other anaerobic sources. H_2S can be readily oxidized by chlorine or ozone to eliminate sulfur (Minnetonka, 1997).

2.4 water treatment

2.4.1 Introduction

Most ground water and surface water sources contain contaminants. The type and concentration of these contaminants determined the treatment method (AWWA, 2003). With the continual growth of dense population areas, there is a great demand on potable water source supplies. Also, improved analytical technology has identified ever increasing number of contaminants in water supplies that have negative impact on public health. This has create a need for the application of water treatment technologies to remove the multiple contaminants and provides high levels of contaminant removal (Marty et al., 2004).

Water treatment is the process of removing undesirable chemicals, biological contaminants, suspended solids and gases from contaminated water. The goal of this process is to produce water fit for a specific purpose. Most water is disinfected for human consumption (drinking water) but water purification may also be designed for a variety of other purposes, including meeting the requirements of medical, pharmacological, chemical and industrial applications. In general the methods used include physical processes such as filtration, sedimentation, and distillation, sand filters or, chemical processes such as flocculation and chlorination and the used of electromagnetic radiation such as ultraviolet light.

2.4.2 Water treatment methods and techniques

Before any engineered water treatment is attempted, source substitution should be considered. Switching to an alternate source may be the best long –term solution for a safe and reliable water supply, even if initial costs are relatively high. Source substitution measures could include switching from ground water to surface water (or vice versa); screening or casing well at certain depth; rainwater harvesting; and sharing or blending of safe supplies. Piped distribution systems should also be considered, either to bring water from a safe source or to maximize the impact of a large treatment plant.

Alternative water sources should be carefully chosen to ensure that the risks from the new source are not greater than from the old source. The relative risks of all available options should also be carefully assessed (Mahmud et al., 2007).

2.4.2.1 Sedimentation

Sedimentation is the removal of suspended solids by gravity. Sedimentation, or gravity settling, is often the first stage of surface water treatment, with the goal of to removing coarse suspended solids that may clog filters or reduce disinfection efficiency. This is especially needed in tropical areas where rivers often have high silt loads.

Sedimentation most commonly takes place in horizontal flow tanks, where water slowly moves from one end to the other. Preliminary sedimentation tanks can remove at least 50%, and up to 90% of turbidity and suspended solids, depending on the nature of the solids in suspension. If the tanks are open to the atmosphere sunlight may promote algae growth. Preliminary sedimentation may be followed by a primary disinfectant dose to enhance color removal, improve subsequent coagulation and to prevent the growth of algae and smile in treatment tanks. This also lowers pathogen loads prior to the main treatment phase.

2.4.2.2 Coagulation

Coagulation is a process which enables small suspended particles in water to stick to each other, forming larger particles that can be easily removed through sedimentation or filtration.

When chemical coagulants are added to the water, they form small solid particles (flocs), which aggregate (flocculate) and settle out of suspension. Following sedimentation, the remaining suspended solids are removed by sand filtration.

The most common coagulants are alum and ferric salts (chloride or sulfate). In some cultures, plant products are used as natural coagulants. The crushed seeds of moringa trees (moringa oleifera lam and moringa peregrine fiori) are particularly effective coagulants, comparing favorably with alum in terms of removal of turbidity. A dosing rate of 200 mg crushed seeds per liter of water is suggested as optimal.

Coagulation also removes many dissolved ions, which are trapped by or bound to the charged floc surfaces. Coagulation can remove some heavy metals, anions (e.g., arsenate, chromate,) and some low-solubility organic contaminants, such as chlorinated pesticides. Doses of coagulants (alum or ferric salts) may be higher for chemical treatment than for removal of suspended solids, on the order of 2-5 mg/L Al or 4-10 mg/L as Fe. Higher doses may be required in the presence of competing solutes: for example, phosphate, bicarbonate and silicate all compete with arsenic.

Coagulation is usually followed by sedimentation and filtration to remove residual solids.

2.4.2.3 Precipitation

Some metals become insoluble at high pH, or in the presence of high levels of carbonate. The most common use of precipitation is lime softening: calcium and magnesium, the principal and magnesium precipitates out as magnesium hydroxide. Addition of soda ash (sodium carbonate) is usually required to allow formation of insoluble calcium carbonate precipitate. Precipitation is followed by sedimentation and filtration to remove sludge. While the principal application in hardness removal, chemical precipitation can also removes metals iron, manganese, cadmium, barium, arsenic, chromium, selenium, radionuclide's and viruses.

Precipitation requires large amount of chemicals (primarily lime), and produces large volumes of waste sludge. Following softening water pH is generally above 10 and must be lowered prior to distribution or consumption. This is most commonly achieved by addition of carbon dioxide.

2.4.2.4 Adsorption

Adsorption is the formation of bonds between dissolved species or small particles and the surface of solid. Usually the solid is in the form of granular media, and water is treated by passing through packed beds. Powdered adsorbents may also be used, and adsorption is a key process during coagulation. Ion exchange can be considered as a special form of adsorption, though its often considered separately.

The efficiency of adsorption depends primarily on the attraction for the media being used and the extent of contact between water and surfaces (controlled by particle size and loading rates). Water chemistry may also be important: positively charged species (like most metals) are more easily removed at high pH, while negatively charged species (like arsenate) are best removed at lower pH. Competition from other dissolved species or clogging of the media by particles can also greatly reduce adsorption of the target chemical. All adsorption media have a limited number of sites where adsorption occurs, and as these sites are filled the media becomes exhausted and must be replaced or regenerated.

