CERTIFICATION OF APPROVAL

Adsorption of Zinc from Aqueous Solution by Using Natural Adsorbents

by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

Several studied have pointed out natural adsorbent efficiently in the removal of heavy metal ion present in aqueous solution. Contact time, pH and adsorbent concentration seem to be the major operating parameters in the metal concentration control. The mechanisms of interactions between metal and solid are a function of pH and are found to be precipitation, adsorption or ion exchange. The objectives of this work were to study the removal of heavy metal in water by sorption onto date seeds, clove, star anise and cinnamon. This research was done on lab scale experiments to study efficiency of date seeds, cloves, star anise and cinnamon powder in removing heavy metals from aqueous solution. Solutions of varying concentrations of heavy metals of 1,10 and 100 ppm were prepared and added with adsorbent than shake in orbital shaker for 1, 3, 6 and 24 hours. Next, the sample of solution been filtered to remove insoluble material and analyzed for concentration of heavy metal ions using spectrophotometer. Concentrations of adsorbent also were varied to study the removal efficiency of heavy metals. Final metal ion concentrations in solution and adsorption isotherm were determined. Base on the experiment, date seeds, clove, star anise and cinnamon shown 92, 91, 82 and 87 percentage of zinc removal. While adsorption capacity was obtained 1.58 mg/g for date, 3.03 mg/g for clove, 0.68 mg/g for star anise and 5.44 mg/g for cinnamon. K_f value for date seed, clove, star anise and cinnamon was 1.41, 3.5, 0.54 and 3.57. While the value for n for date seeds, clove, star anise and cinnamon was 1.48, 1.06, 0.54 and 3.57. The pH for clove, star anise and cinnamon were in range of 4 to 7 pH. While date seeds were in range of 5 to 8 pH. All the results is consistent with the Freundlich parameter that indicate, the smaller the value of 1/n means that adsorption bond is strong.

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1. INTRODUCTION

1.1 Background Of Study

Water, the universal solvent, is required to sustain biological and botanical life. It is broadly used in virtually every aspect of human existence and every single industrial process [1]. Household and commercial water usage produces effluents containing a variety of organic, inorganic, metallic, hydrocarbon, and biological species [1], many of which require treatment. In Malaysia, water is an abundant commodity and most of the areas in the country have a proper water supply. However, same like in any others part n the world, many of the sources of the drinking water has been contaminated.

Water quality management requires not only safe and palatable drinking waters, but also that spent waters and wastewater effluents are made suitable for follow-on uses or are not hazardous to receiving bodies of water (Fair, Geyer, & Okun, 1968). Even though significant advances have been made, wastewater treatment technology lags the pace of changes in the complexity of effluents (McKay, 1995). As waterborne waste becomes an ever more potent hazard to natural water systems, the European Union, the United Kingdom, the United States, Japan, and other developed nations are adopting ever more stringent wastewater treatment standards (McKay, 1995). Therefore, industry faces increasing technical and economic challenges in water treatment requirements (Acar & Zappi, 1995).

1.2 Problem Statement

Adsorption is one of the most utilized waste water treatment processes. Treatment methods used to remove heavy metal ions from waste effluents include precipitation, ion exchange, evaporation, freeze purification, reverse osmosis, electrolysis, cementation, flotation, adsorption, and electro dialysis. These methods are often expensive and cannot consistently accommodate the strict water quality standards now being imposed by public authorities (Kumar & Dara, 1982). Natural adsorbents may provide effective and economical water treatment alternatives.

The benchmark in adsorptive capacity is activated carbon, due to its immense surface area per gram. Most carbonaceous materials are porous and have a natural internal surface area of around 10 m^2/g. The activation process expands the internal surface structure and yields carbons with an internal surface area of approximately 1000 m^2/g. Granular activated carbon (GAC) is the most commonly used adsorbent for removal of toxic organic compounds from wastewater streams and is frequently used for removal of inorganic pollutants, as well. Carbon activation consists of two phases. The first is the carbonization phase, which involves heating the carbon source to a temperature of 600°C in the absence of air. The second phase activates the carbonized char by steam at 1000°C or by chemical treatments with acid or acid salts. The surface area is increased and porosity is developed by the activation process (McKay, 1995).

Other type of activation process is known as chemical activation. Carbon source is impregnated with chemicals such as acids like phosphoric acid or bases like potassium hydroxide, sodium hydroxide or salts like zinc chloride, followed by carbonization at temperatures in the range 450-900 °C. The carbonization and activation step proceeds simultaneously in chemical activation. Chemical activation is preferred over physical activation if lower temperature and shorter time is needed for activating the material.

Although broadly and effectively used across the full spectrum of adsorption system applications, GAC usage does have drawbacks, which include:

a. The cost of activated carbon is approximately $0.50-$3.00 per pound.

b. Activated carbon is loaded into and out of containment vessels using water-carbon slurries, increasing system complexity and cost (Smith, Pettit, & Schofield, 1996).

c. Activated carbon is easily crushed into useless fines under high impact and overburden stresses (Zappi, Graves, Aycock, Subramani, & Tavai, 2000).

d. The spent activated carbon must be removed and transported for regeneration or disposal, increasing operating costs (Smith et al., 1996).

There has been over the last few decades a great deal of interest in alternative or unconventional adsorbent materials. Many agricultural by-products have little or no economic value and are readily available (Smith et al., 1996). Forestry and food processing industries also yield valueless biomass by-products, which must be disposed of if no beneficial uses may be found. Wastewater treatment systems based on locally available, inexpensive natural adsorbent materials can potentially yield significant economic dividends compared to more complex and costly systems based on materials requiring long distance transportation (Kumar & Dara, 1981). Using natural adsorbents for the removal of heavy metals from waste water stream could be most promising if economical disposal and/or regeneration methods can be found (Roy, Greenlaw, & Shane, 1993). The same is true in the application of natural adsorbents for the removal of toxic organic compounds from waste waters. Earlier studies have shown that organic compounds, such as 2-4 DCP and TNT, adsorbed onto kenaf fiber may be fully biodegraded by composting (Subramani, 2002). In the case of heavy metals adsorption onto natural media, the spent adsorbent material may be regenerated via desorption of the metals by adjusting the pH (Roy, Greenlaw, & Shane, 1993).

1.3 Objective and Scope of Study

Since natural adsorbents are a renewable resource cheaply available in Malaysia, biomass adsorbent-based biosorptive processes are expected to be more economical than activated carbon (Zappi *et al.*, 2000; Brown, Gill, & Allen, 2000). Adsorbent in this report are easily prepared by established processing techniques that economically wash, and crush, are conveniently stored, and are extremely stable under high impact and overburden stresses (Zappi *et al.*, 2000). The candidate adsorbents evaluated in this study was date seed, clove, star anise and cinnamon.

In this research the employment of date seeds, clove, star anise and cinnamon, a natural adsorbent, is proposed in place of granular activated carbon for the adsorption heavy metals in aqueous solution. The specific purpose of this research was to evaluate the adsorptive capacity of candidate adsorbents, date seeds and others with respect to the removal of zinc in aqueous solution. Another one is to develop adsorption isotherms and determine the empirical adsorption isotherm constants.

The present work is an attempt to remove metallic ions in aqueous solutions using different date seeds mixture. The aim is to assess the influence of three parameters on the removal of heavy metals which are contact time, metal ion/adsorbent ratio and pH. Experimental methodology was used to identify influential parameters and to assess their interactions.

2. LITERATURE REVIEW

The use of natural adsorbents such as agricultural by-products or waste products, biomass, minerals, and earths is not a new concept. Certainly the self-healing, self-cleansing biosphere in which we live demonstrates the efficacy of naturally occurring processes of adsorption, filtration, purification, biodegradation, and recycling. Due to the costly nature of highly processed adsorbents in commercial and municipal use, a great deal of research work has been done over the past several decades to find inexpensive, more easily disposed or regenerated biobased materials to replace such proven effective materials as activated carbons, engineered zeolites, and ion-exchange resins. Natural materials such as bagasse, flour waste, paddy husk and straw, onion skin, garlic skin (Kumar & Dara, 1981; Kumar & Dara, 1982); green algae and rice hulls (Roy, Greenlaw, & Shane, 1993), chicken feathers (Al-Ahsen, Banat, & Al-Rousan, 2003), cypress, hardwood, and pine bark mulches (Jang, Seo, & Bishop, 2004); activated phosphate (Mouflih, Akil, & Sebti, 2005); banana and orange peels (Annaduri, Juan, & Lee, 2003; Sivaraj, Namasivayam & Kadirvelu, 2000), corncobs (Vaughan, Seo, Marshall, 2001), wheat bran (Farajzadeh & Monjii, 2004), peat (Brown, Gill, & Allen, 2000), peanut hulls (Johnson, Watson, Brown, & Jefcoat, 2002); lysine fermentation wastes (Choi & Yun, 2004), pine bark (Brás, Lemos, Alves, & Pereira, 2004; Vásquez, Antorrena, Gonzalez, & Doval, 1994; Randall, 1977); chitosan (Ahamd, Sumathi, & Hammeed, 2005); and many others have been evaluated for use as adsorbents.

Researchers in India have investigated the use of inexpensive agricultural by-products such as bagasse, flour waste, paddy husk, paddy straw, onion skin and garlic skin for binding metal ions such as Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}. The agricultural by-products were collected from readily available local sources, dried and powdered. Equilibrium and columnar adsorption experiments were conducted to evaluate the capacity of these natural adsorbents (Kumar & Dara, 1981). The powdered bagasse was pretreated with an 8% NaOH solution. The powdered onion skin was treated with formaldehyde and sulfuric acid (NH_2SO_4) to eliminate color leaching into solution and improve physical characteristics. Onion skin showed great efficiency in scavenging heavy metal ions from wastewater, while the other agricultural by-products appeared to have an appreciable capacity, as well, for binding heavy metal ions from solution. Onion skin removed greater than 99.9% of lead ion from an initial 110 ppm solution and 98.8% of cadmium ion from an initial 80 ppm solution. Onion skin adsorption capacities determined from column experiments were 1.35 mg/g, 1.55 mg/g and 1.22 mg/g for lead, cadmium, and zinc removal, respectively. An observed decrease in pH during the sorption of metal ions indicates that the possible mechanism of adsorption is predominantly ion exchange. The sorbed metal ions can be easily stripped from the substrate with dilute nitric acid and washing with water, after which the adsorbent substrate may be reused (Kumar & Dara, 1981).

The adsorption of heavy metals by green algae and ground rice hulls has been studied at Louisiana State University, demonstrating the applicability of inexpensive, readily abundant alternate adsorbents to bind and recover toxic heavy metals from aqueous solutions. The two adsorbing biomass media, algae and rice hulls, were considered because their cellular structure is similar in terms of functional group availability and both are available and abundant worldwide. Characterization of the cellular structure and identification of available functional groups were not given. The study demonstrated that dried *Chlorella minutissima* cells and ground rice hulls are excellent heavy metal adsorbers. Metal adsorption for both, from aqueous test systems, was more than 90% for Sr, Cd, Pb, Zn, Co, Cr, As and removal of Ni approached 80%. Adsorption of heavy metals by algae appeared to be noncompetitive. Adsorption capacity for the ground rice hulls was comparable to that for the algal biomass. Adsorption equilibrium occurred rapidly, within minutes. In contrast to many previous investigations which have focused on divalent cation adsorption, heavy metals such as As and Cr in anionic forms were also evaluated in this study. Algal biomass adsorbed almost 98% of chromium and arsenic, while similar experiments with rice hull biomass resulted in nearly 99% adsorption of Cr and As (Roy, Greenlaw, & Shane, 1993).

The ability of mulches to remove heavy metal ions typically found in urban runoff waters has also been assessed. Urban storm water runoff is the second most common the adsorptive ability of chitosan declines and at pH 2.0 chitosan is unstable. At pH 6.0 - 7.0 chitosan, bentonite, and activated carbon remove residual oil very poorly, because at this pH level chitosan loses its cationic nature and activated carbon and bentonite become very unstable. Applying chitosan in a coagulation treatment system caused a greater than 99 % reduction of residual oil in the supernatant and suspended solids of palm oil mill effluent (Ahmad, Sumathi, & Hameed, 2005).

The evaluation of peanut hulls has been conducted cooperatively by University of Alabama and Mississippi State University as a single use sorbent for the capture of cupric ions from wastewater. Peanut hulls are a cheap and ready available agricultural by product in much of the South, making them an excellent candidate adsorbent product for incorporation into wastewater treatment systems. The peanut hull was tested for adsorption capacity in an unmodified and a pelletized form. The minimum equilibrium time was approximately 40 minutes in this study and optimum copper(II) sorption occurred between pH 6.5 and 7.5 (Johnson et al., 2002).

2.1 ADSORPTION THEORY

The simplest definition of adsorption is the attraction of molecules to a surface. Physical adsorption takes places when weak intermolecular forces provide the attraction, whereas chemisorption utilizes chemical bonding forces to bind a species to a surface (Ebbing, 1996). A soluble chemical species, the adsorbate, is removed from a fluid by contacting a solid surface, the adsorbent. The forces of interaction between adsorbent surface atoms and adsorbate molecules are comparable to Van der Waals forces between adjacent molecules (LaGrega, Buckingham, & Evans, 1994). Both attractive forces and repulsive forces act between molecules. The net force of attraction and repulsion depends on the distance between the surface of the adsorbent and the adsorbate molecule (Cooney, 1999). The combined attractive and repulsive effects may be modeled by the Lennard-Jones "6-12" Potential Function (Atkins, 2001),as follows,

$$\Phi = 4\varepsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}]$$

Where,

Φ = potential function
σ = collision diameter, the distance of separation for which the force of interaction is zero
ε = depth of the potential well
r = distance of separation.

Chemisorption, or chemical adsorption, is not generally relevant to liquid-solid adsorption at normal temperatures. It is more important in gas-phase catalysis (Cooney, 1999). Chemical adsorption takes place at high temperatures, has significant activation energy, involves strong bonds, and is typically irreversible.

Physical adsorption involves weak forces, takes place at low temperatures, and is reversible. Physical adsorption is exothermic (Conney, 1999). Physical adsorption is primarily affected by the surface area of the adsorbent, adsorbent pore structure, adsorbent surface chemistry, nature of the adsorbate, pH of the solution, and the presence of competing adsorbates. These major factors make physical adsorption a complex phenomenon (LaGrega et al., 1994; Cooney, 1999).

The surface area of the adsorbent, like the surface area of a catalyst, is comprised of an external surface area and the internal surface area of the pore walls (Folger, 1999). The external surface of the adsorbent contributes to the external superficial surface area, while the pores of the adsorbent contribute mostly to the internal surface area. Because surface area so strongly affects adsorption capacity, the greater the surface area of the adsorbent becomes, the greater the capacity for physical adsorption (Cooney, 1999). Adsorbent surfaces are typically made up of various surface functional groups. Adsorption of organic adsorbates is particularly dependent on the quantity and nature of surface oxide groups. Carbon/oxygen surface functional groups may occur naturally or may be created by oxidation that occurs if an adsorbent undergoes an activation process. In the case of activated carbon, the activation process involves heating in the absence of air followed by steam or chemical treatment to increase surface area and develop porosity.

Adsorbent surface groups and structures may be modified by surface modification techniques, such as oxidation, reduction, and sonication. These techniques may create or alter surface functional groups (carbon/oxygen groups), create positive or negative charge distributions, and/or clear surface debris and unblock pores or adsorption sites. The pH of a solution is a major adsorption-determining factor, with acidic species generally adsorbing better at low pH, and basic species better at higher pH.

Competition for available adsorption sites on the adsorbent increases when myriad adsorbates are present in solution. In general, competing adsorbates will reduce the adsorption capacity of all adsorbates onto the adsorbent (Cooney, 1999). Adsorption takes place when an adsorbent comes in contact with a liquid containing an adsorbate and adsorption sites on the adsorbent are filled. When all adsorption sites are filled, equilibrium occurs. At equilibrium the rate of adsorption equals the rate of desorption (Cooney, 1999).

The relationship between the amount of adsorbate adsorbed onto the adsorbent surface and the equilibrium concentration of the adsorbate in the solvent at a constant temperature may be estimated by adsorption isotherm models. The most broadly used isotherm model in wastewater treatment is the Freundlich Isotherm Model (Freundlich, 1907). The equation works best at low adsorbate concentrations. Data for the adsorption of adsorbates within a liquid phase are best fitted using the Freundlich model (Cooney, 1999). The Two-Parameter Freundlich model relates the sorbed phase concentration to an equilibrium concentration of the adsorbate at a constant temperature according to the equation:

$$\frac{X}{M} = K_f C_e^{1/n}$$

Where,

X = Mass of solute (adsorbate) adsorbed (mg)
M = Mass of adsorbent (g)
C_e = Final aqueous phase concentration (mg/L)
K, n= Equilibrium constants

The value of the empirical constant K is usually reported at water phase equilibrium concentration of 1 mg/L, that is, $C_e = 1$, when the equation becomes "X/M = K." Therefore, K (adsorptive capacity) has the units of L/g. 1/n is unitless and represents adsorption intensity.

The Freundlich model indicates that the energy distribution of the adsorption sites is exponential in nature (Cooney, 1999). The rates of adsorption and desorption vary with the adsorption energy of the sites. There is also the possibility for more than one monomolecular layer of adsorptive coverage as C_e gets larger, although the Freundlich model does not require that the surface coverage must approach a constant value corresponding to one complete monolayer. The equation fails to fit experimental data at high concentrations (Cooney, 1999).

The equation can also be written as in the logarithmic form:

$$\log\frac{x}{m} = \log K_f + \frac{1}{n}\log C_e$$

Linear regression is performed graphically by plotting log X/M versus log C_e on a rectangular plot. The linear equation from the linear regression allows the Freundlich isotherm constants, K and 1/n, to be determined, where K represents the adsorption capacity in milligrams adsorbate adsorbed per gram of adsorbent (mg/g) and the unitless 1/n represents adsorption intensity. From the form of the linear equation y = mx + c obtained from the plot, 1/n is the slope (m) and log K is the y-intercept. Linear plot of log x/m vs. log C_e shows that the adsorption follows Freundlich isotherm.

Larger value of K_f means the adsorption capacity of the adsorbent is greater. K_f value shows that limestone and granular activated carbon mixture represents beneficial adsorption. The constant 1/n is a function of the strength of adsorbent.

While the Freundlich model is a better model for the adsorption of adsorbates in liquid solutions, the Langmuir model is generally a better model for the adsorption of gases onto solids (Cooney, 1999). The Langmuir Isotherm Model is a two-parameter model of the form,

$$\frac{x}{m} = \frac{bq_m C_e}{1 + bC_e}$$

Where,

X = Mass of solute adsorbed (mg)
M = Mass of adsorbent (g)
C_e= Final aqueous phase concentration (mg/L).

The Langmuir monolayer capacity parameter q_m (mg/g) is the maximum value that X/M can achieve as C_e becomes larger. It is the actual physical concentration of the adsorbate on the surface when one complete monomolecular layer of coverage is attained. The parameter b (L/mg) is the Langmuir isotherm constant corresponding to adsorptive capacity (Langmuir, 1918). A three-parameter isotherm model, the Langmuir-Freundlich Isotherm Model, is given by:

$$\frac{X}{M}=\frac{bq_m C_e^{1/n}}{1+bC_e^{1/n}}$$

Where,

X = Mass of solute absorbed (mg)
M = Mass of adsorbent (g)
C_e = Final aqueous phase concentration (mg/L).

