REMOVAL OF HEAVY METAL FROM INDUSTRIAL WASTEWATER

USING ULTRASONIC ASSISTED BY TEA WASTE AS ADSORBENT

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ABSTRACT

Wastewater from industry can lead to water pollution if untreated, especially due to its high concentration of heavy metals. Heavy metals are considered extremely harmful because they can cause illnesses, disorder and diseases to human. Therefore, industrial wastewater containing heavy metal should be treated before discharge to the water stream but its treatment is very costly. There are several techniques to remove heavy metals from wastewater such as biosorption, filtration and adsorption of heavy metal but there is some limitation such as long treatment time. This research is about the efficiency of combination method between ultrasonic and adsorption process to remove zinc, Zn and nickel, Ni from fertilizer factory wastewater. The parameters analyzed in this research are amounts of adsorbent in solutions from 0.5 g to 2.9 g of tea waste, different ultrasonic temperature from 40° C to 80° C and different sonication time from 5 minute to 29 minutes. After several experiment and analysis of results, it is found that the optimum condition to remove Zn and Ni from 100 ml wastewater is at 24 minute sonication time and 75°C ultrasonic temperature for 2.5 g amount of adsorbent which can remove about 79% of zinc and 71% of nickel. According to the result, the method of ultrasonic assisted by adsorption process to remove heavy metal from industrial wastewater can be use effectively because it can reduce energy, time and cost of treatment.

ABSTRAK

Air sisa dari industri boleh membawa kepada pencemaran air jika tidak dirawat, terutama kerana kepekatan logam berat yang tinggi. Logam berat adalah sangat merbahaya kerana ia boleh menyebabkan penyakit, ketidakupayaan serta wabak kepada manusia. Oleh itu, air sisa industri yang mengandungi logam berat mestilah dirawat sebelum disalurkan ke dalam saliran air tetapi kos rawatannya adalah sangat tinggi. Terdapat beberapa teknik untuk menyingkirkan logam berat daripada air sisa seperti proses penjerapan biologi, penapisan serta penjerapan tetapi terdapat beberapa kekangan seperti masa rawatan yang lama. Kajian ini adalah tentang keberkesanan gabungan antara proses ultrasonik dan penjerapan untuk menyingkirkan zink, Zn dan nikel, Ni daripada air sisa kilang baja. Parameter yang telah dianalisa dalam kajian ini adalah kandungan bahan jerap dalam larutan daripada 0.5 gram hingga 2.9 gram sisa teh, perbezaan suhu ultrasonik daripada 40 hingga 80 darjah Celsius dan perbezaan masa sonikasi dari 5 minit hingga 29 minit. Selepas beberapa eksperimen serta analisa keputusan, didapati keadaan paling optimum untuk menyingkirkan Zn dan Ni daripada 100 mililiter air sisa adalah pada masa sonikasi 24 minit dan 75 darjah Celsius suhu ultrasonik untuk kandungan 2.5 gram sisa teh dimana ia boleh menyingkirkan 79 % zink dan 72 % nikel. Berdasarkan kepada keputusan, kaedah ultrasonik dibantu oleh proses penjerapan untuk menyingkirkan logam berat daripada air sisa industri boleh digunakan secara efektif kerana ia boleh mengurangkan tenaga, masa serta kos rawatan.

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LIST OF ABBREVIATIONS

AAS	-	Atomic Adsorption Spectrometer
Zn	-	Zinc
Ni	-	Nickel
C_o	-	Initial concentration
C_f	-	Final concentration
ppm	-	Part per million
HNO_3	-	Nitric Acid
Cr	-	Chromium
Cu	-	Cuprum
Pb	-	Lead
S	-	Sulphur
M	-	Concentration
V	-	Volume
COD	-	Chemical Oxygen Demand
BOD	-	Biochemical Oxygen Demand
MHz	-	Megahertz

CHAPTER 1

INTRODUCTION

1.1   Background of study

Water pollution is a major problem in the global context. Several industrial wastewater streams may contain heavy metals such as Cr, Cu, Pb, Zn, Ni, etc. including the waste liquids generated by metal finishing or the mineral processing industries. The toxic metals, probably existing in high concentrations, must be effectively treated/ removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment. In recent years, the removal of toxic heavy metal ions from sewage, industrial and mining waste effluents has been widely studied. Among the many methods available to reduce heavy metal concentration from wastewater, the most common ones are chemical precipitation, ion-exchange, adsorption and reverse osmosis (Chao *et al.*, 2005).