Water treatment with granular adsorption media is relatively easy to implement: water is simply passed through packed beds containing the media. Adsorption may improved by pre-treatment such as pH adjustment, oxidation or turbidity removal. One drawback of adsorption treatment systems is that it is not easy to tell when media have become exhausted.

2.4.2.5 Oxidation

Strong oxidants can help to break down organic chemicals, and can in some cases convert inorganic chemicals to a form that is easier to remove. Atmospheric oxygen is the most wiedly available oxidant, but it is weaker than other chemical oxidants such as free chlorine, permanganate and ozone.

The use of ground water for drinking water is in many cases limited by the presence of dissolved iron and, to lesser extent, manganese. These give the water an unpleasant metallic taste and stain food, sanitary ware and laundry. Both metals can be oxidized to form an insoluble precipitate, which can then be removed by filtration. Both metals can be oxidized to some cases be used for the oxidation of dissolved iron, but oxidation is slaw below pH 7, or if the iron is bound with organic matter. Chemical oxidants are generally required to oxidize dissolved manganese or to achieve more rapid oxidation of iron: potassium permanganate is used most commonly.

Much effort has been spent on developing simple methods to remove iron and manganese from water. Most are based on oxidation followed by filtration, though biological processes probably contribute significantly to removal efficiency. While small community-based plants often work well initially, long-term success is less common, due to inadequate maintenance.

2.4.2.6 Ion exchange

Ion exchange is very similar to adsorption; it involves passing water through beds of granular media which remove the target contaminant. The difference is that ion exchange media is made of synthetic resins, which forms easily reversible bonds with ions. This allows much better regeneration than, for example, activated alumina, and ion exchange resins can be reused many times. Salt solutions (brines) are used for regeneration.

The most common application of ion exchange resins is for removal of cations (positively charged ions) that cause hardness, chiefly calcium and magnesium. Cation exchange resins can also remove barium and radium. Other resins target anion (negatively charged ions) and are used to remove nitrate, arsenate, chromate, selenium and uranium. Molybdenum and boron may also be removed to some extent. Anion exchange is the most readily available technology for nitrate removal.

Ion exchange resin should not be used in waters with high salinity or sulfate, because competing ions will be quickly exhausting the media. Also, iron removal may be necessary to prevent fouling of the media with oxide precipitate.

2.4.2.7 Membrane filtration

Synthetic membrane with small pores can remove large molecules while allowing water pass through. Reverse osmosis, the main technology used for desalination can effectively remove most inorganic contaminants but requires a lot of electricity to create pressure needed to drive water through. Nanofilteration, which uses membranes with slightly larger pores, can also remove many ions from water, including arsenic. Electrodialysis is a related removal process that uses an electrical potential rather than water pressure to drive ions through membrane with relatively large pores.

Membrane can easily be fouled by organic matter or iron, so water usually is pretreated. Because of the complexity of operation and high cost, membrane processes are not generally appropriate for use in developing countries (UNICEF, 2008).

2.5 Adsorption

2.5. 1 Introduction

Adsorption is a significant phenomenon in many applications. Sorption on solids is commonly used for purification in water and waste water, most often by using activated carbon. However, many other adsorbents are being used effectively such as silica gel, treated acid clay, and metal oxides. For example, Smith (1998) used recycled iron to remove metals from aqueous solutions. The triple layer surface complexation model was used to characterize the equilibrium of lead, cadmium, and zinc adsorption by using a recycled iron-bearing material. The experiments were conducted using fixed bed and batch reactor systems. The uptake capacity of the recycled iron adsorbent was favorable relative to some commercial adsorbents.

2.5.2 Definition of adsorption

Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it. Adsorption is a surface phenomenon. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction (Ferrari et al., 2010).

2.5.3 Types of adsorption

The adsorption process is generally classified as physisorption (characteristic of weak Van der Waals forces) or chemosorption (characteristic of covalent bonding) it may also occur due to electrostatic attraction.

The fundamental interacting force of physisorption is caused by Van der Waals force. Even though the interaction energy is very weak (~10-100 meV), physisorption plays an important role in nature. For instance, the Van der Waals attraction between surfaces and foot-hairs of geckos provides the remarkable ability to climb up vertical walls (Autumn et al., 2000).

Chemisorptions is a kind of adsorption which involves a chemical reaction between the surface and the adsorbate. New chemical bonds are generated at the adsorbant surface. Examples include macroscopic phenomena that can be very obvious, like corrosion, and subtler effects associated with heterogeneous catalysis. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds (Oura et al., 2003).

2.5.4 Specific affinity of solute for the solid

In this case three types of mechanism are known:

1) Ion exchange.
2) Chemical adsorption.
3) Physical adsorption.

Adsorption due to the electrical attraction of solute to the adsorbent is often called exchange adsorption and fall within the realm of ion exchange. Exchange adsorption is the process by which ions of the substance concentrate at specific changed sites on the surface of the adsorbent.

Adsorption due to the Van der Waal's is termed physical adsorption, which represents cases where the adsorbed molecule is not fixed to specific surface site but is free to move about on the adsorption interface.

Chemical adsorption occurs when the adsorbate and the adsorbent interact chemically. Molecules which are chemically adsorbed are not free to move about the adsorption interface (Collins and Jhonson 1998).