The three constants are q_m (mg/g), b (L/mg), and n, as defined above. The Langmuir-Freundlich model has been mainly used for granular activated carbon adsorption of aqueous benzene and toluene (Hindarso, Ismadji, Wicaksana, Mudjijati, & Indraswati, 2001).

While, the linear form of this equation was:

$$\frac{1}{x/m} = \frac{1}{KbC_e} + \frac{1}{b}$$

There are many isotherm models available for use. The most widely used are the Freundlich and Langmuir models, with the Freundlich model most widely used to model the adsorption of contaminants from waste water streams.

3. MATERIALS AND METHODOLOGY

3.1. Phase 1: Adsorbent materials

3.1.1 Sewage Sludge Ash

A sample of the sewage sludge ash (SSA) was collected from the Universiti Teknologi PETRONAS sewage treatment plant in Tronoh. The samples were treated by the following methods. Initially, the SSA will be dried in open air area about few days. Then it will be dried further by using mechanical oven. Next, the SSA will be grind until it becomes fine particle. Lastly, the SSA will be furnace at 750° C for about 8 hours.

After finishing the experiment using SSA, it was found that the time that been used to prepare the SSA was very lengthy. It took about three days to dry the SSA in natural weather condition. Next, when the SSA was partially dry, it needed two more days to dry it completely using mechanical oven. Base on the data that was collected from the first experiment of the SSA, 200 kilogram of sludge was needed to achieve about 200 gram fully dry SSA. Considering the time duration was not realistic, it is decided to change the adsorbent to petroleum coke.

3.1.2 Petroleum Coke

The petroleum coke that was used as the replacement of petroleum coke was collected from Petronas Penapisan Melaka (PPM). Petroleum coke is a carbonaceous solid derived from oil refinery cracking processes. Petroleum coke has many uses as a fuel, in the manufacturing of dry cells, electrodes, etc. On the other hand, needle coke or acicular coke is a highly crystalline petroleum coke used in the production of electrodes for the steel and aluminum industries. Before the experiments, studied was done on academic journals regarding this new purpose adsorbent. From the research, a few journal indicate that petroleum coke contain high mercury component. Even in few research, there are finding that specify a considerable arsenic component (Jennifer, 2003).

Both elements were considered very hazardous to the human health and environment. But, the possibility to find these two hazardous elements in the petroleum coke from PPM is depending on the source of the petroleum coke. Because of that, the petroleum coke was sent for XRD test. The result from the XRD test was confirming our consent; the petroleum coke did contained mercury arsenide chloride (Hg_2AsC_{12}). Due to health, safety and environmental (HSE) issue, it was decided again to replace the adsorbent.

Referring to the XRD test, the petroleum coke contains Mercury Arsenide Chloride (Hg_2AsCl_2) and Barium Hydrogen Chromium Oxide Arsenate ($Bah(AsCr_2O_{10})$). The graph can be referred in Figure 1 below.

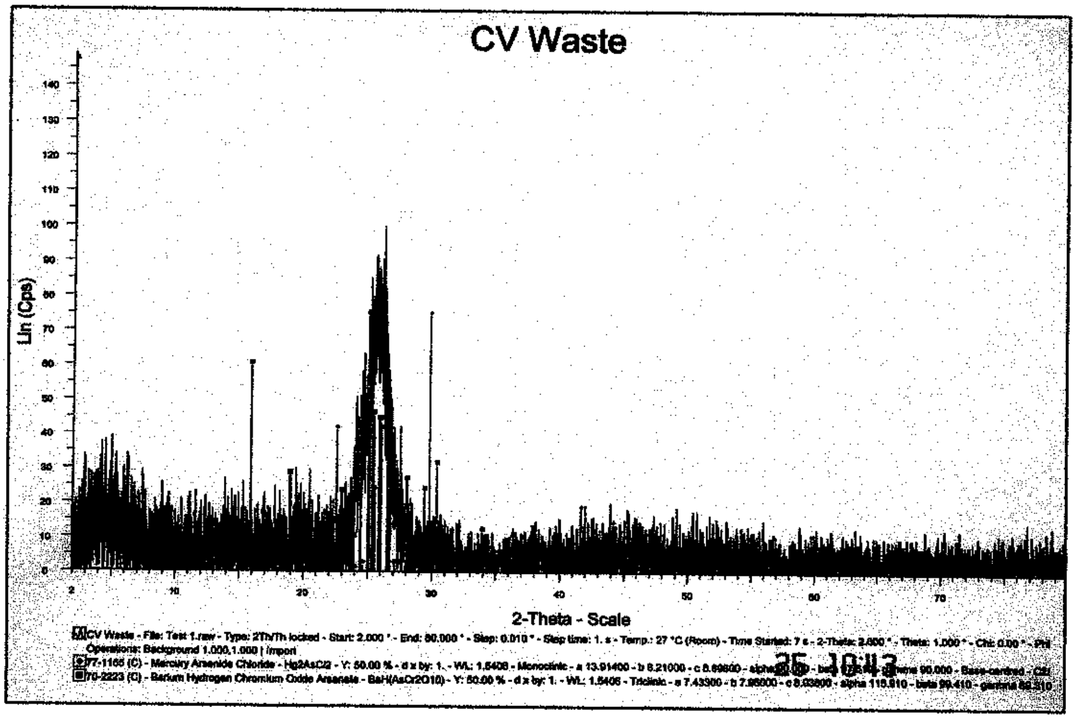

Figure 1: XRD result of test on Petroleum Coke

3.1.3 Molinex (Molecular Sieve)

The latest material that will be use as the adsorbent for this project is molecular sieve or in this case the product is named as molinex by its manufacturer. The material was collected from Aldwich Enviro-Management Sdn Bhd. This company operated at Cukai, Terengganu. Basically, molecular sieve is a material containing tiny pores of a precise and uniform size that is used as an adsorbent for gases and liquids. Molecular sieves are usually utilized in the petroleum industry, especially with purification of gas streams. The mercury content of natural gas is extremely harmful to the aluminum piping and other parts of the liquefaction apparatus - silica gel is used in this case.

As for experiment using concentration of adsorbate at 1 ppm and 10 ppm, the solution was placed for digestion treatment. There is a difference in this method, after filtration, 50 mL of the solution will be added up with 2.5 mL of acid nitric. Then, the solution was heated up at 50° C for two hour. After two hour, the solution was needed to be added up again with distils water until it reaches its original volume of 50 mL. Finally, the concentration of Zinc was determined using the spectrophotometer.

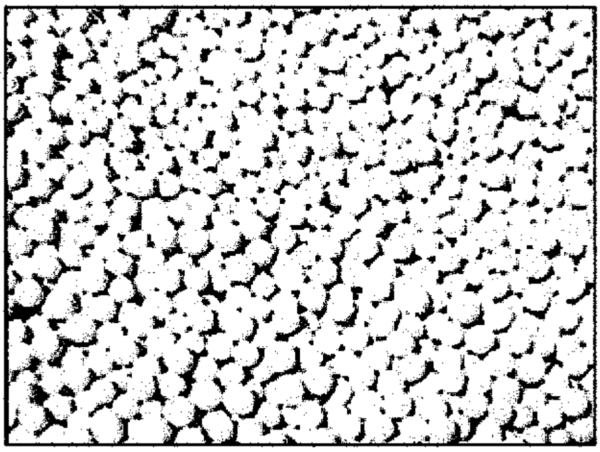

Figure 2: Molinex (Molecular Sieve)

3.1.4 Date Seeds

Due to the incapability of molinex to react as adsorbent, the date seed was proposed to replace it as natural adsorbent for this project. In Malaysia, the fruit is famous in the fasting month of Ramadhan. The date fruits were collected from the date that available in the market. The seeds were extracted manually, washed and placed to dry in the lab. After that, it were put in the mechanical oven to ensure that there were really dried.

Date has been a staple food of the Middle East for thousands of years. They are believed to have originated around the Persian Gulf, and have been cultivated since ancient times from Mesopotamia to prehistoric Egypt, possibly as early as 6000 BC. There is archaeological evidence of date cultivation in eastern Arabia in 4,000 BC.

Dates have high tannin content and are used medicinally as a detersive (having cleansing power) and astringent in intestinal troubles. As an infusion, decoction, syrup, or paste, dates may be administered for sore throat, colds, bronchial catarrh, and taken to relieve fever and number of other complaints. The date seeds were sent to XRD test to investigate the compound available in it. Base on the result the date seeds contain Ferrocenylcarboxylic acid (C3OH31FeN30) and Lithium Uranyl Carbonate (Li4UO2 $(CO_3)_3$). The graph was located at Figure 3.

Figure 3: Date Seed

3.1.5 Clove (Bunga Cengkih)

Cloves (Syzygium aromaticum, syn. Eugenia aromaticum or Eugenia caryophyllata) are the aromatic dried flower buds of a tree in the family Myrtaceae. It is native to Indonesia and used as a spice in cuisine all over the world. The name derives from French clou, a nail, as the buds vaguely resemble small irregular nails in shape. Cloves are harvested primarily in Zanzibar, Indonesia and Madagascar; it is also grown in India, and Sri Lanka.

The clove tree is an evergreen which grows to a height ranging from 10-20 m, having large oval leaves and crimson flowers in numerous groups of terminal clusters. The flower buds are at first of a pale color and gradually become green, after which they develop into a bright red, when they are ready for collecting. Cloves are harvested when 1.5-2 cm long, and consist of a long calyx, terminating in four spreading sepals, and four unopened petals which form a small ball in the centre. The compound responsible for the cloves' aroma is eugenol ($C_{10}H_{12}O_2$). It is the main component in the essential oil extracted from cloves, comprising 72-90%. Eugenol ($C_{10}H_{12}O_2$), is used as antiseptic and anaesthetic in dentistry.

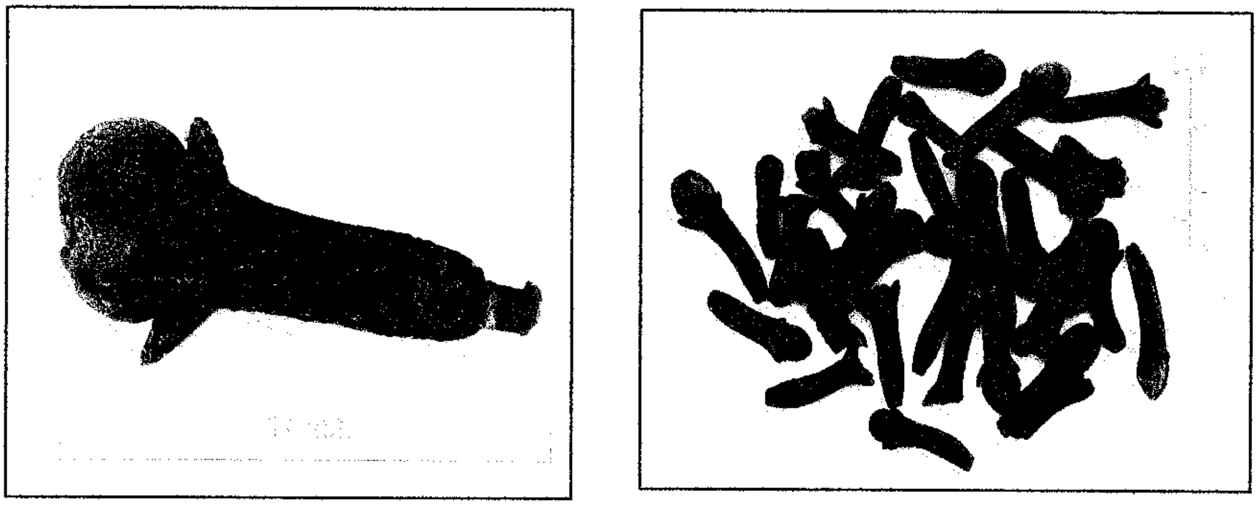

Figure 4: Clove (Bunga Cengkih)

3.1.5 Star Anise (Bunga Lawang)

Star anise, is a spice that closely resembles anise in flavor, obtained from the star-shaped pericarp of Illicium verum, a small native evergreen tree of southwest China. The star shaped fruits are harvested just before ripening. It is widely grown for commercial use in China, India, and most other countries in Asia. Star anise is an ingredient of the traditional five-spice powder of Chinese cooking.

The dried fruits may contain 5 to 8% of essential oil, which dominated by anethole (85 to 90%). The other components are, estragole (methylchavicol), anisic acid, b-caryophylline, anisaldehyde, linalool, anise ketone (methoxyphenylacetone); the polymers of anethole, dianethole and photoanethole; an Egyptian variety carvene, carvone, and alpha-zingiberene. Coumarins, such as bergapten, umbelliferone, scopoletin. Flavonoid glycosides including rutin, isovitexin, quercetin, luteolin, and apigenin glycosides . Phenylpropanoids, including l-propenyl-2-hydroxy-5-methoxy-benzene-2- (2- methyl-butyrate), lipids, fatty acids, sterols, proteins and carbohydrates.

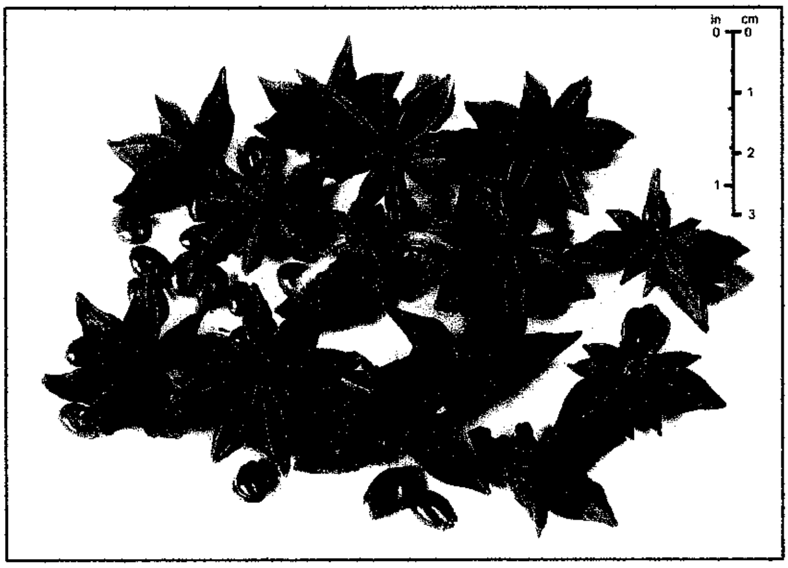

Figure 5: Star Anise (Bunga Lawang)

3.1.5 Cinnamon (Kayu Manis)

Cinnamon (*Cinnamomum verum*, synonym *C. zeylanicum*) is a small evergreen tree 10-15 meters (32.8-49.2 feet) tall, belonging to the family Lauraceae, native to Sri Lanka and Southern India. The bark is widely used as a spice. The leaves are ovate-oblong in shape, 7-18 cm (2.75-7.1 inches) long. The flowers, which are arranged in panicles, have a greenish color, and have a rather disagreeable odor. The fruit is a purple one-centimetre berry containing a single seed.

Its flavor is due to an aromatic essential oil which makes up 0.5 to 1% of its composition. This oil is prepared by roughly pounding the bark, macerating it in sea-water, and then quickly distilling the whole. It is of a golden-yellow colour, with the characteristic odour of cinnamon and a very hot aromatic taste. The pungent taste and scent come from cinnamic aldehyde or cinnamaldehyde and, by the absorption of oxygen as it ages, it darkens in colour and develops resinous compounds. Chemical components of the essential oil include ethyl cinnamate, eugenol, cinnamaldehyde, beta-caryophyllene, linalool and methyl chavicol.

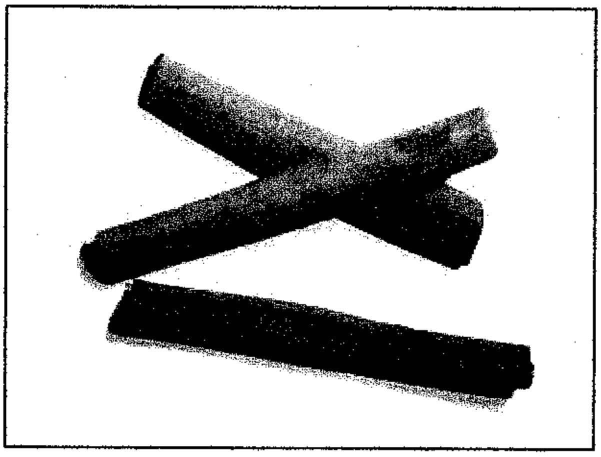

Figure 6: Kayu Manis (Cinnamon)

3.2 Phase 2: Batch experiments

To perform the experiment, working solution (adsorbate) of Zinc (II) was prepared by dissolving the respective metal Zinc Chloride in distilled water to avoid errors in results. If using others than the distilled water, there are possibility that the water are already contaminated with others substances that might affect the experience. The concentrations of adsorbate that used for the experiment were 1 ppm, 10 ppm and 100 ppm.

While, for the adsorbent, was first wash with distilled water to remove all the contaminants such as dust, small insects etc. After cleaning, the adsorbents were put on the tray for the drying process. The drying was carried out in oven for 24 hours with 110 °C temperatures. Next, the adsorbents were grinded using Panasonic Blender and Mill.

The adsorption of heavy metal ion on molecular sieve powder was carried out using batch method. Adsorption studies were conducted using different dosage of 100 mg, 150 mg, 200 mg and 400 mg of adsorbent with 100 ml of solution containing zinc ion concentration in BOD bottles at constant temperature. The bottles were shaken in a mechanical shaker for 1 hour, 3 hours, 6 hours and 24 hours. After shaking, the aqueous solution containing heavy metal ion and adsorbent were filtered up. The initial and final concentrations of zinc were determined using Hach DR 2800 Spectrophotometer.

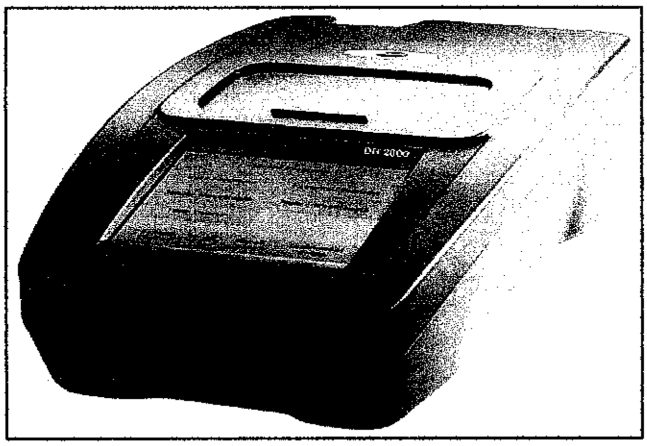

Figure 7: Hach DR 2800

4. RESULTS AND DISCUSSION

4.1 Use of Molinex as Adsorbent

The results of molinex experiment were shown in Figure 8, Figure 9 and Figure 10. The result for experiment using concentration of 100 ppm was shown in Table 1. Before the concentration of the Zinc been test using spectrophotometer, the solution was dilute with 1:100 ratio. The result was multiplied with 100 to achieve the actual result.