Heavy metals are the non-degradable metals .These metals are toxic and posses high density. Heavy metals occur in the earth's crust naturally. Some of the heavy metals are lead, cadmium, mercury, arsenic, chromium and thallium. High concentration of heavy metals causes poisoning. The improper disposal of these heavy metals leads to pollution.

Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters. Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater. Industrial waste constitutes the major sources of various kind of metal pollution in natural waters. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down or metabolized.

Any oxidizable material present in a natural waterway or in an industrial wastewater will be oxidized both by biochemical (bacterial) or chemical processes. The result is that the oxygen content of the water will be decreased. Basically, the reaction for biochemical oxidation may be written as:

Oxidizable material + bacteria + nutrient + $O_2 \rightarrow$ $CO_2 +$ H_2O + oxidized inorganic such as NO_3 or SO_4

Oxygen consumption by reducing chemicals such as sulfides and nitrites is typified as follows:

$$S^{--} + 2\,O_2 \rightarrow SO_4^{--}$$

$$NO_2^- + \tfrac{1}{2}\,O_2 \rightarrow NO_3^-$$
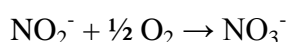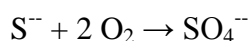
Those biochemical reactions create what is measured in the laboratory as the Biochemical oxygen demand (BOD). Such chemicals are also liable to be broken down using strong oxidizing agents and these chemical reactions create what is measured in the laboratory as the Chemical oxygen demand (COD). Both the BOD and COD tests are a measure of the relative oxygen-depletion effect of a waste contaminant. Both have been widely adopted as a measure of pollution effect. The BOD test measures the oxygen demand of biodegradable pollutants whereas the COD test measures the oxygen demand of oxidizable pollutants.

Ultrasonic is an effective purification and separation technique used in industry especially in wastewater treatment. Ultrasonic generates high-energy which causes the cavitation. Cavitation is the rapid and repeated formation and resulting implosion of micro bubbles in a liquid resulting in the propagation of microscopic shock waves. Microscopic vapor bubbles are created at site of rarefaction as the liquid fractures or tears because of the negative pressure of the sound wave in the liquid. Finally the compression part, which follows the rarefied part, collapses the bubble (Hindu and Takemura, 2006).

The cavitational collapse of bubble generates localized hot spots of temperature as high as 5000° K and pressure of as high as 1000 atmospheres for a life time of a few microseconds thus creating high energy movements of the solvent that results in localized high energy shear forces as shown in figure 1.1. The number of cavitation bubbles collapsing per second may well be in the millions hence their cumulative effect can be significant. Shock waves from cavitation in liquid-solid slurries produce high velocity-inter particle collisions, the impact of which is sufficient to melt most metals. Thus the ultrasonic energy may be effective to remove the sorbed contaminants, like heavy metals, from fine grained soils.
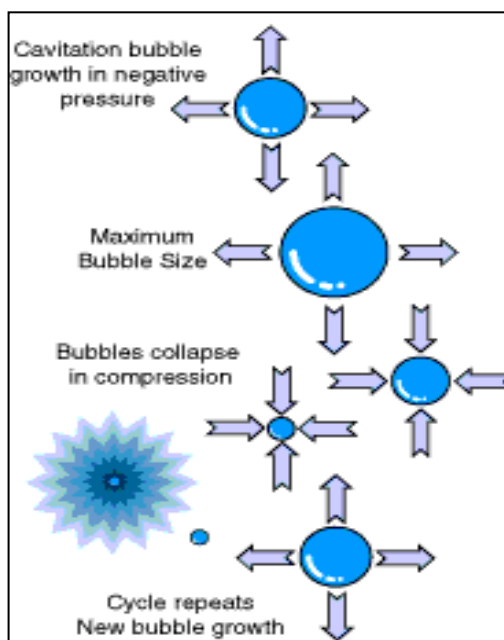
Figure 1.1: Cavitation and implosion phenomena in ultrasonic