2.5.5 Adsorption equilibrium

The equilibrium reached in adsorption is illustrated by plotting the amount of solute, or metal in the case, adsorbed per unit weight of the adsorbent, $q_{e,}$ against the concentration of the solute still remaining in the solution, C. This develops an adsorption isotherm. There are two most used equations for water and wastewater treatment: Langmuir and Freundlich. The capacity of the adsorbents determine the amount of heavy metal that was adsorbed on to the adsorbent, and can be determined through the following mass balance equation

$$q_e = (C_O - C_e)V/m \quad (1)$$

Where q_e represents the number of moles of solute adsorbed per unit weight of adsorbent after equilibrium (mg adsorbate/g absorbent), V represents the total volume of solute solution (in L), C_O represents the initial concentration of the solute (in mg/L),C_e represents the concentration of the solute at equilibrium (in mg/L) and m represents the weight of the adsorbents used (in g) (Douglas, 1984).

2.5.6 Adsorption isotherms

The adsorption isotherm can be viewed as a map in which an adsorbate solute distributes itself between the adsorbent and the solvent (Hassler, 1974). It describes the equilibrium of the sorption of material at surface (more general at a surface boundary) at constant temperature. It represents the amount of material bound at the surface (the sorbate) as a function of the material present in the gas phase and/or in the solution. Sorption isotherms are often used as empirical models, (Atkins, 1998) which do not make statements about the underlying mechanisms and measured variables. They are obtained from measured data by means of regression analysis. The most frequently used isotherms are the linear isotherm, Freundlich isotherm, the Langmuir isotherm, and the BET model.

2.5.7 The Langmuir equation

Langmuir's Adsorption Isotherm may be used for monolayer adsorption on to a surface containing a finite number of identical sites, and assumes uniform energies of adsorption on the surface, in addition to no transmigration of the adsorbate in the plane of the surface. The Langmuir isotherm model determines the maximum capacity of the adsorbent from complete monolayer coverage of the adsorbent surface. Langmuir's isotherm non linear equation is

$q_e = q_o b C_e / 1+bCe$

Where q_e represents the amount adsorbed at equilibrium time (in mg/g), q_o and b are Langmuir constants that depend on the maximum monolayer adsorption capacity and adsorption equilibrium constant that relates to the energy of adsorption respectively. They can be calculated from the $1/q_e$ vs 1/C figure, where q_o is 1/intercept'and b is equal to the intercept * 1/slop (Douglas, 1984).

2.5.8 BET equation

A different equation is more likely to describe adsorpation where adsorbate exceeds a monolayer. The Brunauer-Emmett-Teller (BET) equation is:

$q = q_m k_b C/\{C_s - C\}\{1 +(k_b - 1)(C/C_s)\}$

where C_s = concentration at which all layers are filled

k_b = a coefficient

Its assumptions are:

- Enthalpy of adsorption is the same for anylayer
- Energy of adsorption is the same for layers other than the first
- A new layer can start before another is finished.

It is important that many unusual adsorption isotherms are fitted well by the BET equation. This is to be expected when there are three coefficients to manipulate. The maximum loading, Q_m, just multiplies to move the entire curve up and down. The coefficient, k_b, has amajor effect on a shape. The concentration at which all sites are saturated (may be several layers) can be adjusted to get a portion of the isotherm. In other words, you can look at just part of the curve. As C approaches C_s, the denominator of the equation becomes small, and the curve shoots up (Howard, 2000).

2.5.9 Freundlich adsorption isotherm

May also be used for heterogenous surface energies and is commonly used to compare powder carbon in the treatment of water. The isotherm portrays that the ratio of the quantity of the solute adsorbed on known mass of adsorbent to the concentration of the solute in the solution differs at different concentrations. Langmuir's energy term, b, varies here as a function of q_e due to the variations in the heat of adsorption. The Freunlich equation is as follows:

$q_e = k_f C^{1/n}$

Where k_f and n are constants, with k_f being the Freundlich constant defining the adsorption coefficient that indicate the relative adsorption capacity of the adsorbent of the bonding energy, and is proportional to $RT_n be^{\Delta H/RT}$ and with $n>1$.

Data obtained are fitted into the logarithmic equation:

$\mathrm{Log}\, q_e = \mathrm{Log} k_f + 1/n \mathrm{Log} C$

With an intercept of k_f and straight lined-slop of 1/n, where k_f roughly indicates the adsorption capacity, and 1/n the adsorption intensity (Douglas, 1984)

2.5.10 Factors influencing adsorption

- **Nature of the Adsorbent**

The adsorption process is mainly a surface phenomenon in which adsorption depends on the portion of the total surface area available to the adsorption process. The adsorption capacity is directly proportional to the specific surface area (Weber, 1972). Vernon et al. (1967) found that the physiochemical nature of the surface of carbon is an important factor in the adsorption process, and should be considered in selection or preparation of carbons for specific applications.

- **Nature of the Adsorbate**

The adsorption process is mainly affected by the nature of the adsorbate in the sense of it is solubility in the solute. The adsorption capacity is inversely proportional to the solubility of an adsorbate in a solute, and this is the Lundelius rule, one of two rules used to predict the effect of a solute’s chemical character on it is uptake (Weber and walter, 1972). The greater the solubility, the stronger the solute-solvent bond is and therefore the smaller the extent of adsorption. The molecular size of the adsorbate is of significance too. The molecular size relates to the rate of uptake of solutes from aqueous solution by porous adsorbents so that the smaller the molecular size, the faster the reaction is. However, it must be kept in mind that the adsorption process dependence on molecular size can be generalized only within a particular chemical class. For example, large molecular size of certain type of chemical series may be adsorbed more rapidly than smaller ones of another class. Moreover, the rate of uptake dependence on the molecular size is expected only for rapidly agitated batch reactors which are of limited interest in water and wastewater systems. In contracts to the molecular size effects, the variations in the geometry and structure of the molecules have smaller effects on the equilibrium condition (Faust, 1998).