The spectrophotometer can only detect between 0.3 mg/L to 3 m.0 mg/L concentration of Zinc. The experiment was conducted to use 1 ppm concentration instead of 10 ppm. In this experiment, the solution had digestion treatment first, before the Zinc concentration being test using spectrophotometer. The result from 1 ppm concentration was observed as shown observed in Figure 8 below.

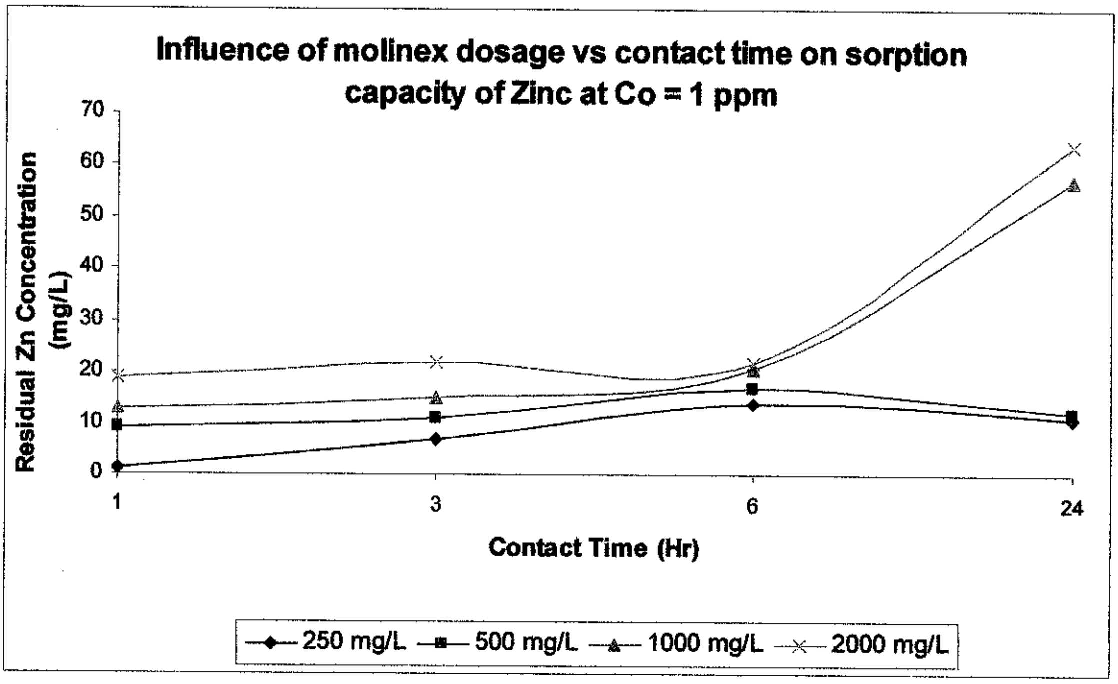

Figure 8: Influence of molinex dosage vs contact time on sorption capacity of Zinc Co = 1 ppm

The result from the experiment the blank solution (molinex mix with distilled water) indicates that the Zinc concentration is 1.52 ppm. The result was supposed to show the Zinc concentration declining, but it was vice versa, in other word, the longer the contact time, the higher Zinc concentration.

Base on the result, it was assumed that instead of absorb Zinc the material was actually leaching it. But, to confirm the presumption, another experiment was conducted using 10 ppm at contact time of one and six hour. The result was shown on Table 5 and in Figure 10. The result was compared with the solution of molinex without metal solution at same contact time of one and six hour. The absorbent also was sent to have X-ray crystallography (XRD) test to ensure it molecular structure.

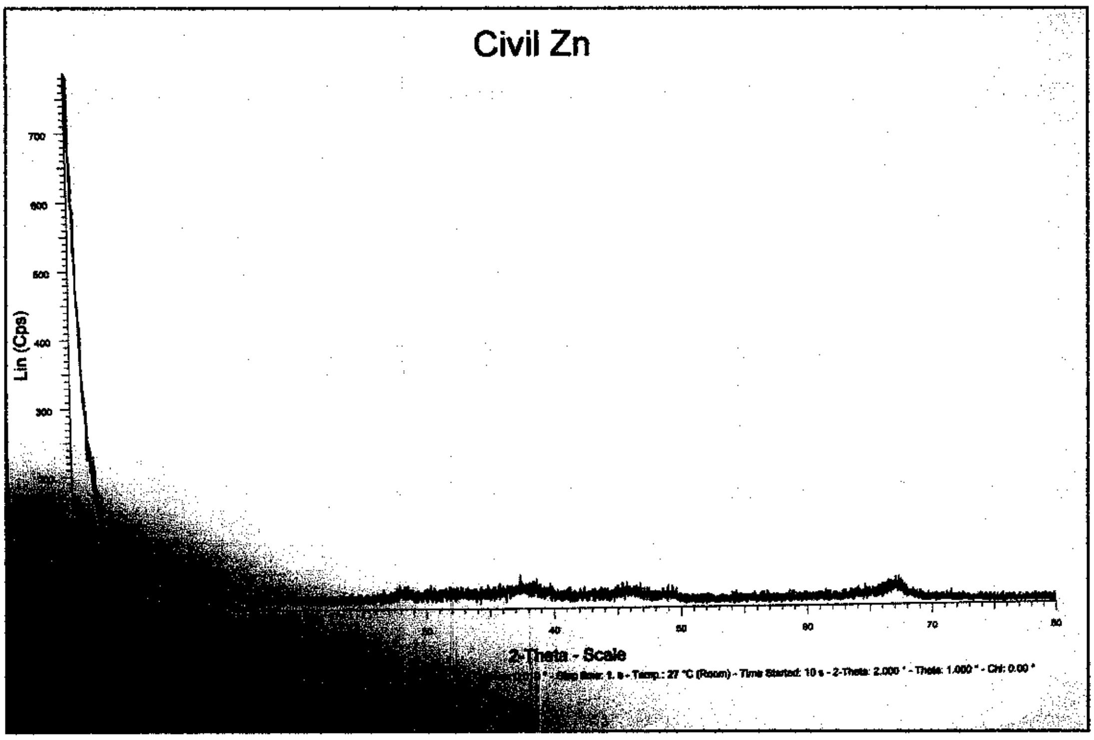

Figure 9: XRD Test Result on Molinex

The result from the leachability test was observed as shown in Figure 10. While in Figure 9 above, the finding from the XRD test can be observed. Base on the X-ray crystallography (XRD) result, there were no any heavy metal element been detected. There are a few possibilities that lead to it, one of it was because the Zinc element is too high or too low for the device range. Thus it cannot indicate any trace of Zinc element in the substance.

Base on the finding it was proven that molinex is actually leaching Zinc into the concentration. The materials itself contain heavy metal. Because of that molinex is not suitable to be taken as natural adsorbent in this project.

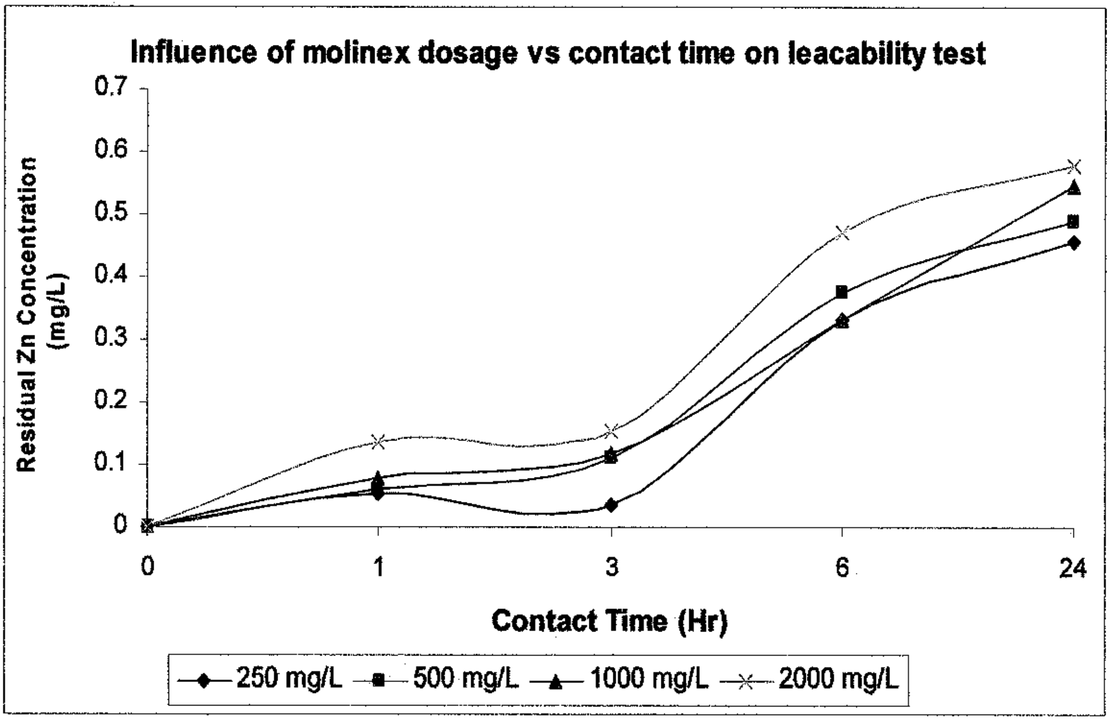

Figure 10: Zinc Concentration on Leacability Test

4.2 Use of Date Seeds as Natural Adsorbent

4.2.1 Adsorption of Zinc

Firstly, the date seeds were been clean of thoroughly by using distilled water. Next, the seeds were then dried using mechanical oven at 37° C for two day to ensure that it dried.

The result from the experiment with solution of Zinc at 1 ppm can be observed at Figure 11. The graph shown an inclination curve which is a good indicator that date seeds perform well as adsorbent. Base on the result, the best curve is in concentration of 2000 mg/L. The percentage of removal for the best result was 92 % which is 4000 mg/L concentration at 24 hours contact time.

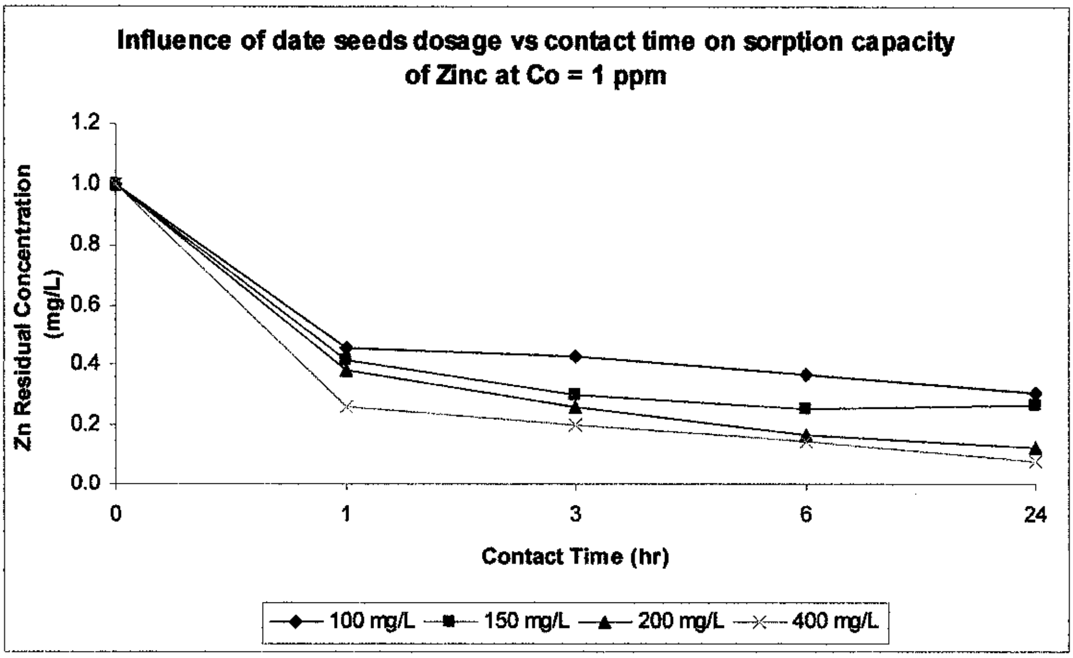

Figure 11: Influence of date seeds dosage vs contact time on sorption capacity of Zinc Co = 1 ppm

The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration. This result is the best comparing with other experiments using different concentration of adsorbate. We can conclude that date seeds show highest efficiency in adsorbing zinc at lower concentration.

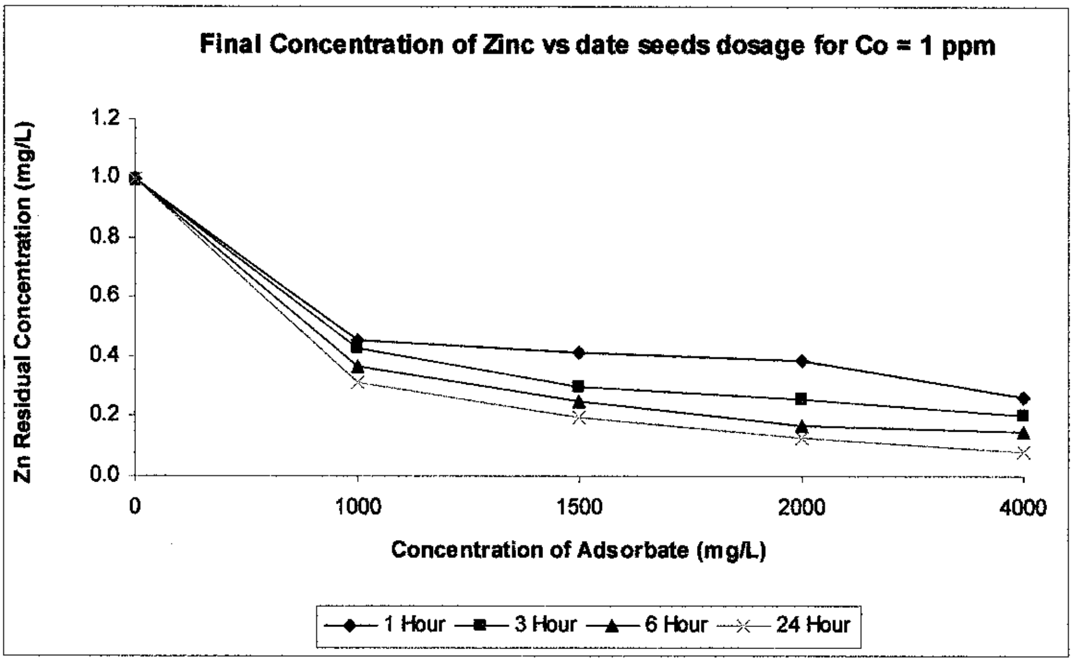

Figure 12: Final Concentration of Zinc vs adsorbent for Co = 1 ppm

Figure 12 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was date seeds in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows that the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

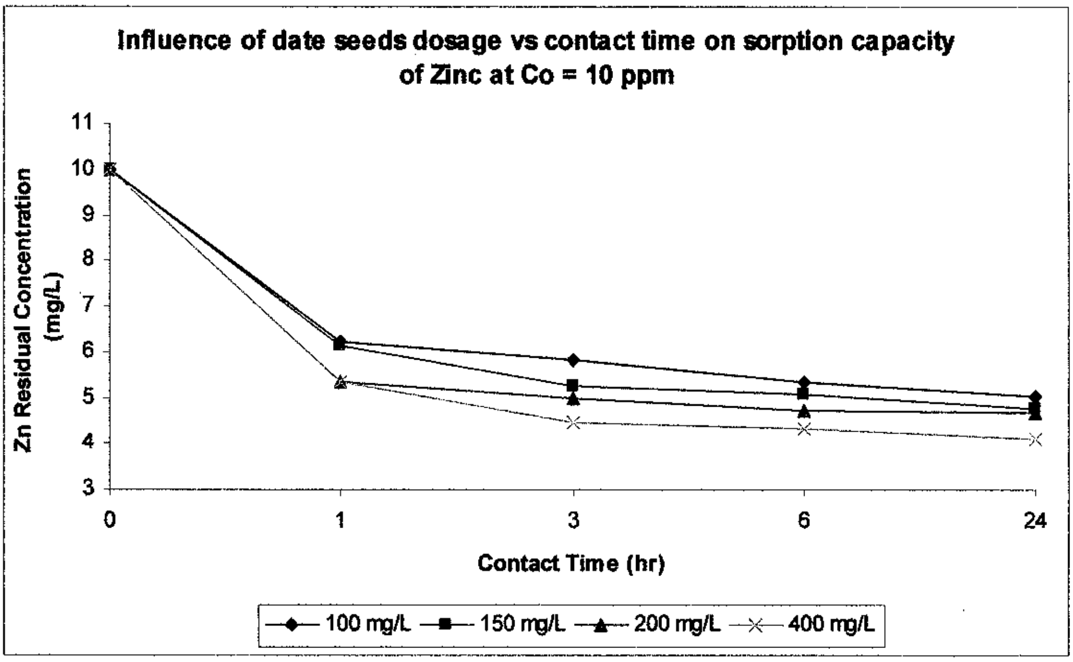

Figure 13: Influence of date seeds dosage vs contact time on sorption capacity of Zinc Co = 10 ppm

Figure 13 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 10 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Referring to the graph, lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 10 ppm of zinc, the best result is shown using 400 mg of date seeds in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 4.1 mg/L which mean 59 % of initial zinc is being absorbed.

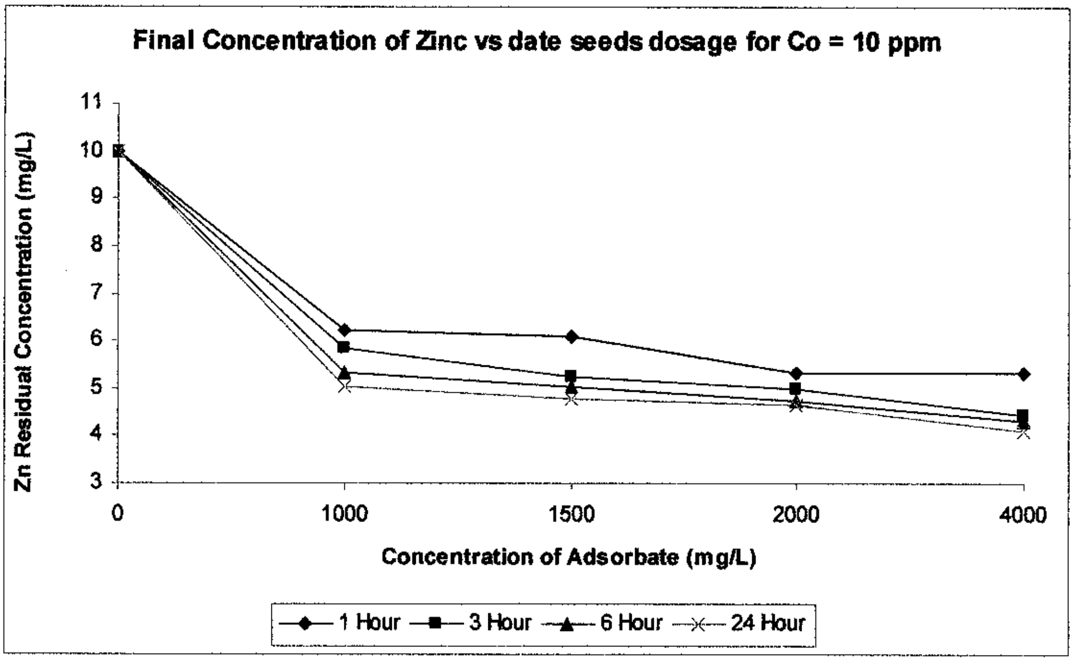

Figure 14: Final Concentration of Zinc vs adsorbent for Co = 10 ppm

Figure 14 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was date seeds in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows that the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

For these experiments, we can see that the difference between the graphs was not significant. This can be indication that after certain hour contact times the absorbability of date seed does not change much.