According to (Fuchs, F.J.2002), in elastic media such as air and most solids, there is a continuous transition as a sound wave is transmitted. In non-elastic media such as water and most liquids, there is continuous transition as long as the amplitude or "loudness" of the sound is relatively low. As amplitude is increased, however, the magnitude of the negative pressure in the areas of rarefaction eventually becomes sufficient to cause the liquid to fracture because of the negative pressure, causing a phenomenon known as cavitation. Cavitation bubbles are created at sites of rarefaction as the liquid fractures or tears because of the negative pressure of the sound wave in the liquid. As the wave fronts pass, the cavitation bubbles oscillate under the influence of positive pressure, eventually growing to an unstable size. Finally, the violent collapse of the cavitation bubbles results in implosions, which cause shock waves to be radiated from the sites of the collapse. The collapse and implosion of myriad cavitation "bubbles" throughout an ultrasonically activated liquid result in the effect commonly associated with ultrasonic.

However, there is relative lack of information in the literature about removal heavy metal from wastewater by ultrasonic combined by adsorption. Adsorption of heavy metal ions onto activated carbon is an efficient and well established method for their removal from contaminated waters, but high costs limit its widespread use. Thus, in recent years much research has been undertaken to develop comparably effective but less expensive adsorbents. Adsorption is one of the methods commonly used to remove heavy metal ions from various aqueous solutions with relatively low metal ion concentrations. The efficiency of adsorption relies on the capability of the adsorbent to adsorb metal ions from the solutions onto its surfaces. Different naturally occurring adsorbents like activated carbon, tea waste, egg shells, mineral mixtures, and rice husks are used as adsorbents for industrial waste management (Ghaffar, A. 2008).

An economical adsorbent is defined as one which is abundant in nature, or is a by-product or a waste from industry and requires little processing. Cost is an important parameter for comparing the sorbent materials. Byproducts of soybean and cottonseed hulls, rice straw and sugarcane were evaluated as metal ion adsorbents in aqueous solutions. Commonly, tea waste consist of Carbon 48.60% wt/dm, Nitrogen 0.50% wt/dm and Hydrogen 5.50% wt/dm make it as suitable natural absorbent to remove heavy metal from wastewater due to its properties and its cost.

In this research, metal of interest were zinc, Zn and nickel, Ni due to their potential pollution impact on the environment. According to (Zuorro and Lavecchia, 2010), Zn, in particular, is one of the most common environmental contaminants due to its wide use in petroleum, mining, paint and pigments, ceramics and weapons industries. Its accumulation in the body may cause several pathological states, including brain damage, kidney failure and serious developmental, learning and behavioral problems in children.

1.2   Problem statement

Several industrial wastewater streams may contain heavy metals such as Sb, Cr, Cu, Pb, Zn, Co, Ni, etc. including the waste liquids generated by metal finishing or the mineral processing industries. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, while the direct discharge into the sewerage system may affect negatively the subsequent biological wastewater treatment.

The purpose of this research is to improve the method to remove heavy metal from industrial wastewater. It's important to ensure there are no harmful heavy metals in the water stream because it can accumulate in the environment elements such as food chain and pose a significant danger to human health. Ultrasonic was used because this method offers many potential advantage in energy saving, process enhancement and processing time to remove heavy metal. In this research, tea waste was used as an adsorbent to assist ultrasonic process because of its cost and its efficiency to remove heavy metal.