Ionization also plays a rule in the uptake capacity, where may components of water and wastewater exist as ionic species, for example, fatty acids, amines and pesticides have the property of being ionized under appropriate conditions of pH. The ionization of some of some chemical components and classes is believed to be of significance for the carbon adsorption process due to the fact that activated carbon commonly exists with a net negative charge in water. It has also been observed that as long as the compounds are structurally simple, the uptake capacity decreases for the charge species and increases for the natural ones. As compounds become more complex, the effect of the ionization becomes less important. Thus, the adsorption capacity was on the decrease by the increasing of the ionization for many different types od simple organic acids. To conclude, it has been observed that a polar solute will tend to be strongly absorbed by a polar adsorbent in a non polar solvent.

Also, it was found that the order of increasing pk for the first hydrolysis product (e.g., $PbOH^+$) of metal ions affect the adsorption magnitude of heavy metals by increasing the adsorption under the acidic conditions (pH 5.0) (Elliott et al., 1986).

- **Solution pH**

The uptake capacity of adsorbates from the aqueous solution is affected by the value of the pH of the solution. This is due mainly to the fact that hydrogen and hydroxide ions are being adsorbed strongly by activated carbon, so the adsorption of other ions is influenced by the pH of the solution. Furthermore, since the ionization has an effect on the uptake capacity of the adsorbates from the solvent, pH affects the adsorption as well in that it governs the degree of the ionization of acidic or basic compounds. The adsorption of the organic pollutants from the aqueous solution is increased by decreasing the pH. This can occur to the fact the lowering the pH of the aqueous solution results in neutralizing the negative charges at the surface of the carbon by increasing the hydrogen-ion concentration. Therefore it releases more available active surface of the carbon. The phenomenon varies for different carbons according to the composition of the raw materials and on the technique of the activation (Weber and Walter, 1972).

Osvaldo et al. (2007) investigated the adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. He found that the removal of metal ions from aqueous solutions by adsorption is dependent on solution pH as it affects adsorbent surface charge. The removal of Pb, Cu, and Cd ions from aqueous solution increases with the increase in pH. Maximum removal of Cd was observed above pH 6 and in case of Pb and Cu, above pH 5.0 and 5.5 respectively.

- **Effect of temperature**

The uptake capacity of the adsorbates from aqueous solution tends to increase with decreasing temperature due to the fact that the adsorption process is normally exothermic. However, small variations in temperature will not affect the adsorption process to a significant extent. The rate of adsorption is related to the activation energy and temperature dependence of equilibrium capacity where the dependence of rate of adsorption is expressed as activation energy (Ea), and the temperature dependence of equilibrium capacity for adsorption is known as ΔH. Although the energy parameters, Ea and ΔH, are useful for delineating the adsorption process, the normal temperature variations in water and wastewater treatment have minor effects on the adsorption process (Weber and Walter, 1972).

Osvaldo et al. (2007) investigated the adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. He found that the removal of metal ions from aqueous solutions by adsorption is dependent on solution pH as it affects adsorbent surface charge. The removal of Pb, Cu, and Cd ions from aqueous solution increases with the increase in pH. Maximum removal of Cd was observed above pH 6 and in case of Pb and Cu, above pH 5.0 and 5.5 respectively.

2.5.11 Application and modes of operation

This can be conducted by the following techniques:

A/ Batch system

Most of researches conducted on adsorption of metals using waste water materials underwent batch tests to analysis how the adsorbate and the adsorbent perform under various conditions. These conditions include pH levels, initial concentration of metals solution, concentration of the adsorbent, temperature, agitation speed, and contact time. All of these conditions produce different results once changed; however, the magnitude and significance of change alters between the different conditions as each has different effect on the adsorption process. As adsorption is a process which involves reactions between the adsorbate and the adsorbent, varying the conditions may improve or exacerbate the rate and amount of the adsorption. pH affects adsorption reaction through H^+ and OH ions that are emitted into solution. A more acidic solution releases more H^+ ions that may react with the adsorbent or adsorbate, hence affecting results. Likewise an alkaline solution releases OH^- which may also react with the adsorbent or adsorbate(Walter, 1974). Hence, it is crucial when performing batch test to evaluate the process at different pH levels. Unfortunately, a universal pH value cannot, be determined and sett due to the different types of adsorbents used and their chemical constitution. Hence tested need to be performed to determine the most efficient value of pH, contact time is another crucial factor to consider when performing testes. This is also significant as adsorbents used as organic materials, which may release additional organic material in the system. Not allowing for enough contact time will not effectively complete the adsorption process, hence, results obtained will be incomprehensible and void. The greater the contact time, the greater the possibility that equilibrium has been reached, and hence, adsorption has reached its potential. Agitation speed is another important criterion to be test, as this either speeds up or slaws down adsorption. However, a higher agitation speed does not necessarily mean a higher rate of adsorption. Adsorption is highest at a certain speed that needs to be determined through experimentation. Different initial concentrations of the metal solution evaluate the capacity of the adsorbent in its ability to adsorb and remove the metals from the solution. Usually, the lower the concentration of adsorbate, and hence, have a higher adsorption capacity. These adsorbents are thus favorable due to their capacity. Also, to test the capacity of the adsorbent, the concentration dosage in the liquid solution needs to be evaluated. If only a small quantity is required to remove a large portion of the adsorbate, then the adsorbent is favorable as its capacity is low. One way to reduce the quantity of adsorbent is to increase the surface area. This can be achieved by using very small diameters of the adsorbent. Larger surface areas are a lot more successful in adsorption, and hence, the same adsorbent may require smaller dosages once ground compared to its larger counterpart.