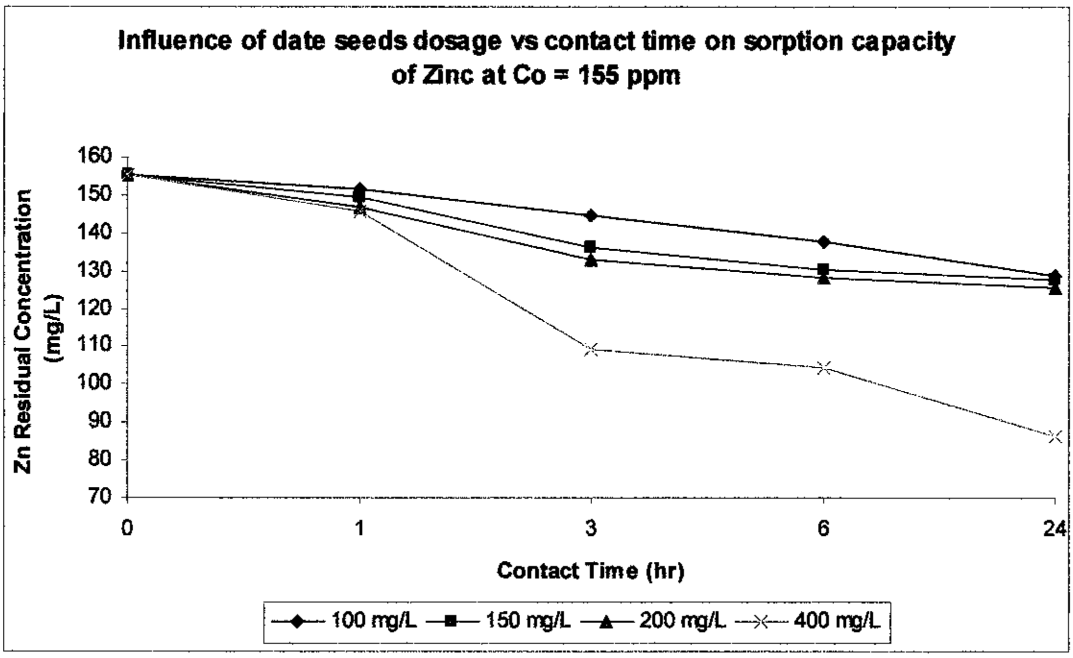

Figure 15: Influence of date seeds dosage vs contact time on sorption capacity of Zinc Co = 155 ppm

Figure 15 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 100 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Base on the performance of all experiments using date seeds as the adsorbent, the lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 100 ppm of zinc, the best result is shown using 400 mg of date seeds in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 87 mg/L which mean 44 % of initial zinc is being absorbed. The graph also indicating that the adsorption is slowly reaching it limit.

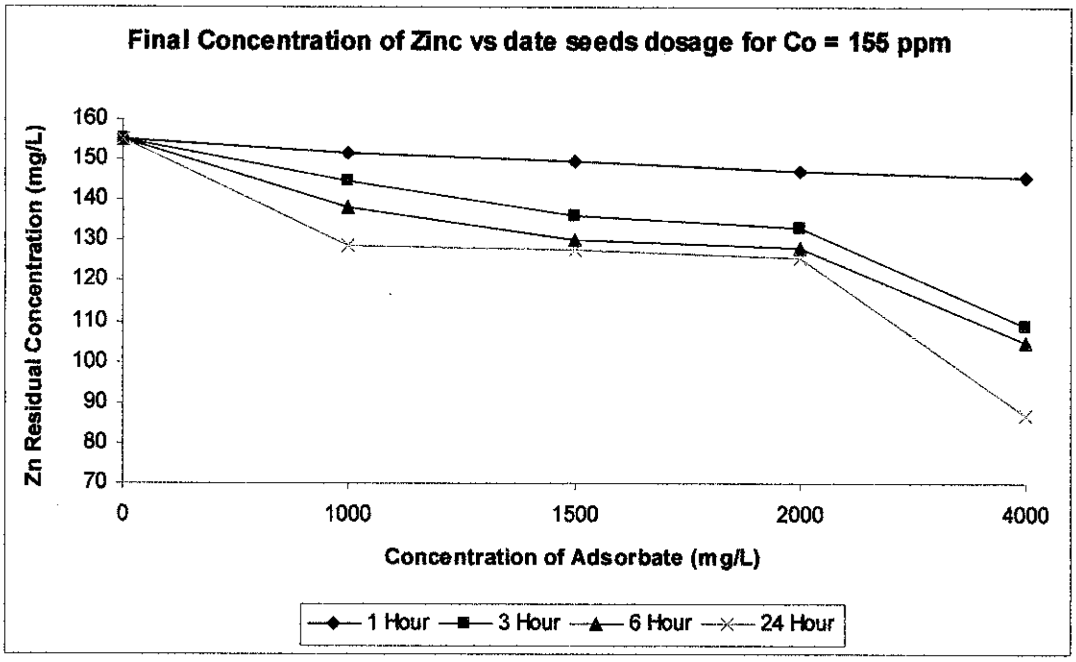

Figure 16: Final Concentration of Zinc vs adsorbent for Co = 155 ppm

Figure 16 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was date seeds in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows is same like the above graph, the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

For these experiments, there are significant prove that the higher the amount of adsorbent permitted the lower residual of zinc at the end of the experiment. Thus, date seed are more capable react as a good adsorbent with higher amount of dosage with lower concentration of adsorbate.

Base on the experiments results, date seeds shown higher absorbability when the concentration of Zinc is at the lowest, which is 1 ppm. The best graph show that at 1 ppm of Zinc, using 400 mg of date seeds as adsorbent at 24 hour of contact time has the best performance by adsorbing 92 percent of the initial zinc concentration.

The pH is detected between the range of 8 to 5 pH. Depending on the mass of the adsorbate, the higher the adsorbate the lower the pH. A statistical analysis was conducted on the results of the experiment. Analysis of variance (ANOVA) performed on the results showed that, 5% level of significant; the zinc removal was significantly affected by time of contact time and weight of adsorbent used.

4.2.2 Adsorption Isotherm

The relation between the initial concentration of Zinc and its percentage removal from solution was studied for all adsorbents included in the study. The initial concentrations of Zinc studied were 1, 10 and 100 mg/L at an adsorbent concentration of 100, 150, 200 and 400 mg/L. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e.

The Langmuir constants q_m and b are related to the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage) and energy of adsorption, respectively. The highest value of adsorption capacity q_m (maximum uptake) of date seeds is 1.58 mg/g using 1 ppm of Zinc at 24 hour contact time. While the value of b, the Langmuir constant is indicate at 0.441. Linear plots of 1/q versus $1/C_e$ in Figure 17 were employed to determine the value of q_m (mg/g) and b (L/mg).

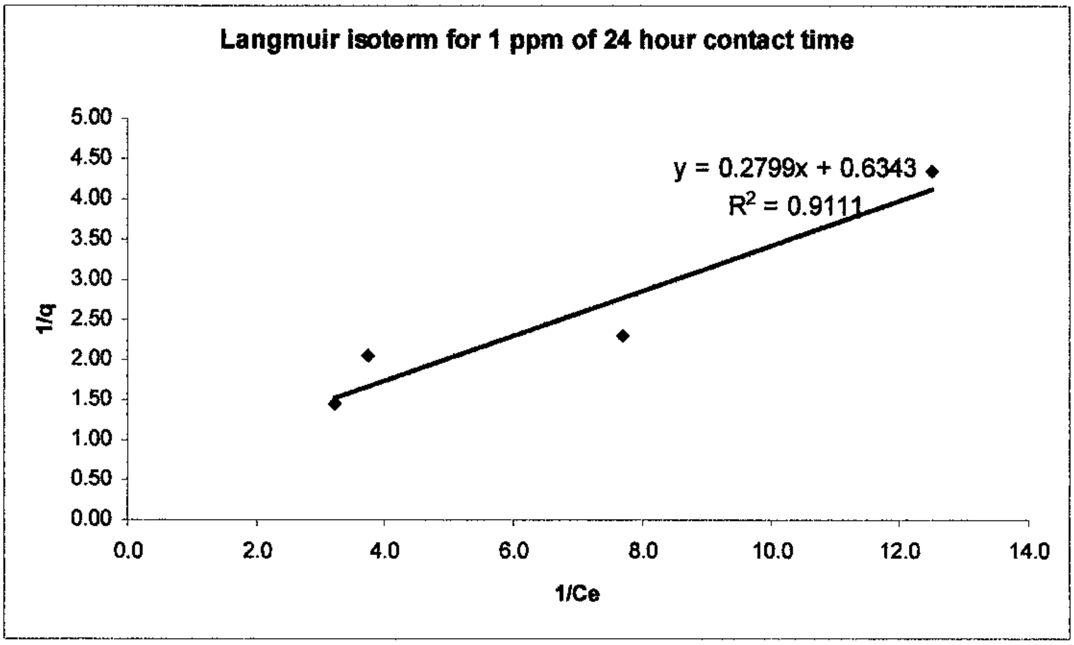

Figure 17: Langmuir plot for the adsorption of Zinc by date seeds, adsorbate 1 ppm and contact time 24 hour

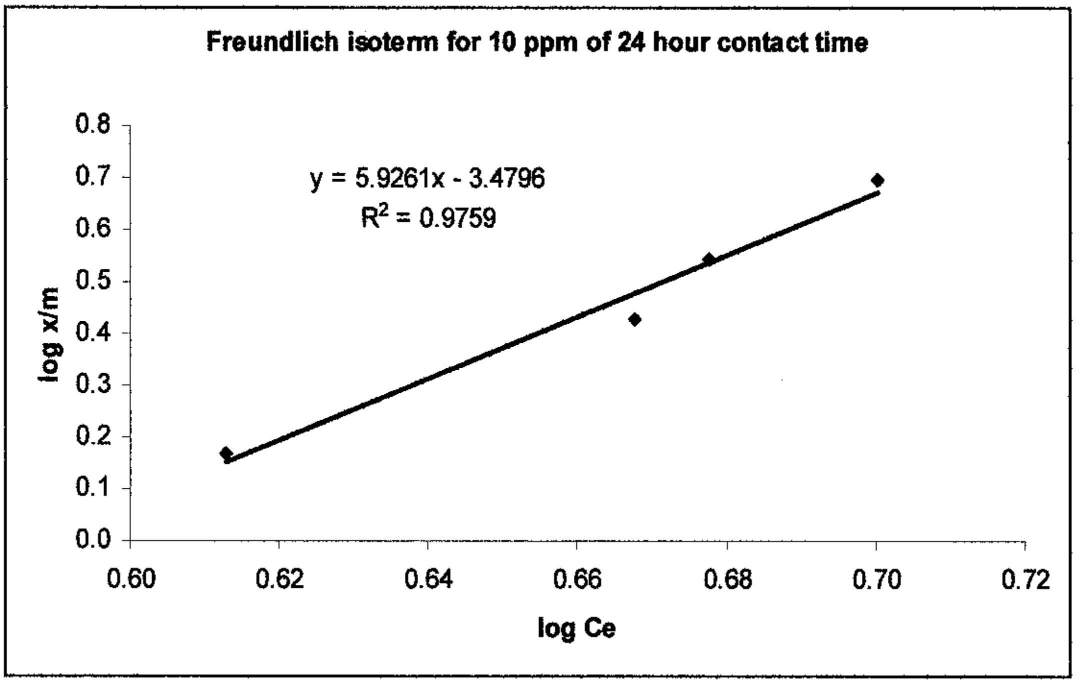

Figure 18: Freundlich plot for the adsorption of Zinc by date seeds, adsorbate10 ppm and contact time 24 hour

The constants K_f and n of Freundlich Isotherm were calculated base on the plots in Figure 18 above. The highest value of Freundlich constant, K_f is 1.41 while n value is 1.48. This is base on experiment using 10 ppm of Zinc at 24 hour contact time.

4.3 Use of Clove as Natural Adsorbent

4.3.1 Adsorption of Zinc

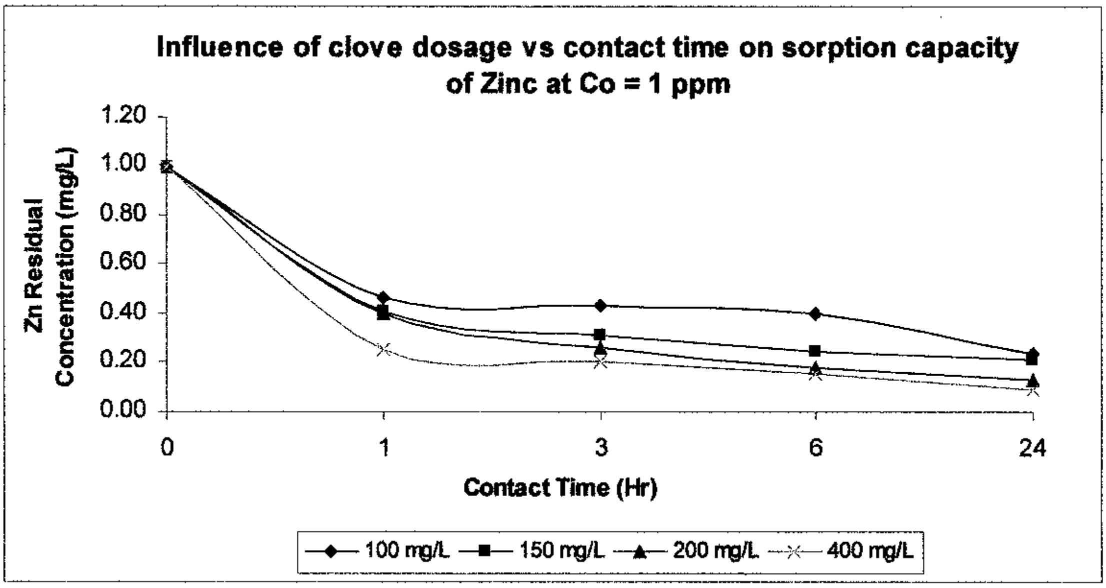

Figure 19: Influence of clove dosage vs contact time on sorption capacity of Zinc Co = 1 ppm

Figure 19 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 1 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Base on the performance of all experiments using clove as the adsorbent, the lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 1 ppm of zinc, the best result is shown using 400 mg of clove in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 0.09 mg/L which mean 91 % of initial zinc is being absorbed.

This result is the best comparing with other experiments using different concentration of adsorbate. We can conclude that clove show highest efficiency in adsorbing zinc at lower concentration.

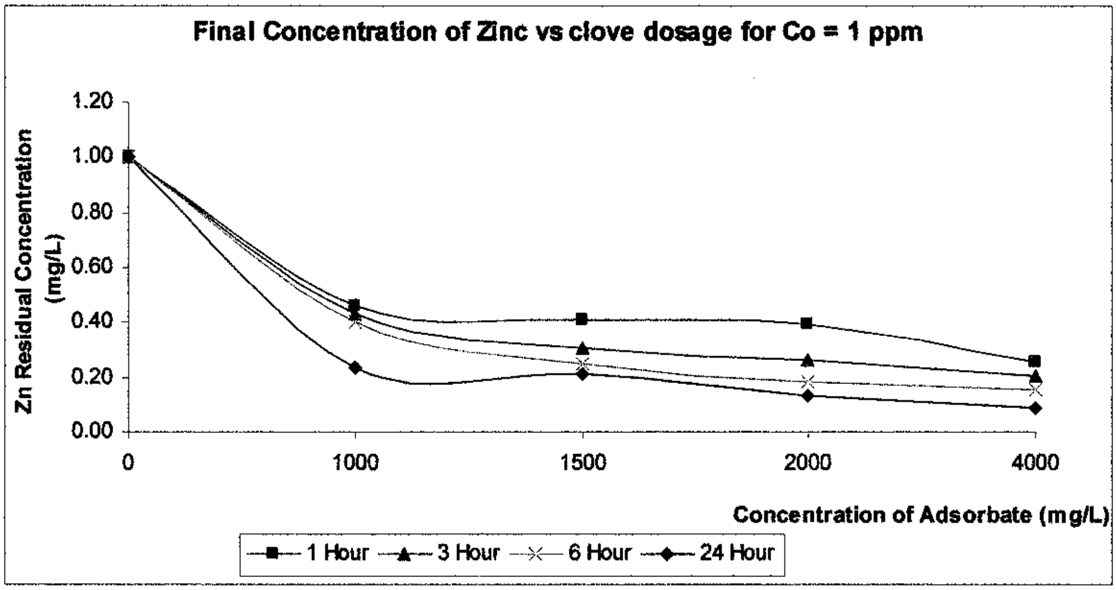

Figure 20: Final Concentration of Zinc vs adsorbent for Co = 1 ppm

Figure 20 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was clove in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows that the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

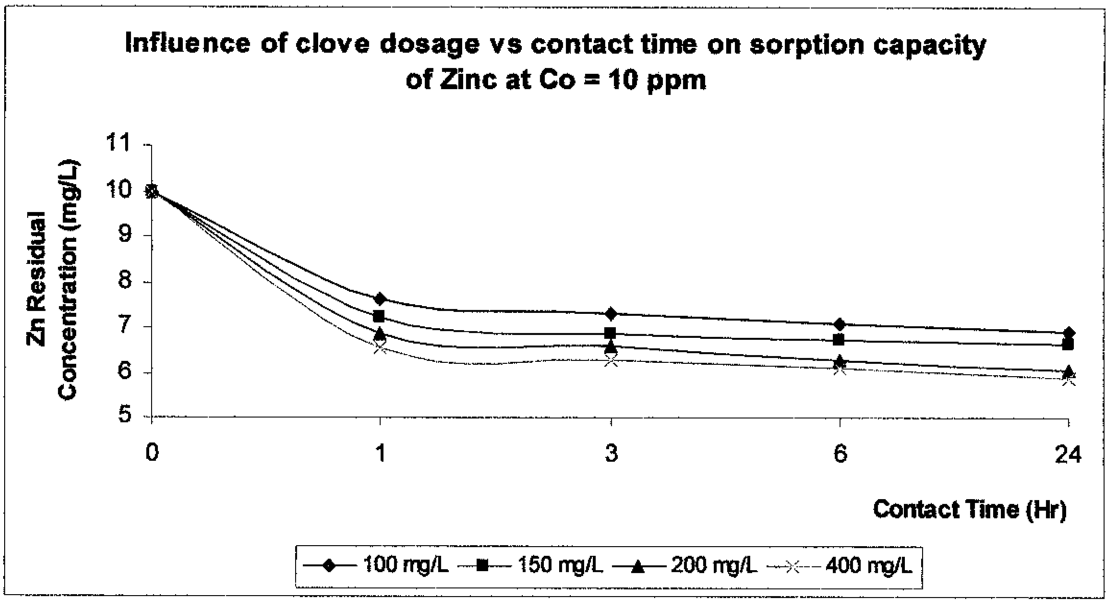

Figure 21: Influence of clove dosage vs contact time on sorption capacity of Zinc Co = 10 ppm

Figure 21 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 10 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Referring to the graph, lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 10 ppm of zinc, the best result is shown using 400 mg of clove in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 5.9 mg/L which mean 41 % of initial zinc is being absorbed.