1.3 Research objective

The purpose of this study is to determine the optimum condition to remove heavy metal from industrial wastewater by using ultrasonic assisted by tea waste as adsorbent.

1.4 Scope of research

The scope has been identified in this research in order to achieve the objective. The scopes of research are listed as below:

a) Study the effect of different amount of adsorbent weight

b) Study the effect of different reaction temperature

c) Study the effect of different sonication time on the percentage removal of heavy metal from industrial wastewater

1.5 Significance of the study

The rationales of significances of this study are:

a) To improve current research by increasing the percentage of heavy metal degradation from wastewater using ultrasonic assisted by tea waste as adsorbent.

b) To open up opportunities to increase the demand on wastewater treatment by using ultrasonic assisted by natural absorbent as proven by researchers that it's have a lot of benefits.

c) To prevent the heavy metal concentration release to the water stream which can causes foul odor and toxicity that can be potential hazard to human health and environment.

d) To reduce the cost of wastewater treatment by using tea waste to assist the ultrasonic process on heavy metal degradation.

1.6   Thesis outline

This research presents about the efficiency of combination method between ultrasonic and adsorption process to remove heavy metal which is zinc, Zn and nickel, Ni from fertilizer factory wastewater. The following chapter (Chapter 2), give a brief summary about what has been done in the past (literature review) regarding on the method to remove heavy metal from wastewater. Chapter 3 presents methodology used in this research where all the parameter involved explained clearly. Analysis results and the experimental data for the percentage removal of heavy metal after treatment for effect of different adsorbent amount, sonication time and different reaction temperature with detailed discussion will be discussed in Chapter 4. Finally, some important conclusion for the present and future work suggestion were given in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter reviews the current technique to remove heavy metal from wastewater with related theory and information about this research. An important parameter that affects the percentage removal of heavy metal after treatment as the main interest in this study will also be review. Besides that, a brief summary about ultrasound and adsorption mechanism was also discussed.

2.2 Introduction

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and agriculture and can encompass a wide range of potential contaminants and concentrations.

According to (Mahvi *et al*., 2008), water used in industries creates a wastewater that has a potential hazard for our environment because of introducing various contaminants such as heavy metals into soil and water resources. Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment. Industrial waste constitutes the major source of various kinds of metal pollution in natural waters. The important toxic metals i.e. Cd, Zn, Ni, and Pb find its way to the water bodies through waste waters. Heavy metals can accumulate in the environment elements such as food chain, and thus may pose a significant danger to human health.

2.3 Toxicology of heavy metal

According to Saifuddin and Kumaran (2005), at least 20 metals are classified as toxic and half of these are emitted to the environment in quantities that pose risk to human health.

Metals of interest in this research was zinc and nickel due to their potential pollution impact on the environment and also because it is found in the wastewater sample for this project. Heavy metals are metallic elements with high atomic weights, examples mercury, chromium, magnesium and zinc. Heavy metals are widely distributed in nature, in places such as water, soil, air and various forms of organisms.

Nickel is silvery-white, hard, malleable and ductile metal. It is of the iron group and it takes on a high polish. It is a fairly good conductor of heat and electricity. Nickel is bivalent in its familiar compounds even though it assumes other valences. It also forms a number of complex compounds. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but like iron, becomes passive when treated with nitric acid.

Zinc is a lustrous bluish-white metal. It is found in group II b of the periodic table. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen.

Table 2.1: Toxicology of Heavy Metal

Heavy Metal	Toxicology
Zn	- Stomach cramps - Skin irritations - Vomiting - Nausea - Anemia - Damage the pancreas - Disturb the protein metabolism - Cause arteriosclerosis
Ni	- Higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer - Sickness and dizziness after exposure to nickel gas - Lung embolism - Respiratory failure - Birth defects

Source: http://www.lenntech.com/periodic/elements/zn.htm

There are several technique to remove heavy metal from wastewater and one of popular method is using ultrasonic process that produce high frequency waves which cause the formation of microscopic bubbles, or cavitations.