B/ Column type

Colum tests, also known as bed columns, are used for industrial applications (Yasemin, 2010).

For the column testes to tack place, previous researchers placed the adsorbent in a pipe where the ends are sealed off with rubber to support the adsorbent. A thin tube is placed on either side of the pipes, where one tube the inflow, transports the water being tested into the pipe with the aid of a pump, and where the other tube, the outflow, transports a treated water into basin to be tested and discarded (Walter and weber, 1974).

2.5.12 Low cost materials

Adsorption is low-cost process as it uses relatively cheap materials. The method to obtain and prepare material is effortless and does not require the use of other resources, chemicals, or processes. Low cost material that only requires through washing and drying to remove moisture before being sieved is the latest research material being employed for successful adsorption (Neama, 2011). Evaluation of tree leaves (Ahalya, 2006), date pits (Azza, 2008), agricultural waste etc has been done to test adsorption capability on different metals at different concentrations. Condition that are tested for include obtaining optimal pH, contact time, agitation speeds, and initial concentrations of metals and dosage of adsorbent. Different conditions yield different results for different metals and adsorbents. Hence, what may apply for a certain combination of experimental conditions, metals, and adsorbents, may not apply for another.

2.5.13 Activated graphite granules

Activated carbon and graphite are widely used materials in the industry as catalytic support in industrial reactions mainly because of its inertness, low cost, high surface area, and low deactivation (Davis, 2007). Their low applications are in the water and wastewater treatment and as adsorbent of heavy metals and organic compounds. Activated carbon has oxygen and nitrogen groups on its surface, which gives many of its chemical properties (.thermal or chemical pretreatments are known to introduce these groups and change the texture of the material surface.

In this study, the raw material was collected from dry batteries, the rod was crushed and sieved in different particle size (mesh).

2.5.14 Adsorption of heavy metals

Adsorption is accumulation of substances at a surface or interface. It could be occurring between liquid-liquid, liquid-solid, gas-liquid, or gas-solid. The material adsorbed or concentrated at a surface or interface of another medium is called adsorbate, while the adsorbing phase is known as the adsorbent. The term sorption includes both adsorption and absorption (Weber, 1972). Absorption is the interpenetration of the molecules or atoms of one phase to another to form a solution with the second phase. In contrast, adsorption is the accumulating of something such as a gas, a liquid, or a solute, on the surface of the solid or a liquid. For example, the removal of the undesirable dissolved gases from water may be achieved by gas stripping (absorption) or by their adsorption onto a substance such as activated carbon (Bartleby, 2009).. The dissolved substances in aqueous systems are divided to either hydrophilic, water liking, or hydrophobic, water disliking. The hydrophobic substances tend to be adsorbed from aqueous solution more likely than the hydrophilic ones (Weber and walter, 1972). In addition to the cause of adsorption, the adsorption rate depends on the mixing strength of the solution, pH, nature of the adsorbate, and temperature (Chen and Minsheng, 2001).

- **Lead adsorption**

Kadirvelu (2001) stated that parameters such as agitation time, metal ion concentration, adsorbent dose and pH will affect the adsorption of lead from aqueous solution to the adsorbent. Smith and Afshin (2000) studied the removal of lead by using recycled iron Adsorption of Heavy metals. They successfully recycled waste shot-blast fines produces from the manufacturing of cast iron in order to efficient and inexpensive adsorbent to remove heavy metals from industrial and hazardous wastewater. By conducting fixed-bed experiment, they found that removal efficiency of lead by using recycled iron material is equal or greater than other those implemented by other adsorbents such as activated carbon for instance, for an influent lead of 10 ppm and pH 5.5, the sorbent yield a solid phase uptake capacity of almost 40 mg/g.

- **Cadmium adsorption**

Reed and Matsumoto (1993) studied cadmium adsorption by using two different commercially available activated carbons. They conducted several experiments at different pH values and metal and carbon concentrations. They found that the cadmium removal strongly depends on the solution pH values, where increasing the solution pH values significantly increases the cadmium adsorption. The surface area of the sorbent was observed to be more important parameter for organic adsorbents rather than heavy metals.

Ozer (1998) used activated carbon produced from sugar beet to remove cadmium from aqueous solutions. The adsorption ability was investigated according to a change in temperature, pH, values, contact time, and adsorbent dosage. Ozer stated in his study that effective removal efficiency of cadmium was found to be at 6.3 or greater, moreover, the maximum removal percentage for cadmium was 99,0, 78.0, 57.0, by using 2.5 gm/l for initial concentration of 100, 250, and 500mg/l respectively at optimum 20^{o}C for a contact time of 120 min.