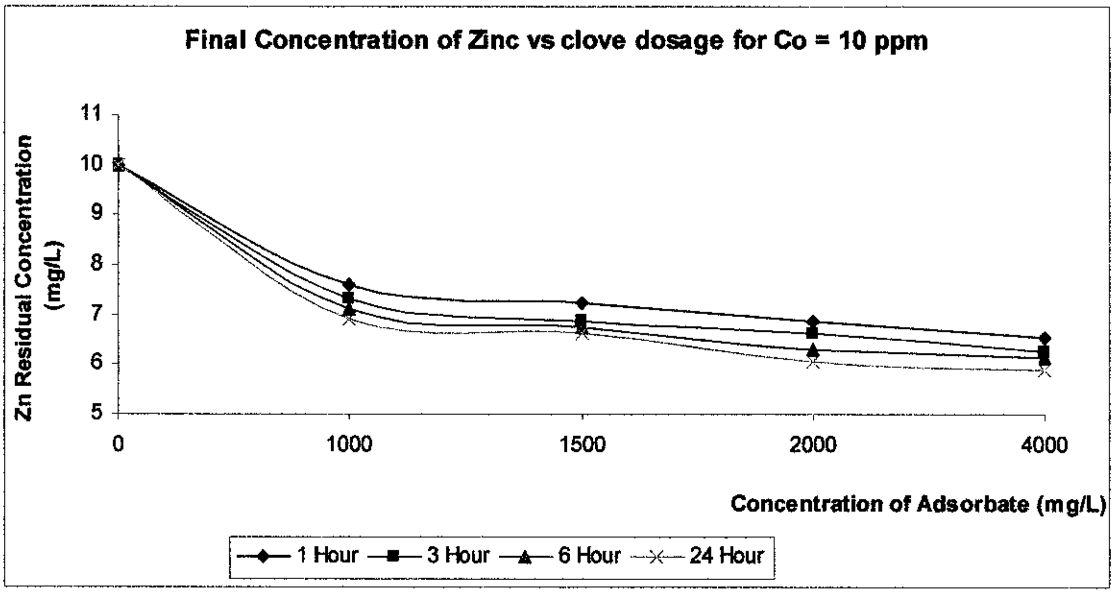

Figure 22: Final Concentration of Zinc vs adsorbent for Co = 10 ppm

Figure 22 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was clove in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows that the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

For these experiments, we can see that the difference between the graphs was not significant. This indicates that the amount of adsorbent was not varying enough to give a better graph. Particularly this is only for concentration of 10 ppm.

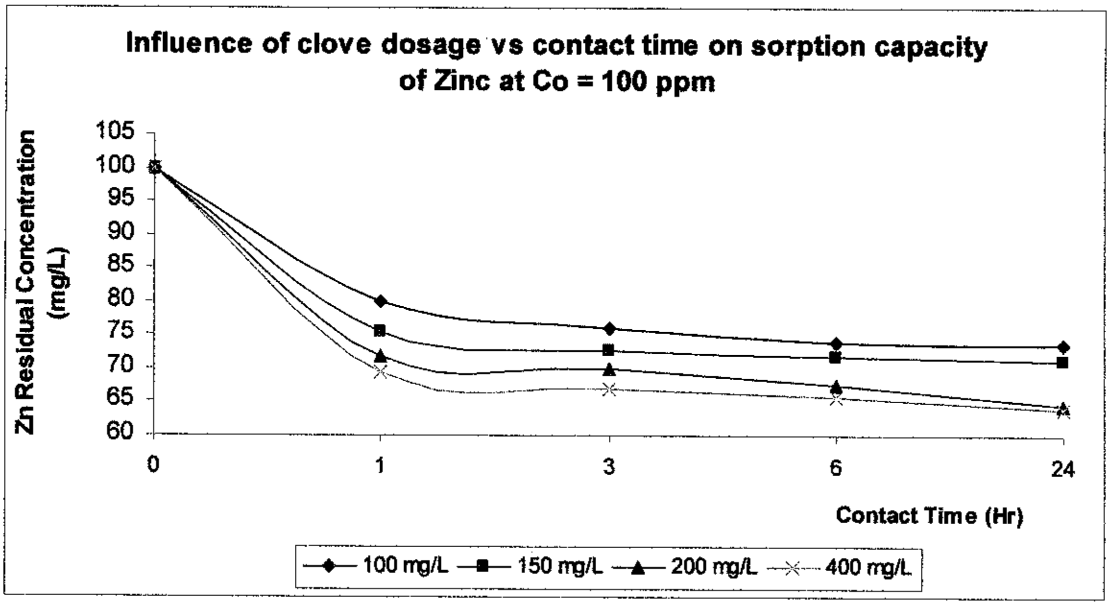

Figure 23: Influence clove dosage vs contact time on sorption capacity of Zinc Co = 100 ppm

Figure 23 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 100 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Base on the performance of all experiments using clove as the adsorbent, the lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 100 ppm of zinc, the best result is shown using 400 mg of clove in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 64 mg/L which mean 36 % of initial zinc is being absorbed. The graph also indicating that the adsorption is slowly reaching it limit.

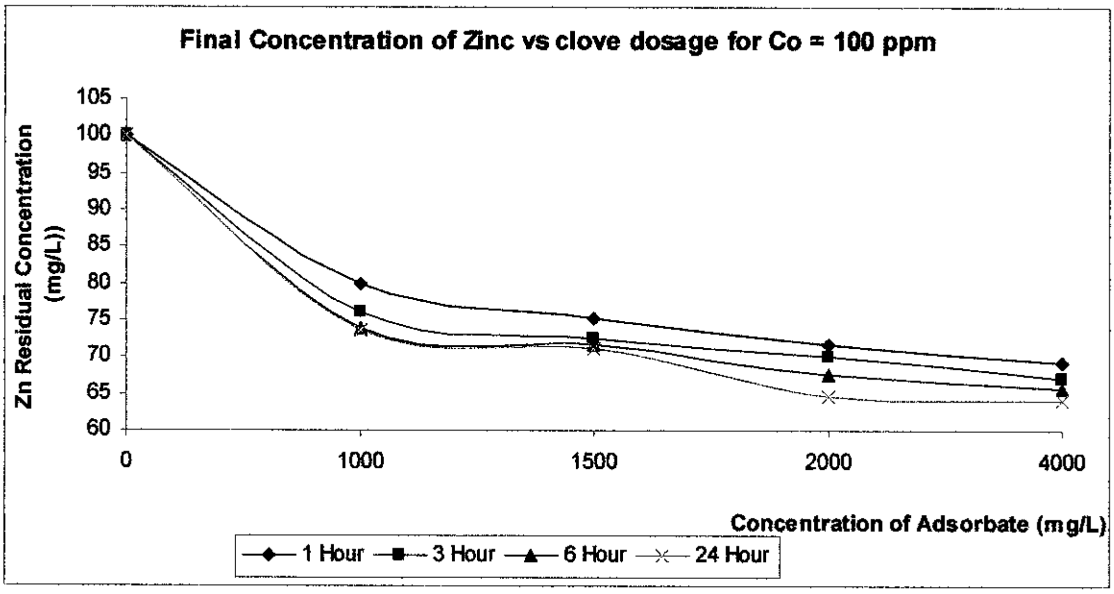

Figure 24: Final Concentration of Zinc vs adsorbent for Co = 100 ppm

Figure 24 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was clove in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows is same like the above graph, the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

For these experiments, there are significant prove that the higher the amount of adsorbent permitted the lower residual of zinc at the end of the experiment. But, comparing with others concentration of adsorbate, the result show the lowest capability of clove to adsorb zinc.

Base on the experiments results, clove shown higher absorbability when the concentration of Zinc is at the lowest, which is 1 ppm. The best graph show that at 1 ppm of Zinc, using 400 mg of clove as adsorbent at 24 hour of contact time has the best performance by adsorbing 91 percent of the initial zinc concentration.

The pH is detected between the range of 7 to 4 pH. Depending on the mass of the adsorbate, the higher the adsorbate the lower the pH. A statistical analysis was conducted on the results of the experiment. Analysis of variance (ANOVA) performed on the results showed that, 5% level of significant; the zinc removal was significantly affected by time of contact time and weight of adsorbent used.

4.3.2 Adsorption Isotherm

The relation between the initial concentration of Zinc and its percentage removal from solution was studied for all adsorbents included in the study. The initial concentrations of Zinc studied were 1, 10 and 100 mg/L at an adsorbent concentration of 100, 150, 200 and 400 mg/L. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e.

The Langmuir constants q_m and b are related to the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage) and energy of adsorption, respectively. The highest value of adsorption capacity q_m (maximum uptake) of clove is 3.03 mg/g using 1 ppm of Zinc at 24 hour contact time. While the value of b, the Langmuir constant is indicate at 1.23. Linear plots of 1/q versus $1/C_e$ in Figure 25 were employed to determine the value of q_m (mg/g) and b (L/mg).

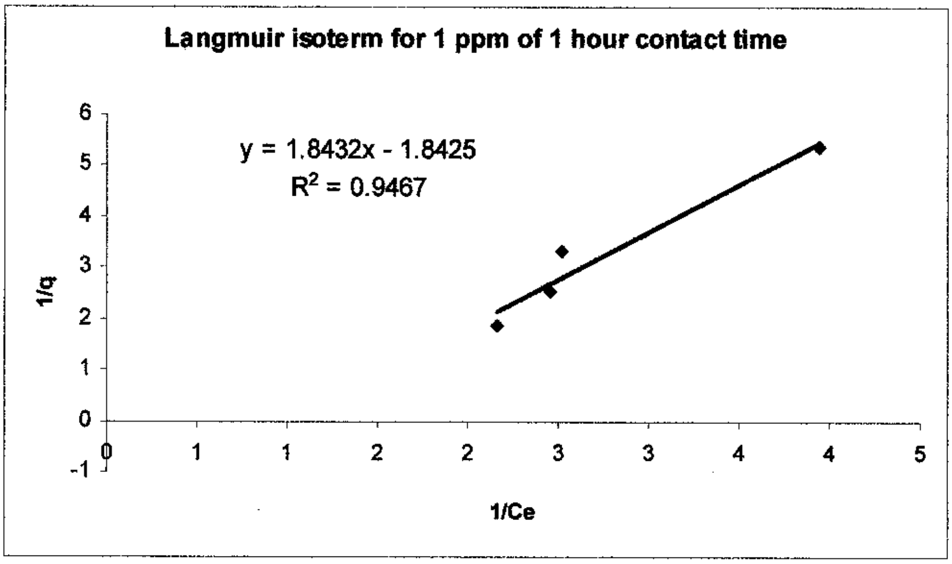

Figure 25: Langmuir plot for the adsorption of Zinc by clove, adsorbate 1 ppm and contact time 1 hour

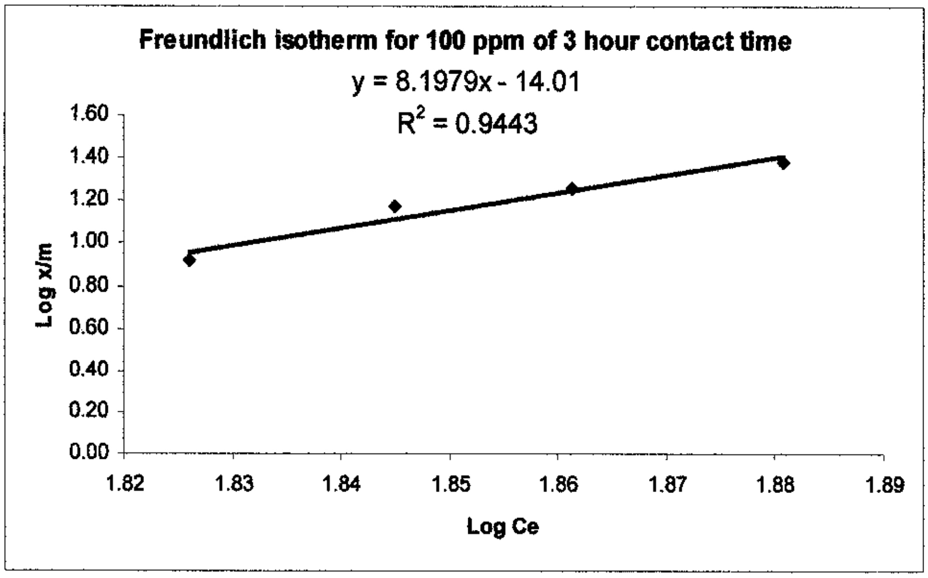

Figure 26: Freundlich plot for the adsorption of Zinc by clove, adsorbate 100 ppm and contact time 3 hour

The constants K_f and n of Freundlich Isotherm were calculated base on the plots in Figure 26 above. The highest value of Freundlich constant, K_f is 3.25 while n value is 1.06. This is base on experiment using 1 ppm of Zinc at 24 hour contact time.

4.4 Use of Star Anise as Natural Adsorbent

4.4.1 Adsorption of Zinc

Figure 27 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 1 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Base on the performance of all experiments using star anise as the adsorbent, the lower the concentration, the lower the final residual of zinc that left. In this particular experiment using 1 ppm of zinc, the best result is shown using 400 mg of star anise in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 0.18 mg/L which mean 82 % of initial zinc is being absorbed. This result is the best comparing with other experiments using different concentration of adsorbate.

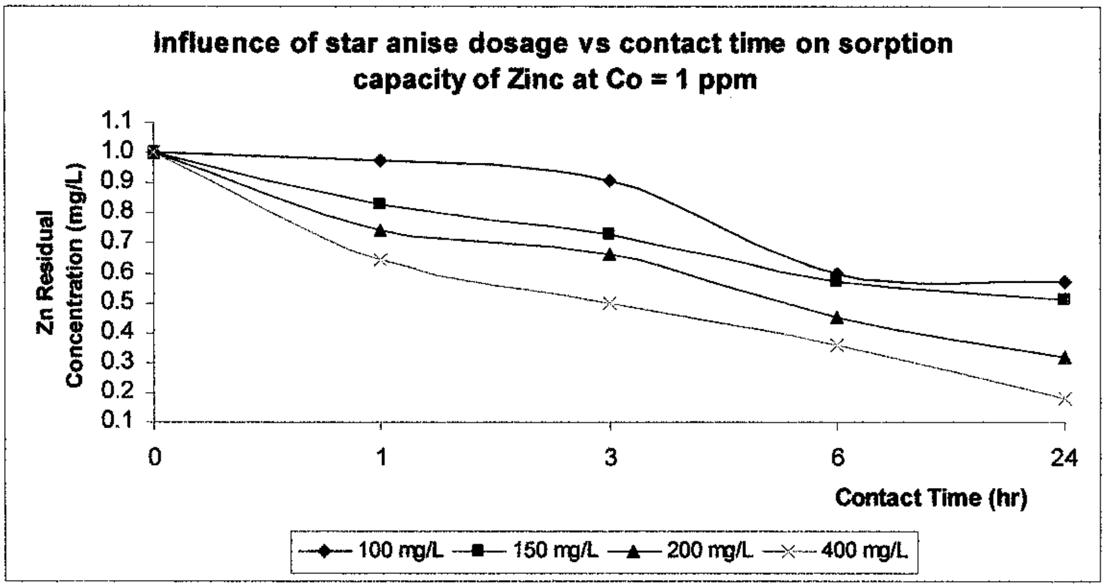

Figure 27: Influence of star anise dosage vs contact time on sorption capacity of Zinc Co = 1 ppm

Figure 28 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was star anise in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows that the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

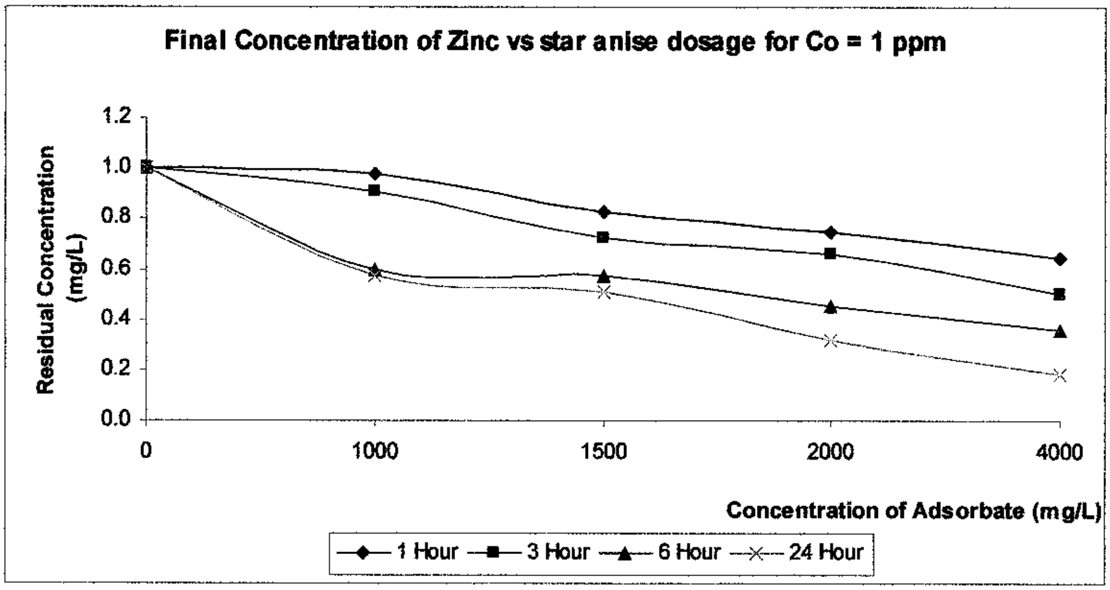

Figure 28: Final Concentration of Zinc vs adsorbent for Co = 1 ppm

Figure 29 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 10 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Referring to the graph, lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 10 ppm of zinc, the best result is shown using 400 mg of star anise in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 7.77 mg/L which mean 22.3 % of initial zinc is being absorbed.