2.4 The Theory of Sound Waves

According to (Fuchs, F.J.2002), in order to understand the mechanism of ultrasonic, it is necessary to first have a basic understanding of sound waves, how they are generated and how they travel through a conducting medium. The dictionary defines sound as the transmission of vibration through an elastic medium which may be a solid, liquid, or a gas. A sound wave is produced when a solitary or repeating displacement is generated in a sound conducting medium, such as by a shock event or vibratory movement. We are probably most familiar with sound waves generated by alternating mechanical motion. There are also sound waves which are created by a single shock event. Azar, L. (2009), states that the term ultrasonic represents sonic waves having a wave frequency above approximately 20 kHz and includes both the traditional ultrasonic cleaning spectrum which extends in frequency from approximately 20 kHz to 500 kHz, and the more recently used mega sonic cleaning spectrum which extends in frequency from about 0.5 MHz to about 5 MHz. The device used for cell disruption has traditionally been the ultrasonic horn. This device works at a fixed frequency, normally between 20 and 50 kHz, and is designed to be resonant in the longitudinal mode of vibration.

2.5 Ultrasound Mechanism

Ultrasound energy is sound waves with frequencies above 20,000 oscillations per second, which is above the upper limit of human hearing. In liquid, this high frequency waves cause the formation of microscopic bubbles, or cavitation. When the bubbles collapse, they generate tiny but powerful shock waves. We needed to agitate the border layer of liquid to get the liquor through the barrier more quickly, and these shock waves seemed like the perfect stirring mechanism, Aravin, P.P. (2009).

According to Chitra et al., (2004) instead of chemical treatment, the application of high power ultrasound (US) for the destruction of organic pollutants has recently drawn much attention. It is an advanced oxidation process wherein it can affect organic oxidation in three different mechanisms: nucleation, growth and cavitation.

Based on this theory, the effect of ultrasound arises from the longitudinal vibration in liquid molecules through a series of compression and rare factional cycles resulting in the tearing of solvent layers during rarefaction. Cavities are formed at the point where the pressure in the liquid drops well below its vapor pressure. These cavities turn into bubbles and are filled with vapor of the solvent molecules. Bubbles start reverberating with the propagating ultrasound wave and grow in size after every rarefaction cycle until an optimum stage is attained where the energy supplied by the wave is no longer capable of sustaining these bubbles. At this stage the bubble implodes, thereby allowing solvent molecules from the bulk to rush into the void space of relatively low pressure in the form of micro jets.
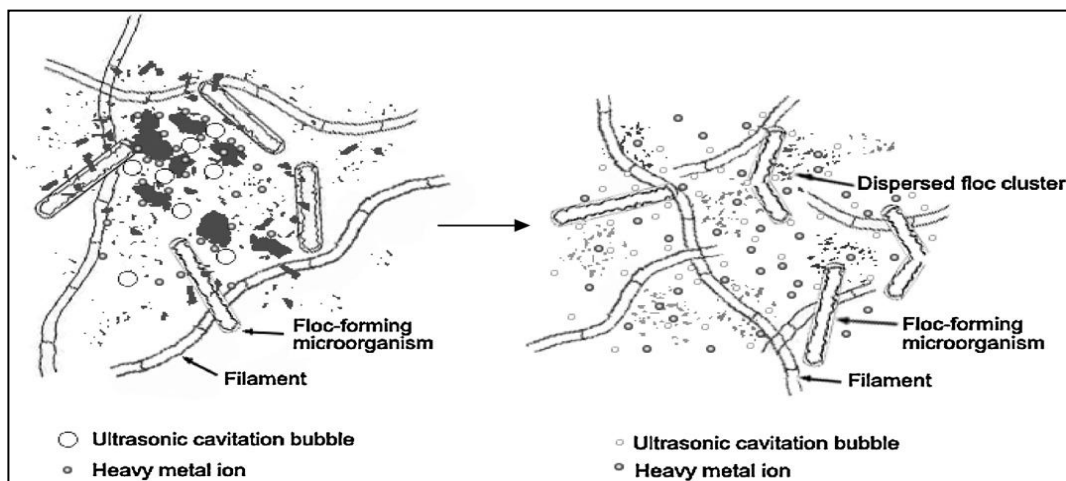