- **Copper adsorption**

Manktelow and paterson (2005) investigated the removal of copper associated with cyanide from aqueous solution by activated carbon. They used a coal-based activated carbon ith initial concentration of 244 to 2441mg/l for cyanide in addition to 61 to 610 mg/l copper, and they found that the concentrations were reduced to a minimum of 3.6 mg/l cyanide and 0.6 mg/l copper.

Sulaymon et al. (2009) has investigated the removal of copper from aqueous solution using granular activated carbon in a fixed bed volume. The granular activated carbon was found to be suitable adsorbent for the removal of pb, Cu, Cr, and Co from aqueous solution. Their study showed that as flow rate and the initial metal ion concentration increase, and the bed height decreases the time of the breakthrough point decreases.

- **Adsorption of Zinc**

Adsorption of Ni(II) and Zn(II)from aqueous solution by various adsorbents were assessed by Ajay kumar Meena et al (2005). Based on the experimental studies , treated granular activated carbon showed 98% and 94% and carbon aerogel 92% adsorptive removal of Ni(II) and Zn(II) respectively under optimized conditions of pH 8 and dosage 1.2 gm/100ml for 3mg/l Ni(II) and Zn(II) from aqueous solutions in 48 hour contact time. The Langmuir model was found to be in good agreement and obeyed pseudo-second order kinetic model.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Materials and Methods

Laboratory experiments presented in this chapter were carried out in order to evaluate the adsorption efficiency of the activated carbon prepared from used graphite rods collected from dry batteries. Series of experiments were conducted to determine adsorption capacity of the activated graphite granules for removal of some heavy metals; namely, cadmium, lead, copper, and zinc. Batch method was followed in all experments.

3.2. Instruments

Atomic Adsorption Spectrophotometer AAS (flammenAAS.jpg).

Heating molten.

Electronic weighing balance. ,

Furnace.

Crusher.

3.3 Glassware

Conical flasks, funnel, beakers, , round bottles, , , sample bottles, , spatula, , measuring cylinders, glass rod, dropper, and volumetric flasks.

3.4 Chemicals

Nitric acid5%.

Cadmium nitrate ($Cd(NO_3)_2.4H_2O$).

Lead nitrate ($Pb(NO_3)_2$).

Copper nitrate ($Cu(NO_3)_2.3H_2O$).

Zinc chloride ($ZnCl_2$).

3.5 Mateials

Graphite rods

3.6 Experimental methods

3.6.1 Preparation of graphite activated carbon (GAC)

The graphite rods were grinded and sieved to 100 and 200 mesh. 50 g of 100 mesh GAC were placed in 500 ml flask and 500 ml of 5% nitric acid were added. The mixture was refluxed for 12 hour at $100^{o}C$. The activated granules were filtrated, washed with a continuous flow of distilled water and dried at $100^{o}C$ for 12 hour.

The same method was repeated using 200 mesh GAC. The produced GAC was used for adsorption of heavy metals using batch method.

3.6.2 Preparation of cadmium solution:

A stock solution of cadmium was prepared by dissolving 0.٨٧ g of cadmium nitrate ($Cd(NO_3)_2.4H_2O$) in distilled water (DW) and the volume was completed to 1000 ml to get a concentration of 100 ppm. From this stock solution 50, 25, and 10 ppm were prepared by dilution.

3.6.3 Preparation of lead solution:

A stock solution of lead was prepared by dissolving 0.1٥٩g of lead nitrate $Pb(NO_3)_2$ in distilled water and the volume was completed to 1000 ml to get a concentration of 100ppm, From this stock solution 50, 25, and 10 ppm were prepared by dilution

3.6.4 Preparation of copper solutions:

A stock solution of copper was prepared by dissolving 0.38١ g of copper nitrate ($Cu(NO_3)_2.3H_2O$) in distilled water and the volume was completed to 1000 ml to get a concentration of 100ppm, From this stock solution 50, 25, 10ppm were prepared by dilution.

3.6.5 Preparation of zinc solutions:

A stock solution of zinc was prepared by dissolving 1.08g of zinc chloride $ZnCl_2$ in distilled water and the volume was completed to 1000 ml to get a concentration of 100ppm, from this stock solution, 50, 25, and 10ppm were prepared by dilution.

3.7 Removal of Cu (II) ions at different concentrations by GAC

The sorption capacity of GAC was determined by shaking 25ml of copper metal ion solution at 10, 25, 50, and 100ppm with 0.20 grams of GAC at optimum pH and room temperature. After shaking for 30 minutes the solution was filtered with filter paper, acidified with nitric acid and stored for analysis.

The same procedure was repeated for Pb^2, Cd^{2+}, and Zn^{2+} ions.

٣.8 Effect of mesh of GAC on removal efficiency of heavy metals

The sorption capacity of GAC was determined by shaking 25ml of copper metal ion solution at 10, 25, 50, and 100ppm with 0.20 grams of GAC with mesh 200 at optimum pH and room temperature. After shaking for 30 minutes the solution was filtered with filter paper, acidified with nitric acid and stored for analysis.

The same procedure was repeated by using GAC at mesh 100 and for other metals Pb^2, Cd^{2+}, and Zn^{2+} ions.

CHAPTER FOUR
RESULTS AND DISCUSSIONS

4.1.1 Effect of mesh on removal of copper ions by GAC

Table (4.1):

Effect of mesh on removal of copper ions by GAC

Mesh	Initial concentration ppm	Absorbed concentration ppm	Remaining concentration ppm	% removal
200	5.7	5.301	0.399	93
100	5.7	4.845	0.855	85
200	14.25	12.398	1.852	87
100	14.25	11.258	2.992	79
200	28.5	22.80	5.700	80
100	28.5	19.95	8.55	70
200	57	42.18	14.82	74
100	57	35.91	21.09	63

Table (4.1) shows the removal percentage of copper ions by GAC.The effect of mesh at constant concentration.