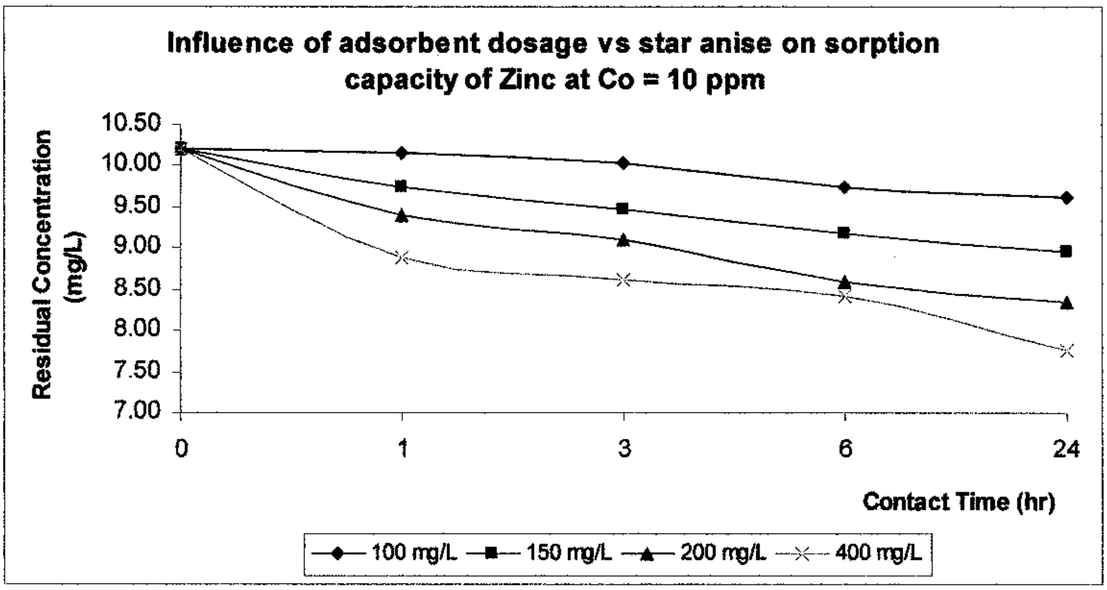

Figure 29: Influence of star anise dosage vs contact time on sorption capacity of Zinc Co = 10 ppm

Figure 30 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was star anise in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows that the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

It is consistence with the previous graph that indicates solution with the largest volume of adsorbent with the longest contact time will have best sorption capacity.

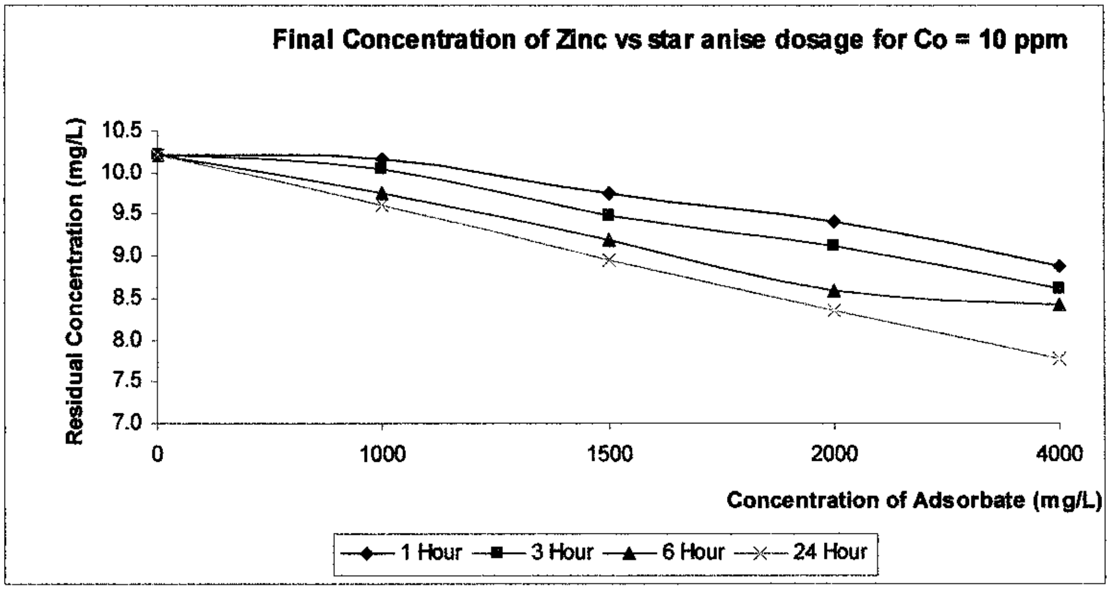

Figure 30: Final Concentration of Zinc vs adsorbent for Co = 10 ppm

Figure 31 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 100 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Base on the performance of all experiments using star anise as the adsorbent, the lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 100 ppm of zinc, the best result is shown using 400 mg of star anise in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 83.67 mg/L which mean 16.33% of initial zinc is being absorbed.

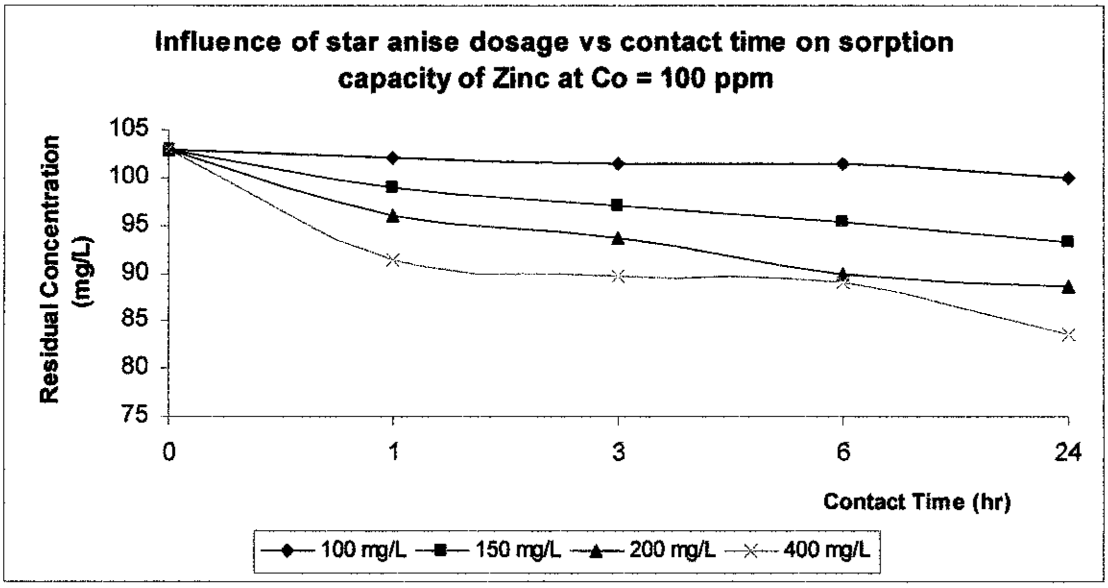

Figure 31: Influence of star anise dosage vs contact time on sorption capacity of Zinc Co = 100 ppm

Figure 32 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was star anise in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows is same like the above graph, the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

For these experiments, there are significant prove that the higher the amount of adsorbent permitted the lower residual of zinc at the end of the experiment. However, comparing with others concentration of adsorbate, the results show the lowest capability of star anise to adsorb zinc.

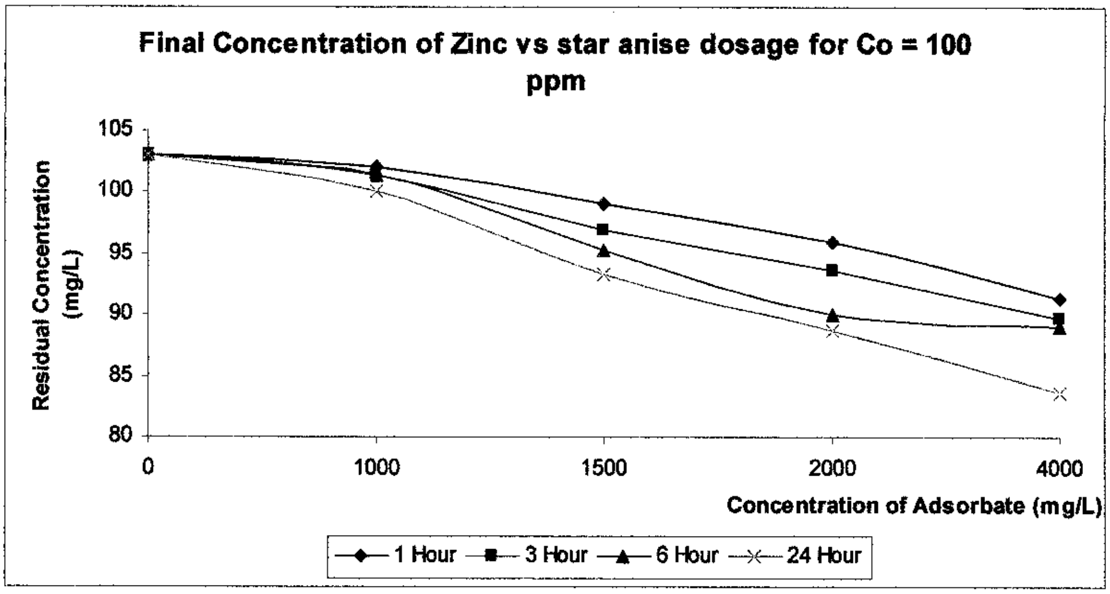

Figure 32: Final Concentration of Zinc vs adsorbent for Co = 100 ppm

Base on the experiments results, star anise shown higher absorbability when the concentration of Zinc is at the lowest, which is 1 ppm. The best graph show that at 1 ppm of Zinc, using 400 mg of star anise as adsorbent at 24 hour of contact time has the best performance by adsorbing 82 percent of the initial zinc concentration.

The pH is detected between the range of 7 to 4 pH. Depending on the mass of the adsorbate, the higher the adsorbate the lower the pH. A statistical analysis was conducted on the results of the experiment. Analysis of variance (ANOVA) performed on the results showed that, 5% level of significant, the zinc removal was significantly affected by time of contact time and weight of adsorbent used.

4.4.2 Adsorption Isotherm

The relation between the initial concentration of Zinc and its percentage removal from solution was studied for all adsorbents included in the study. The initial concentrations of Zinc studied were 1, 10 and 100 mg/L at an adsorbent concentration of 100, 150, 200 and 400 mg/L. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e.

The Langmuir constants q_m and b are related to the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage) and energy of adsorption, respectively. The highest value of adsorption capacity q_m (maximum uptake) of star anise is 0.68 mg/g using 1 ppm of Zinc at 24 hour contact time. While the value of b, the Langmuir constant is indicate at 0.402. Linear plots of 1/q versus $1/C_e$ in Figure 33 were employed to determine the value of q_m (mg/g) and b (L/mg).

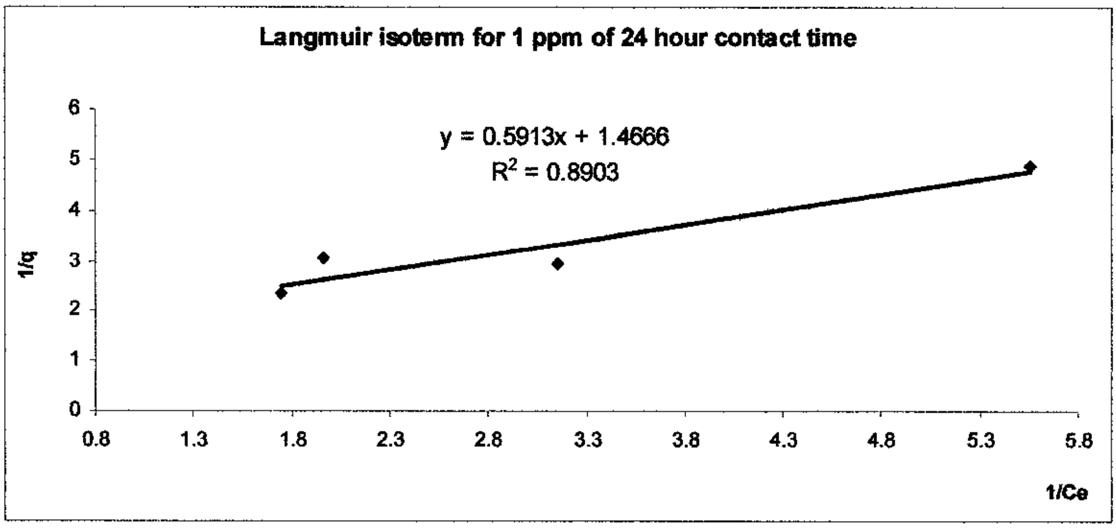

Figure 33: Langmuir plot for the adsorption of Zinc by star anise, adsorbate 1 ppm and contact time 24 hour

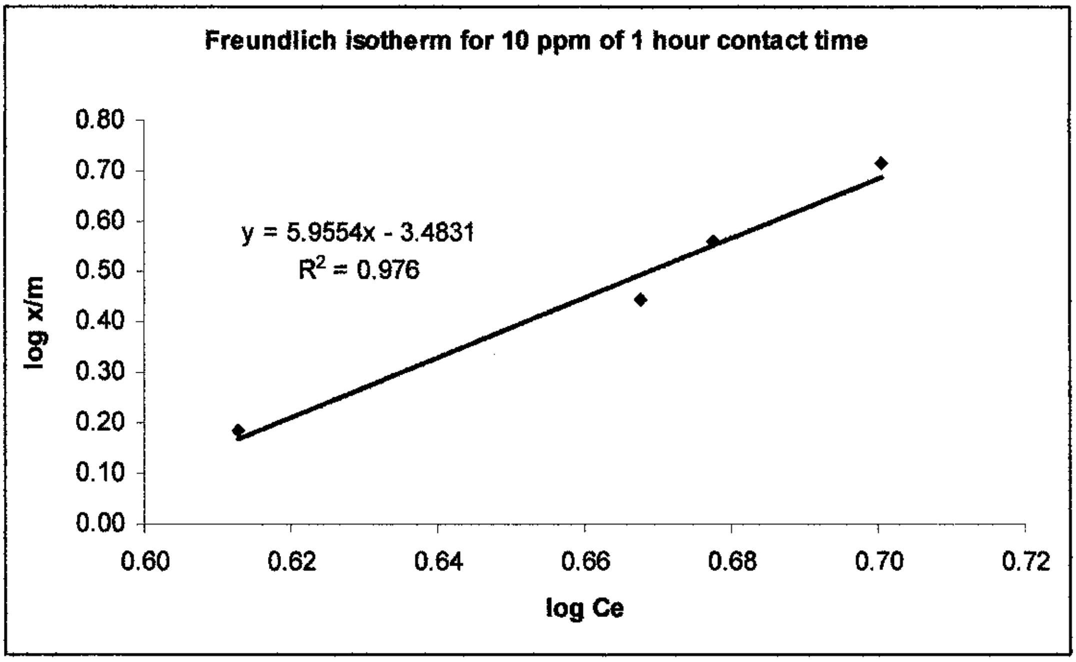

Figure 34: Freundlich plot for the adsorption of Zinc by star anise, adsorbate 10 ppm and contact time 1 hour

The constants K_f and n of Freundlich Isotherm were calculated base on the plots in Figure 34 above. The highest value of Freundlich constant, K_f is 0.54 while n value is 1.89. This is base on experiment using 1 ppm of Zinc at 24 hour contact time.

4.5 Use of Cinnamon as Natural Adsorbent

4.5.1 Adsorption of Zinc

Figure 35 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 1 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Base on the performance of all experiments using cinnamon as the adsorbent, the lower the concentration, the lower the final residual of zinc that left. In this particular experiment using 1 ppm of zinc, the best result is shown using 400 mg of star anise in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 0.13 mg/L which mean 87 % of initial zinc is being absorbed. This result is the best comparing with other experiments using different concentration of adsorbate.

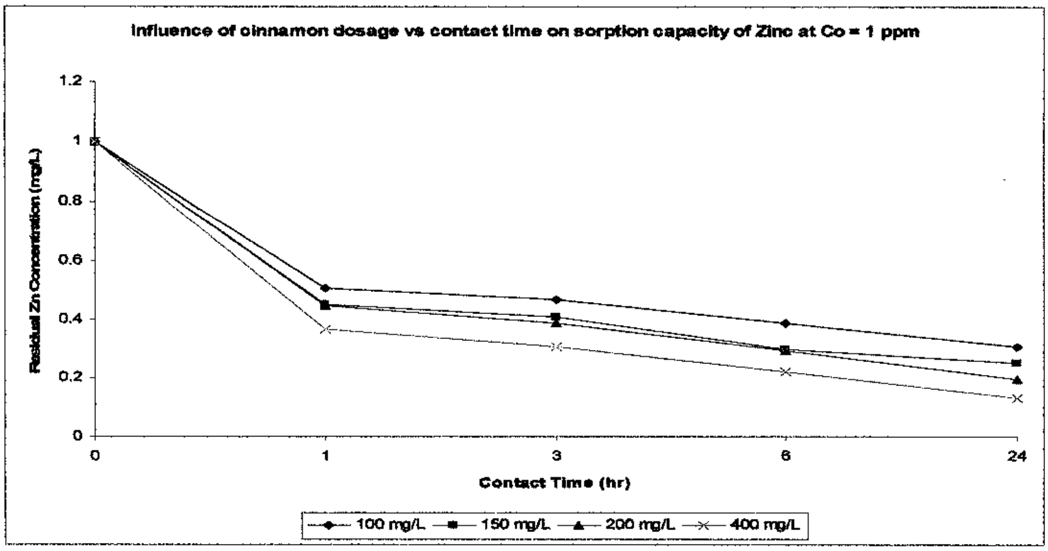

Figure 35: Influence of date cinnamon vs contact time on sorption capacity of Zinc Co = 1 ppm

Figure 36 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was star anise in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows that the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

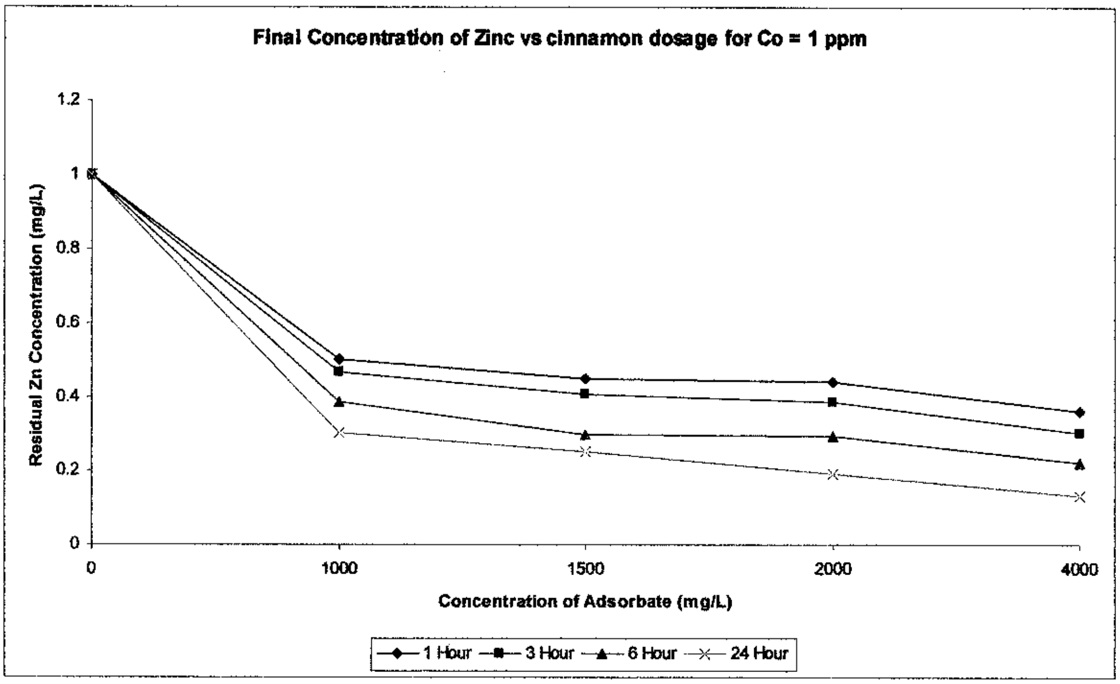

Figure 36: Final Concentration of Zinc vs adsorbent for Co = 1 ppm

Figure 37 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 10 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Referring to the graph, lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 10 ppm of zinc, the best result is shown using 400 mg of star anise in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 6.3 mg/L which mean 37 % of initial zinc is being absorbed.