Figure 2.1: Mechanism of heavy metal release from sludge flocs by ultrasound.

Azar, L. (2009), states that once the cavitation is generated, a cavitation bubble may undergo two different kinds of radial oscillations. One may oscillate nonlinearly during many cycles of the acoustic wave; termed "stable cavitation" .The other may grow rapidly and collapse violently in one or two acoustic cycles, termed "transient cavitation." During bubble implosion, surrounding fluid quickly flows to fill the void created by the collapsing bubble. This flow results in an intense shock wave which is uniquely suited to substrate surface cleaning. Specifically, bubble implosions that occur near or at the substrate surface will generate shock waves that can dislodge contaminants and other soils from the substrate surface. When the bubble collapses, pressure up to 20,000 psi and a high local temperature, possibly in the order of 5,000K are achieved.

It is important to maximizing ultrasonic process in order to get the most efficient condition to remove heavy metal from wastewater by consider any parameter that help to maximize the ultrasonic process.

2.6   Maximizing Ultrasonic Process

Effective application of the ultrasonic process requires consideration of a number of parameters. While time, temperature and chemical remain important in ultrasonic as they are in other technologies, there are other factors which must be considered to maximize the effectiveness of the process. Especially important are those variables which affect the intensity of ultrasonic cavitations in the liquid.

According to (Fuchs, F.J.2002), maximizing cavitations of the cleaning liquid is obviously very important to the success of the ultrasonic process. Several variables affect cavitations intensity. Temperature is the most important single parameter to be considered in maximizing cavitations intensity. This is because so many liquid properties affecting cavitations intensity are related to temperature. Changes in temperature result in changes in viscosity, the solubility of gas in the liquid, the diffusion rate of dissolved gasses in the liquid, and vapor pressure, all of which affect cavitations intensity. In pure water, the cavitations effect is maximized at approximately 160°F. For most effective cavitations, the cleaning liquid must contain as little dissolved gas as possible. Gas dissolved in the liquid is released during the bubble growth phase of cavitations and prevents its violent implosion which is required for the desired ultrasonic effect. The amount of dissolved gas in a liquid is reduced as the liquid temperature is increased.
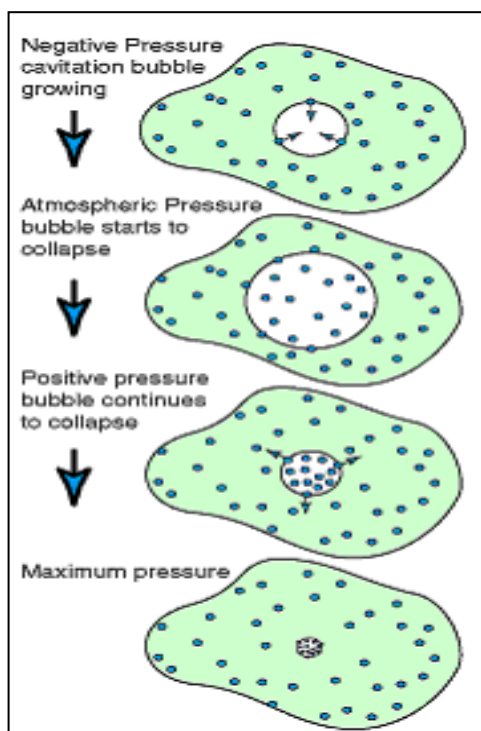
Figure 2.2: Mechanism of minimize dissolved gas