The effect of Cu^{2+} concentration on removal efficiency of GAC granules (200 and 100 Mesh size) was studied with addition of 0.2 grams of activated adsorbent to Cu^{2+} solution at different concentrations. The maximum efficiency was obtained at 5.7 ppm Cu^{2+} concentrations. A little decrease in removal percentage was observed with increasing initial heavy metal concentrations in the solutions. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and as metal concentration increases, these sites became saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available

4.1.2 Effect of concentration on removal of copper ions by GAC

Table (4.2):

Effect of concentration on removal of copper ions by GAC

Mesh	Initial Concentration ppm	% Removal
200	5.7	93
	14.25	87
	28.5	80
	57	74
100	5.7	85
	14.25	79
	28.5	70
	57	63

Table (4.2) shows the removal percentage of copper ions by GAC at constant mesh and a different concentration.

Batch studies showed that 93% and 85% of copper metal at 5.7 ppm concentration were removed when 200 and 100 mesh were used respectively. The removal percentages continue to decrease with increasing concentration. When the concentration of Cu^{2+} reached to 57 ppm the removals are 74% and 63% for 200 and 100 mesh of GAC respectively. Dosing of adsorbents was 0.2gm per 25 ml and it was kept for 30 minutes. From these results it is clear that adsorbent of 200 mesh size is able to remove more Cu ions from aqueous solution than that of 100 mesh size adsorbent. Therefore, it may be concluded from the present studies that GAC granules can be used as an efficient adsorbent for the removal of Cu ions from aqueous solution at optimum conditions.

4.1.3 Effect of mesh on removal of zinc ions by GAC

Table (4.3):

Effect of mesh on removal of zinc ions by GAC

Mesh	Initial concentration ppm	Absorbed concentration ppm	Remaining concentration ppm	% removal
200 100	5.62	5.615 5.610	0.0049 0.0095	100 100
200 100	14.05	14.021 14.008	0.029 0.042	100 100
200 100	28.1	28.010 27.830	0.090 0.112	100 100
200 100	56.2	55.980 55.916	0.219 0.280	100 100

Table (4.3) shows the removal percentage of zinc ions by GAC, The effect of mesh at constant concentration.

The effect of Zn^{2+} concentration on removal efficiency of GAC granules (200 and 100 Mesh size) was studied with addition of 0.2 grams of activated adsorbent to Zn^{2+} solution at different concentrations. The maximum efficiency was obtained at all ppm Zn^{2+} concentrations. There is no decrease was found from this value. Later on, removal efficiency was detected with increasing initial heavy metal concentrations in the solutions. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and as metal the concentration increases, these sites became saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available.

4.1.4 Effect of concentration on removal of zinc ions by GAC

Table (4.4):

Effect of concentration on removal of zinc ions by GAC

Mesh	Initial concentration ppm	% Removal
200	5.62	100
	14.05	100
	28.1	100
	56.2	100
100	5.62	100
	14.05	100
	28.1	100
	56.2	100

Table (4.4) shows the removal percentage of zinc ions by GAC at constant mesh and a different concentration.

Batch studies showed that 100% of zinc metal at5.62 ppm concentration were removed when 200 and 100 mesh were used respectively. Dosing of adsorbents was 0.2gm per 25 ml and it was kept for 30 minutes. From these results it is clear that adsorbent of 200 mesh size and 100 mesh size have the same ability to remove Zn ions from aqueous solution at different concentration. Therefore, it may be concluded from the present studies that GAC can be used as an efficient adsorbent for the removal of Zn ions from aqueous solution at optimum conditions.

4.1.5 Effect of mesh on removal of cadmium ions by GAC

Table (4.5):

Effect of mesh on removal of cadmium ions by GAC

mesh	Initial concentration ppm	Absorbed concentration ppm	Remaining concentration ppm	% Removal
200 100	5.85	4.329 3.81	1.521 2.04	74 65
200 100	14.625	9.507 8.925	5.118 5.70	65 61
200 100	29.25	11.7 9.07	17.55 20.18	40 31
200 100	58.5	4.39 1.58	54.11 56.92	7.5 2.7

Table (4.5) shows the removal percentage of cadmium ions by GAC, The effect of mesh at constant concentration.

The effect of Cd^{2+} concentration on removal efficiency of GAC granules (200 and 100 Mesh size) was studied with addition of 0.2 grams of activated adsorbent to Cd^{2+} solution at different concentrations. The maximum efficiency was obtained at5.85 ppm Cd^{2+} concentrations. A little decrease in removal percentage was observed with increasing initial heavy metal concentrations in the solutions. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and as metal concentration increases, these sites became saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available.

4.1.6 Effect of concentration on removal of cadmium ions by GAC

Table (4.6):

Effect of concentration on removal of cadmium ions by GAC

Mesh	Initial concentration ppm	% Removal
100	5.85	65
	14.625	61
	29.25	31
	58.5	2.7
200	5.85	74
	14.625	65
	29.25	40
	58.5	7.5

Table (4.6) shows the removal percentage of cadmium ions by GAC at constant mesh and a different concentration.