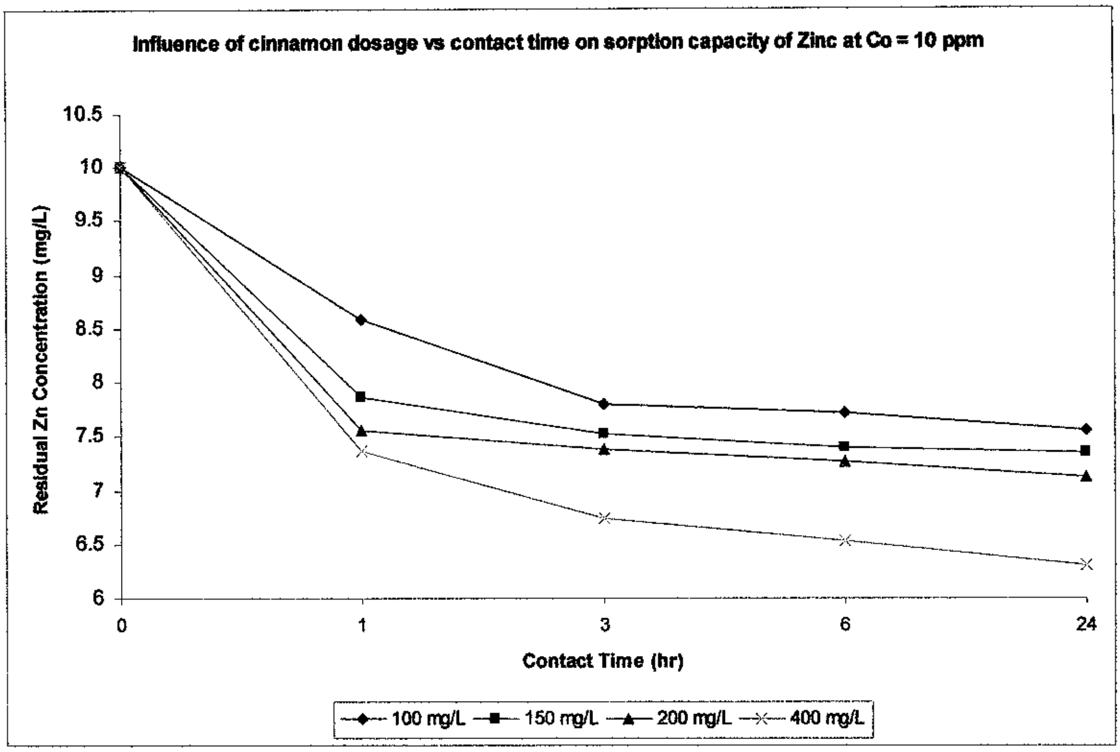

Figure 37: Influence of cinnamon dosage vs contact time on sorption capacity of Zinc Co = 10 ppm

Figure 38 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was cinnamon in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows that the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

It is consistence with the previous graph that indicates solution with the largest volume of adsorbent with the longest contact time will have best sorption capacity.

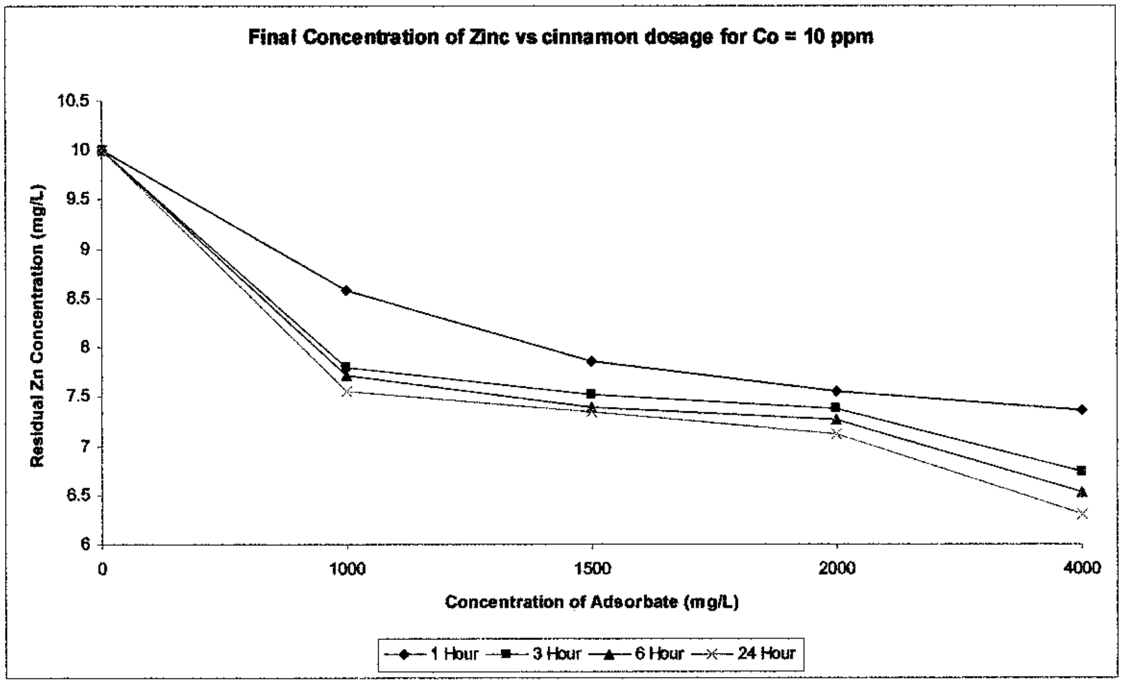

Figure 38: Final Concentration of Zinc vs adsorbent for Co = 10 ppm

Figure 39 shows final concentration of zinc against adsorbent dosage for zinc against adsorbent dosage for zinc initial concentration of 100 mg/L by varying time at 1, 3, 6 and 24 hours. The graph shows that the same hour contact hour, the higher the adsorbent dosage, the lower final concentration becomes. For the same amount of adsorbent dosage, longer contact time resulted in lower final concentration compared with shorter duration.

Base on the performance of all experiments using cinnamon as the adsorbent, the lower the concentration, the lower the final residual of Zinc that left. In this particular experiment using 100 ppm of zinc, the best result is shown using 400 mg of star anise in 100 milliliter zinc solution. The result prove that after 24 hours the zinc is left at 68 mg/L which mean 32% of initial zinc is being absorbed.

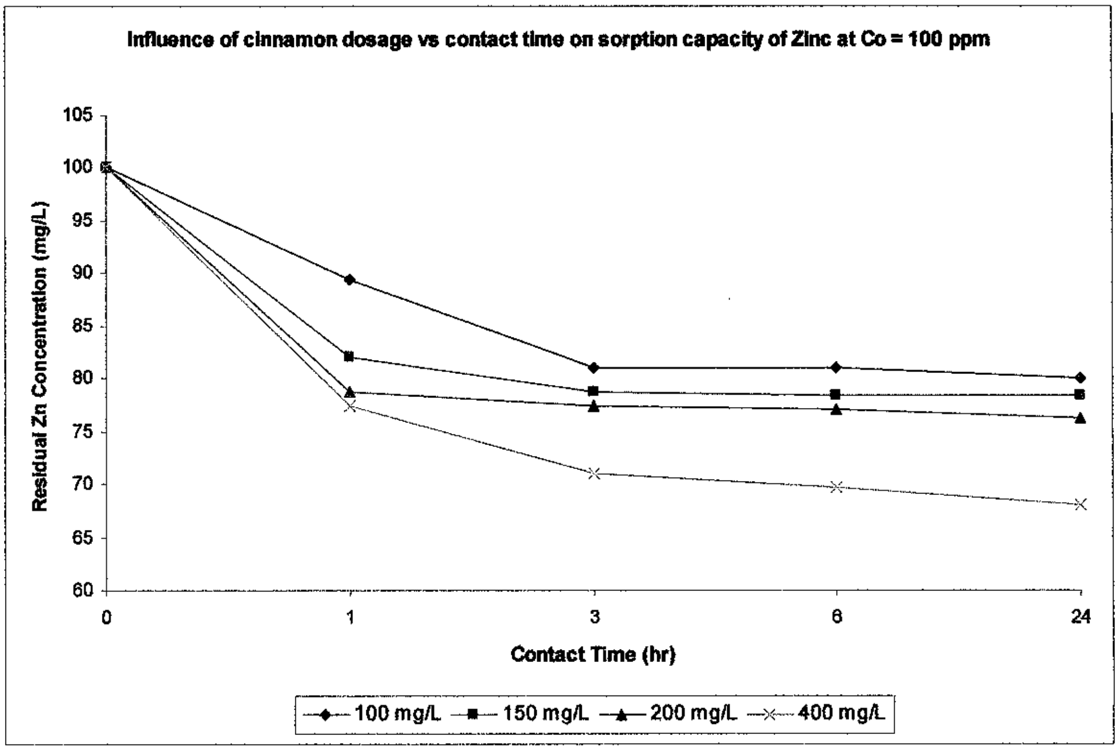

Figure 39: Influence of cinnamon dosage vs contact time on sorption capacity of Zinc Co = 100 ppm

Figure 40 shows final concentration of zinc against time 1, 3, 6, and 24 hours at varied adsorbent quantity. The adsorbent used was cinnamon in amount of 1000, 1500, 2000 and 4000 mg/L.

The trend shows is same like the above graph, the longer contact time resulted in lower final concentration. For the same period of contact time, larger dosage removed more zinc compared to less adsorbent used. The result show that the best result is at 24 hour contact time with the highest dosage of adsorbent.

For these experiments, there are significant prove that the higher the amount of adsorbent permitted the lower residual of zinc at the end of the experiment. However, comparing with others concentration of adsorbate, the results show the lowest capability of star anise to adsorb zinc.

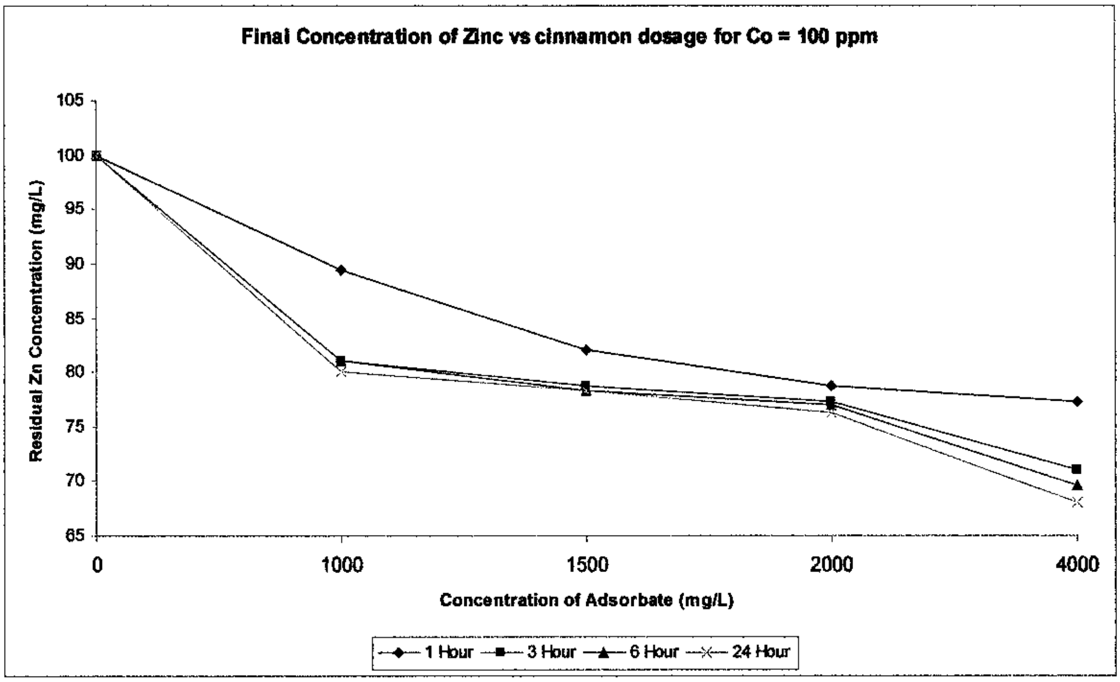

Figure 40: Influence of cinnamon dosage vs contact time on sorption capacity of Zinc Co = 100 ppm

Base on the experiments results, star anise shown higher absorbability when the concentration of Zinc is at the lowest, which is 1 ppm. The best graph show that at 1 ppm of Zinc, using 400 mg of cinnamon as adsorbent at 24 hour of contact time has the best performance by adsorbing 87 percent of the initial zinc concentration.

The pH is detected between the range of 7 to 4 pH. Depending on the mass of the adsorbate, the higher the adsorbate the lower the pH. A statistical analysis was conducted on the results of the experiment. Analysis of variance (ANOVA) performed on the results showed that, 5% level of significant, the zinc removal was significantly affected by time of contact time and weight of adsorbent used.

4.5.2 Adsorption Isotherm

The relation between the initial concentration of Zinc and its percentage removal from solution was studied for all adsorbents included in the study. The initial concentrations of Zinc studied were 1, 10 and 100 mg/L at an adsorbent concentration of 100, 150, 200 and 400 mg/L. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e.

The Langmuir constants q_m and b are related to the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage) and energy of adsorption, respectively. The highest value of adsorption capacity q_m (maximum uptake) of cinnamon is 3.66 mg/g using 100 ppm of Zinc at 3 hour contact time. While the value of b, the Langmuir constant is indicate at 0.33. Linear plots of 1/q versus $1/C_e$ in Figure 33 were employed to determine the value of q_m (mg/g) and b (L/mg).

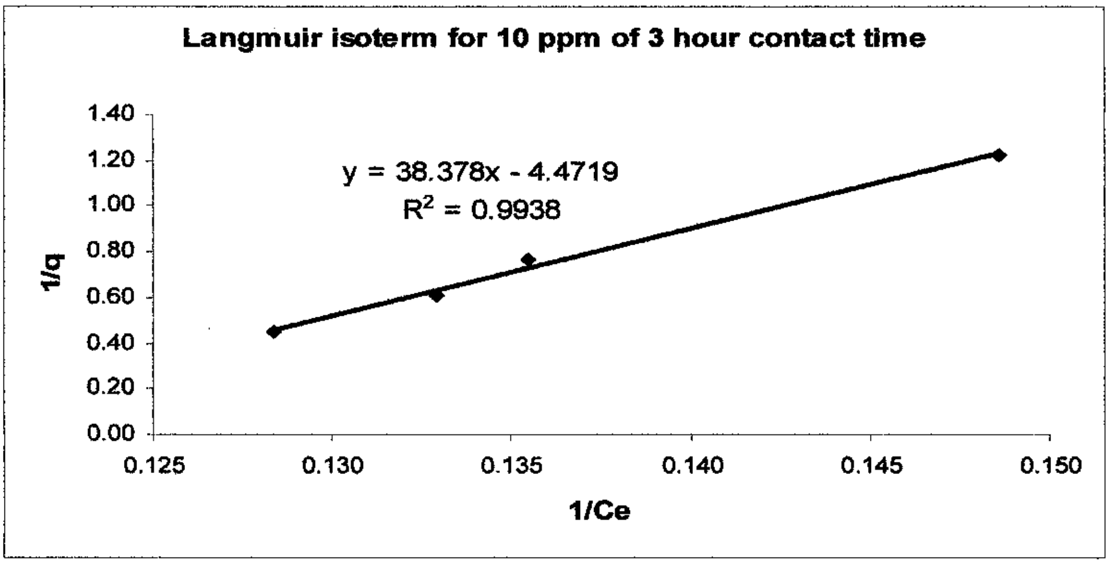

Figure 41: Langmuir plot for the adsorption of Zinc by cinnamon, adsorbate 10 ppm and contact time 3 hour

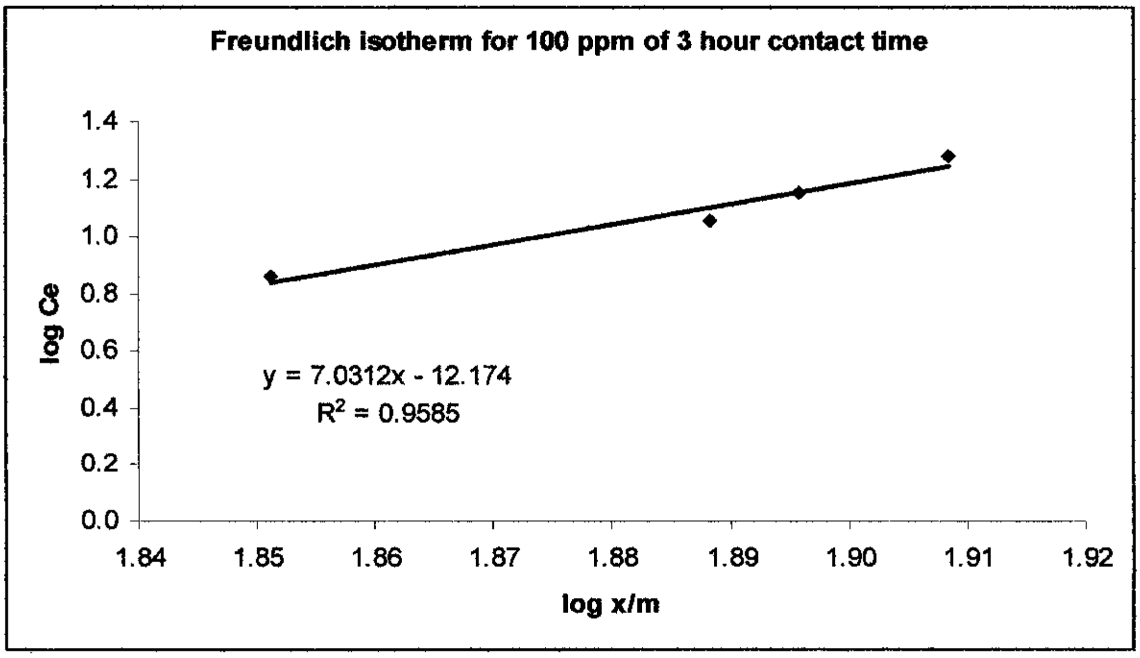

Figure 42: Freundlich plot for the adsorption of Zinc by cinnamon, adsorbate 100 ppm and contact time 3 hour

The constants K_f and n of Freundlich Isotherm were calculated base on the plots in Figure 34 above. The highest value of Freundlich constant, K_f is 5.44 while n value is 3.57. This is base on experiment using 1 ppm of Zinc at 1 hour contact time.