During the negative pressure portion of the sound wave, the liquid is torn apart and cavitations bubbles start to form. As a negative pressure develops within the bubble, gasses dissolved in the cavitations liquid start to diffuse across the boundary into the bubble. As negative pressure is reduced due to the passing of the rarefaction portion of the sound wave and atmospheric pressure is reached, the cavitations bubble starts to collapse due to its own surface tension. During the compression portion of the sound wave, any gas which diffused into the bubble is compressed and finally starts to diffuse across the boundary again to re-enter the liquid. This process, however, is never complete as long as the bubble contains gas since the diffusion out of the bubble does not start until the bubble is compressed. And once the bubble is compressed, the boundary surface available for diffusion is reduced. As a result, cavitations bubbles formed in liquids containing gas do not collapse all the way to implosion but rather result in a small pocket of compressed gas in the liquid.

Adsorption is an effective purification and separation technique used in industry especially in water and wastewater treatments, (Mahvi et al., 2009). It has been proved can assist common technique such as ultrasonic process to remove heavy metal from wastewater by increasing the percentage removal of heavy metal after treatment of wastewater.

2.7   Adsorption Mechanism of Heavy Metal on Adsorbent

The adsorption separation is based on three distinct mechanisms: steric, equilibrium, and kinetic mechanisms. In the steric separation mechanisms, the porous solid has pores having dimension such that it allows small molecules to enter while excluding large molecules from entry. The equilibrium mechanism is based on the solid having different an ability to accommodate different species, that is the stronger adsorbing species is preferentially removed by the solid. The kinetic mechanism is based on the different rates of diffusion of different species into the pore; thus by controlling the time of exposure the faster diffusing species is preferentially removed by the solid, (Duong, D.D. 1998).

The porous solid of a given adsorption process is a critical variable. The success or failure of the process depends on how the solid performs in both equilibrium and kinetics. A solid with good capacity but slow kinetics is not a good choice as it takes adsorbate molecules too long a time to reach the particle interior. This means long gas residence time in a column, hence low throughput. On the other hand, a solid with fast kinetics but low capacity is not good either as a large amount of solid is required for a given throughput. Thus, a good solid is the one that provides good adsorptive capacity as well as good kinetics.

To satisfy these two requirements, the following aspects must be satisfied:

a) The solid must have reasonably high surface area of micropore volume

b) The solid must have relatively large pore network for the transport of molecules to the interior

To satisfy the first requirement, the porous solid must have small pore size with a reasonable porosity. This suggests that a good solid must have a combination of two pore ranges: the micropore range and the macropore range. The classification of pore size as recommended by IUPAC is often used to delineate the range pore size:

Micropores $d<2nm$

Mesopores $2<d<50nm$

Macropores $d>50nm$

According to Chen *et al*., (2001), the adsorption efficiency of the sorbents are influenced by operating temperature, the chlorine or sulfur content in the feed waste, kinds of sorbents, sorbent size, amount of sorbent additive, and air flow rate. Among these factors, operating temperature, chlorine content, and sorbent size are most important. When heavy metals are heated, some volatilized metals exist in the gas phase, some form particles, and some are captured by sorbents through heterogeneous condensation and chemical adsorption. The third mechanism is particle capture. Most metal particles can be captured by sorbents through coagulation, coalescence, and scavenging. This is evident when the surface of sorbents is stickier, such as a glassy surface or sorbents coated with a layer of sticky material.

There are three general types of adsorption: physical, chemical, and exchange adsorption. Physical adsorption is relatively nonspecific and is due to the operation of weak forces of attraction or van der Waals' forces between molecules. The adsorbed molecule is not affixed to a particular site on the solid surface, but is free to move about over the surface. In addition, the adsorbed material may condense and form several superimposed layers on the surface of the adsorbent. Chemical adsorption, on the other hand, is the result of much stronger forces, comparable with those leading to the formation of chemical compounds.