Batch studies showed that 74% and 65% of cadmium metal at 5.85ppm concentration were removed when 200 and 100 mesh were used respectively. The removal percentages continue to decreased with increasing concentration. When the concentration of Cd^{2+} reached to 58.5 ppm the removals are 7.2% and 2.7% for 200 and 100 mesh of GAC respectively. Dosing of adsorbents was 0.2gm per 25 ml and it was kept for 30 minutes. From these results it is clear that adsorbent of 200 mesh size is able to remove more Cd ions from aqueous solution than that of 100 mesh size adsorbent. Therefore, it may be concluded from the present studies that GAC granules can be used as an efficient adsorbent for the removal of Cd ions from aqueous solution at optimum conditions.

4.1.7 Effect of mesh on removal of lead ions by GAC

Table (4.7):

Effect of mesh on removal of lead ions by GAC

Mesh	Initial concentration ppm	Absorbed concentration ppm	Remaining concentration ppm	%removal
75 150	5.929	4.447 4.151	1.482 1.778	75 70
75 150	14.82	9.337 8.596	5.483 6.224	63 58
75 150	29.645	16.601 13.341	16.044 16.304	56 45
75 150	59.29	21.938 20.752	37.352 38.53	37 35

Table (4.7) shows the removal percentage of lead ions by GAC . The effect of mesh at constant concentration

The effect of Pb^{2+} concentration on removal efficiency of GAC granules (200 and 100 Mesh size) was studied with addition of 0.2 grams of activated adsorbent to Pb^{2+} solution at different concentrations. The maximum efficiency was obtained at5.9 ppm Pb^{2+} concentrations. A little decrease in removal percentage was observed with increasing initial heavy metal concentrations in the solutions. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and as metal concentration increases, these sites became saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available.

4.1.8 Effect of concentration on removal of lead ions by GAC

Table (4.8):

Effect of concentration on removal of lead ions by GAC

Mesh	Initial concentration ppm	%removal
200	5.929	75
	14.82	63
	29.645	56
	59.29	37
100	5.929	70
	14.82	58
	29.645	45
	59.29	35

Table (4.8) shows the removal percentage of lead ions by GAC at constant mesh and a different concentration.

Batch studies showed that 75% and70% of lead metal at 5.9 ppm concentration were removed when 200 and 100 mesh were used respectively. The removal percentages continue to decreased with increasing concentration. When the concentration of Pb^{2+} reached to 59 ppm the removals are 37% and 35% for 200 and 100 mesh of GAC respectively. Dosing of adsorbents was 0.2gm per 25 ml and it was kept for 30 minutes. From these results it is clear that adsorbent of 200 mesh size is able to remove more Pb ions from aqueous solution than that of 100 mesh size adsorbent. Therefore, it may be concluded from the present studies that GAC granules can be used as an efficient adsorbent for the removal of Pb ions from aqueous solution at optimum conditions.

4.9 Discussion

Heavy metals affect human health because they are toxic. Nevertheless, a lot of heavy metals were used in the industry and they join to food chain. In this respect, wastewater coming from polluted sources must be treated to decrease their concentration down to the limits given in water regulations before send to the environment. The main methods of removal of heavy metals are: chemical precipitation of metal ions as –hydroxide or –sulphide, Adsorption, ion exchange, membrane filtration and reverse osmosis etc. Removal of metals from water with classical methods was not sufficient enough, practically and economically. Ion exchange method may be used after pretreatment operation. Most of the heavy metal recovery was not easy from the precipitate and economic. For this reason, adsorption process may be preferred to the other applications.

In this investigation GAC, as an adsorbent was used for removal of lead, cadmium, zinc, and copper and found very effective at different working conditions. Graphite granules were sieved to different mesh and activated with concentrated nitric acid.

CHAPTER FIVE

CONCLUSION AND RECOMONDATIONS

5 Conclusion and Recommendations

5.1 Removal of heavy metal by activated graphite granules

Adsorption is a process that has been developed immensely as environmental issues rise. Adsorption has been used to remove many pollutants from water and wastewater. Whether, sea water or industrial waste water, purifying drinking water, or as a polishing phase at the end of sewage treatment. These pollutants include heavy metals, which is the focus of this work. Heavy metals are toxic and hazardous to humans, marine life and the water body in which it is contained. The metals studies in this work include copper, zinc, lead, and cadmium, due to their abundance in water, in addition to their toxicity. The adsorbent used was graphite rods collected from dry batteries due to their availability. Copper gave a maximum percentage removal of 93% cadmium 74%, zinc 100%, and 75% lead.

The effect of concentration of heavy metals on removal efficiency was studied. As concentration of metal increases, the removal percentage decreased.

5.2 Recommendation for future work

Future researches can be conducted to study:

1. The effect of temperature, contact time and speed of shaking on removal efficiency of heavy metal can be studied as they were kept constant in this study.
2. Studying the adsorption efficiency of other metal by GAC.
3. Studying the adsorption efficiency of some organic pollutants by this GAC.
4. Studying the chemical process and behavior of metals that occurs with varying experimental conditions (such as pH, initial concentration, temperature, etc), over varying experimental combinations of metals, will prove beneficial.

5. Evaluation of efficiency of other materials that are also readily available is recommended.
6. It is also recommended to study the effect, feasibility, and practicality of having two treatment processes in series in real life: one with acidic pH and other with basic pH as these gave the best treatment. Depending on the best pH for the metal exiting in the water, the treatment tanks can be placed in series and studied to determine the removal efficiency of the metal.

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