5. CONCLUSIONS

In this study, batch adsorption experiments for the removal of Zinc from aqueous solutions have been carried out using four different adsorbents. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and adsorbent dosages. The obtained results can be summarized as follows:

a) Molecular sieve or by the market named, molinex was not a suitable material that can function as adsorbent. We can safely justify that molinex containing zinc element, base on the result from the experiment. Thus, it was not suitable to be candidate as natural adsorbent in this research.

b) Sewage sludge ash (SSA) also was not practical to be use as adsorbent in this FYP project due to the time consuming preparation. It was highly recommended that SSA research can be further study by the post graduate students, due to it high potential possibility to be use as natural adsorbent due to it abundance and low cost.

c) For all experiments involving clove, star anise and cinnamon, pH is between range of 7 to 4 pH. For all case the higher the concentration of the adsorbent, the solution will become more acidic. While, for date seed the pH was recorded between 5 to 8 pH. The higher the concentration of date seeds in the solution, the pH will become more alkaline in nature. Base on the solubility curve, zinc will start precipitate on pH 10. It proves that there is no possibility of precipitation of zinc in all of the experiments

d) The highest percentage of removal of zinc using date seeds was 92 % with 4000 mg/L concentration at 24 hours contact time. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both the models were fitted well. The highest adsorption capacity was obtained 1.58 mg/g for date seed. While the Kf value was 1.41 and n value was 1.48.

e) For clove, the highest percentage of removal of zinc was 91 % using 4000 mg/L concentration at 24 hours contact time. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both the models were fitted well. The highest adsorption capacity was obtained 3.03 mg/g for clove. While the Kf value was 3.5 and n value was 1.06.

f) The highest percentage of removal of zinc using star anise was 82 % with 4000 mg/L concentration at 24 hours contact time. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both the models were fitted well. The highest adsorption capacity was obtained 0.68 mg/g for star anise. While the Kf value was 0.54 and n value was 1.89.

g) While for cinnamon, the highest percentage of removal of zinc was 87 % using 4000 mg/L concentration at 24 hours contact time. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both the models were fitted well. The highest adsorption capacity was obtained 5.44 mg/g for cinnamon. While the Kf value was 5.44 and n value was 3.57.

Adsorbents	**Highest Percentage Removal of Zinc (%)**	**Maximum Adsorption capacity (mg/g)**	**Kf**	**n**
Date Seeds	92	1.58	1.41	1.48
Clove	91	3.03	3.5	1.06
Star Anise	82	0.68	0.54	1.89
Cinnamon	87	5.44	5.44	3.57

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APPENDIXES

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Removal of Cu^{2+} and Zn^{2+} in Aqueous Solutions by Sorption onto Fly Ash and Fly Ash Mixtures

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KEYWORDS : Fly ash, sorption, metal ions, water treatment

ABSTRACT

Several studies have pointed out ash efficiency in the removal of heavy metal ions present in aqueous solutions. Contact time, pH and ash origin seem to be the major operating parameters in the metal concentration control. The mechanisms of interactions between metal and solid are a function of pH and are found to be precipitation, adsorption or ion exchange as discussed in previous papers. The objectives of this work were to study the removal of Cu^{2+} and Zn^{2+} in water by sorption onto fly ash and fly ash mixtures. The stability of the resulting cake was also approached in term of leaching capability. Experimental design methodology was used in order to identify influential parameters and to evaluate their interactions. Temperature, fly ash to ion concentration ratio, and ash quality were particularly studied. Different ashes and a mixture were investigated. Fly ash and fly ashes mixture investigated in this study, have alkaline reaction in water, especially one of them, and allow to control the pH of the solution without lime addition. Final metal ion concentration in solution, sorption capacity and ion leaching were determined. The results are discussed in order to get the optimal operating parameters in terms of ion control and industrial developments to remove and stabilize heavy metal ions present in wastewater.

INTRODUCTION

Because of the widespread pollution of water and soil by industrial activities, water treatments have been the subject of numerous investigations. Elsewhere control and reduction of waste volume in landfills are being taken into account. As a matter of fact, fly ash is considered as a waste. Nevertheless, so far fly ash has been the more often used as an additive in cement industry [1] due to the pozzolanic and cementitious properties [2, 3]. Moreover, fly ash is an efficient adsorbent for water treatment concerning removal of DOC (Dissolved Organic Carbon) [4, 5] and suspended solids [6, 7]. Several studies have also pointed out its efficiency in the removal of heavy metallic ions in aqueous phase [8 - 11]. Coal fly ash is a cheap adsorbent since they are widely available. Their alkaline property makes them interesting for use in water treatment for the precipitation of metallic ions, by analogy with lime treatment, as it was already shown [8]. The aim of this study was to assess the influence of three parameters on the removal of Cu^{2+} and Zn^{2+} : temperature, metal ion/adsorbent ratio and ash quality. Two fly ashes and a mixture of them were investigated. The pH of the solution was controlled without lime addition. Experimental design methodology was used to identify influential parameters and to assess their interactions. The stability of the resulting cake was also approached in term of leaching capability.

MATERIAL AND METHODS

Adsorbent

Coal fly ash used in these experiments result from different pulverised-coal power plants in France. The fly ashes were used without pre-treatment. Table 1 shows the chemical composition of the fly ashes.

Table 1. Chemical composition of three different fly ashes (% by weight)

Constituent	A fly ash	B fly ash	C Fly ash
Lime	16.7 %	0.6 %	0.1 %
CaO	23.6 %	6.8 %	2 %
SiO_2	16.2 %	48 %	52.3 %
Al_2O_3	7.2 %	22.8 %	36.4 %
Fe_2O_3	5.5 %	9.6 %	4.2 %
Unburned particles	1.2 %	9.6 %	2.7 %

The mixture has been prepared with the A fly ash and C fly ash in ratio providing a final lime composition of 5%. In this case, fly ashes were mixed in water, and then dried at 105°C.

Adsorption experiments

Experiments were carried out in 1 L glass flashes tightly closed at two temperatures, 30°C and 60°C, introducing sorbent in 0.5 L of $ZnCl_2$ or $CuCl_2$ ion solution (500 $mg.L^{-1}$ of Zn^{2+} or Cu^{2+}). The pH was set at the desired value with HCl 36% and 1M and NaOH 1M. The pH was maintained at 5 ± 0.5. For each experiment, control and regulation of pH were made every day. The salinity of the solution was adjusted to 5 $g.L^{-1}$ with NaCl. Solutions were stirred continuously. 7 days were necessary to reach equilibrium conditions of experiments. Every day, samples were filtered through 0.45 μm membrane, and metallic ion concentrations were determined by a flame atomic absorption spectrometer (Perkin Elmer model 2280).

Leaching experiments

Leaching experiments were carried out on contaminated sorbents after a drying period of one week, using a procedure derived from French standard [15]. A liquid / solid mass ratio of 10 (5 g of solid for 50 mL of solution) was observed and solutions were stirred for 24 hours at 150 rpm in a rotating movement. Three leaching solutions were used, either characterized by their resistivity (permuted water with a resistivity at least equal to 0.2 MΩ.cm) or their pH (pH 2, pH 4.6) set by adding HCl 1 M, NaOH 1 M and acetic / acetate buffer solution.

RESULTS AND DISCUSSION

Factorial design for adsorption experiments

The influence of the parameters, temperature, metal/adsorbent ratio and fly ash composition, on the removal of ions onto fly ash, were studied through a screening design [16].

The adsorption experimental conditions are presented in table 2, as well as the parameters and their two levels (-1; +1).

Table 2. Screening design for adsorption experiments

Exp.	Temperature (°C)	Metal/adsorbent mass ratio
# 1	30	0.005
# 2	60	0.005
# 3	30	0.01
# 4	60	0.01
Level -1	30	0.005
Level +1	60	0.01

The results were interpreted by computation of the parameter weights. The influence of the parameters on adsorption is screened on table 3. The information reported is the importance of the factor (weight) and the eventual interaction between the factors. Responses considered for the adsorption are the equilibrium concentration C_e and the equilibrium adsorption capacity Q_e accounting the initial concentration and the adsorbent mass involved.

Table 3. Experimental results given in $mg.L^{-1}$ for adsorption of Cu^{2+} and Zn^{2+} ; A : average, T : temperature, R : metal/adsorbent ratio, T.R : interaction between the two factor

	A fly ash		A/C fly ash		B fly ash	
			Copper			
Parameter	C_e ($mg.L^{-1}$)	Q_e ($mg.g^{-1}$)	C_e ($mg.L^{-1}$)	Q_e ($mg.g^{-1}$)	C_e ($mg.L^{-1}$)	Q_e ($mg.g^{-1}$)
A	71	6	76,2	5,8	88,1	5,7
T	-25,5	0,4	-31,6	0,5	-53,9	0,9
R	16,5	1,6	17,2	1,7	26,4	1,6
T.R	-15,8	0,4	-5,9	0,2	-18,0	0,5
			Zinc			
Parameter	C_e($mg.L^{-1}$)	Q_e($mg.g^{-1}$)	C_e($mg.L^{-1}$)	Q_e($mg.g^{-1}$)	C_e($mg.L^{-1}$)	Q_e($mg.g^{-1}$)
A	338,9	1,6	317,4	1,9	293,7	2,2
T	-32,26	0,4	-60,9	0,8	-91,4	1,4
R	39,99	-0,1	34,7	0,2	59,3	-0,1
T.R	-1,61	0,1	11,0	0,1	31,2	0

Table 4. Experimental results given in percentage for adsorption of Cu^{2+} and Zn^{2+} ; A : average, T : temperature, R : metal/adsorbent ratio, T.R : interaction between the two factor

	A fly ash		A/C fly ash		B fly ash	
			Copper			
Parameter	C_e	Q_e	C_e	Q_e	C_e	Q_e
A	55,1%	71,4%	58,2%	70,7%	47,3%	65,5%
T	**19,8%**	4,8%	**24,1%**	6,1%	**28,9%**	10,3%
R	12,8%	**19%**	13,1%	**20,7%**	14,2%	**18,4%**
T.R	12,3%	4,8%	4,5%	2,4%	9,6%	5,8%

	Zinc					
Parameter	C_e	Q_e	C_e	Q_e	C_e	Q_e
A	82,1%	72,8%	74,8%	63,3%	61,7%	59,5%
T	7,8%	**18,2%**	**14,4%**	**26,7%**	**19,2%**	**37,8%**
R	**9,7%**	4,5%	8,2%	6,7%	12,5%	2,7%
T.R	0,4%	4,5%	2,6%	3,3%	6,6%	0%

According to these results, globally the greatest removal is achieved for copper. In term of C_e results, adsorption is optimized with an increasing temperature. Temperature is the most influential parameter for adsorption of Cu^{2+} and Zn^{2+}. In term of Q_e, addition of fly ash decreased the adsorption capacity. The ratio parameter has a lowest influence on zinc removal. Zinc is less adsorbed than copper and an addition of fly ash would change the equilibrium less efficiently. The quality of fly ash has a low influence on zinc removal. However, differences are shown between fly ashes. A fly ash (high lime composition) is the most efficient for the removal of copper. The fly ash mixture is slightly more efficient than B fly ash.

Leaching experiments

The solutions used for leaching tests had either a pH of 4.6 and 7, or a strong resistivity. The results obtained are reported in the tables 4, 5 and 6. The responses considered for the leaching tests, are the leached concentration of Cu^{2+} and Zn^{2+} ions ($C_{leached}$) and the leached percentage ($P_{leached}$).

Table 5 : Leachability of Cu^{2+} and Zn^{2+} for B fly ash

		final pH	$[Cu^{2+}]_{leached}$ (mg.L^{-1})	$P_{leached}$ % $[Cu^{2+}]$	final pH	$[Zn^{2+}]_{leached}$ (mg.L^{-1})	$P_{leached}$ % $[Zn^{2+}]$
# 1	Acetate buffer	4,8	288,2	77,3	4,6	74,6	76,1
	pH 2	4,8	170,5	45,7	4,2	61,0	62,2
	Permuted water	7,9	0,1	0	7,2	2,1	2,1
# 2	Acetate buffer	4,8	288,9	64,6	4,7	223,5	59,4
	pH 2	4,6	150,3	33,6	4,6	124,8	33,2
	Permuted water	7,3	0,2	0	7,3	1,6	0,4
# 3	Acetate buffer	4,7	236,4	80,1	4,6	42,3	124,4
	pH 2	4,5	165,4	56,1	4,0	37,1	109,1
	Permuted water	6,9	0,1	0	6,5	5,4	15,9
# 4	Acetate buffer	4,7	319,6	74,7	4,6	124,1	70,9
	pH 2	4,7	139,7	32,6	4,4	93,4	53,4
	Permuted water	6,8	0,2	0	6,8	6,4	3,6

Table 6 : Leachability of Cu^{2+} and Zn^{2+} for A/C fly ash mixture

		pH final	$[Cu^{2+}]_{leached}$ (mg.L^{-1})	$P_{leached}$ % $[Cu^{2+}]$	final pH	$[Zn^{2+}]_{leached}$ (mg.L^{-1})	$P_{leached}$ % $[Zn^{2+}]$
# 1	Acetate buffer	4,7	381,8	99,2	4,7	88,3	94,9
	pH 2	5,1	89,7	23,3	5,3	62,2	66,9
	Permuted water	6,3	1,0	0,25	6,2	14,8	15,9
# 2	Acetate buffer	4,3	379,4	87	4,6	196,3	81,4
	pH 2	4,9	72,1	16,5	5,3	79,9	33,1
	Permuted water	6,5	0,2	0	6,6	9,4	3,9
# 3	Acetate buffer	4,7	354,6	104	4,6	53,9	98
	pH 2	5,0	75,7	22,2	5,0	35,6	64,7
	Permuted water	6,2	1,1	0,3	5,9	10,9	19,8
# 4	Acetate buffer	4,5	418,8	101	4,7	138,2	93,4
	pH 2	5,0	56,5	13,7	5,5	56,3	38
	Permuted water	6,8	0,15	0	6,7	7,7	5,2

The leaching test for the A fly ash has been realized on a metallic ions solution issued from an industrial effluent. In this case, pH has not been controlled during the adsorption phase. Metal ions were entirely removed by fly ash during adsorption. The leaching experiments are summarised in table 6.

Table 7 : Leachability of Cu^{2+} and Zn^{2+} for A fly ash

		pH final	$[Cu^{2+}]_{leached}$ (mg.L^{-1})	$P_{leached}$ % $[Cu^{2+}]$	final pH	$[Zn^{2+}]_{leached}$ (mg.L^{-1})	$P_{leached}$ % $[Zn^{2+}]$
# 1	Acetate buffer	5,2	5,8	62,4	5,2	119,9	56,8
	pH 2	12,3	0,1	1,1	12,3	0	0
	Permuted water	12,4	0,1	1,1	12,4	0	0
# 2	Acetate buffer	5,0	4,7	50,5	5,0	83,2	39,4
	pH 2	11,9	0,1	1,1	11,9	0	0
	Permuted water	12,3	0,1	1,1	12,3	0,1	0
# 3	Acetate buffer	5,2	24,3	66,4	5,2	503,0	55,1
	pH 2	12,4	0,1	0,3	12,4	1,2	0,1
	Permuted water	12,5	0,1	0,3	12,5	1,5	0,2
# 4	Acetate buffer	5,1	19,9	54,4	5,1	404,2	44,3
	pH 2	12,2	0,2	0,5	12,2	0,8	0,1
	Permuted water	12,5	0,2	0,5	12,5	0,7	0,1

According to the leaching experiments, pH is a major parameter. The leached percentage decreases as soon as pH exceeds a value around 5. Precipitation as well as adsorption is then supposed to occur between metal and solid.

CONCLUSION

The results obtained for adsorption of copper, and zinc ions onto fly ash show an increasing removal capacity with increasing temperature. Considering the isotherms Q_e versus C_e, three mechanisms, competition, adsorption, and precipitation, are observed. Removal efficiency of Cu^{2+} and Zn^{2+} is a function of fly ash quality, lime and silica composition. The effect of lime addition by mixing fly ash provides an equilibrium between the influence of lime on adsorption and the pH value on precipitation. In the case of fly ashes mixture, the stability of cake in term of leaching capability is obtained with permuted water leaching solution. Nevertheless, other formulations of the fly ashes mixture are needed to be realized in order to increase the removal of metal ions from industrial effluent and stability the resulting cakes.

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	(mg)	(mg/L)	1			Average	3			Average	6			Average	24			Average
1	25	250	0.01	0.04	0.11	**0.05**	0.02	0.07	0.02	**0.04**	0.37	0.46	0.17	**0.33**	0.55	0.45	0.37	**0.46**
2	50	500	0.06	0.04	0.08	**0.06**	0.25	0.06	0.02	**0.11**	0.39	0.35	0.38	**0.37**	0.22	0.67	0.58	**0.49**
3	100	1000	0.06	0.07	0.11	**0.08**	0.06	0.14	0.15	**0.12**	0.41	0.23	0.36	**0.33**	0.45	0.58	0.61	**0.55**
4	200	2000	0.12	0.11	0.18	**0.14**	0.15	0.12	0.19	**0.15**	0.55	0.60	0.36	**0.47**	0.69	0.44	0.61	**0.58**

Table 1: Result On Leachability Test (mollnex)

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
				1			Average	3			Average	6			Average	24			Average
1	25	250	155.00	153.00	149.00	152.00	**151.33**	147.00	134.00	153.00	**144.67**	136.00	146.00	132.00	**138.00**	129.00	134.00	123.00	**128.67**
2	50	500		146.00	150.00	153.00	**149.67**	130.00	143.00	136.00	**136.33**	127.00	125.00	139.00	**130.33**	142.00	132.00	109.00	**127.67**
3	100	1000		148.00	147.00	146.00	**147.00**	129.00	134.00	136.00	**133.00**	122.00	130.00	133.00	**128.33**	117.00	136.00	124.00	**125.67**
4	200	2000		148.00	143.00	146.00	**145.67**	130.00	123.00	74.00	**109.00**	65.00	120.00	129.00	**104.67**	8.00	123.00	129.00	**86.67**

Table 2: Result On Zinc Concentration Using Dates Seed as Adsorbent at 155 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
				1			Average	3			Average	6			Average	24			Average
1	100	1000	10.00	5.70	6.35	6.55	**6.20**	5.60	5.95	5.95	**5.83**	5.00	5.55	5.40	**5.32**	5.25	5.10	4.70	**5.02**
2	150	1500		6.35	5.60	6.35	**6.10**	5.15	5.20	5.35	**5.23**	4.40	5.40	5.35	**5.05**	4.45	5.05	4.78	**4.76**
3	200	2000		4.45	5.60	5.95	**5.33**	5.10	5.00	4.90	**5.00**	4.85	4.65	4.70	**4.73**	4.95	4.53	4.48	**4.65**
4	400	4000		5.15	5.60	5.20	**5.32**	4.30	4.40	4.60	**4.43**	4.00	4.65	4.35	**4.33**	4.00	4.25	4.05	**4.10**

Table 3: Result On Zinc Concentration Using Dates Seed as Adsorbent at 10 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
				1			Average	3			Average	6			Average	24			Average
1	100	1000	1.00	0.43	0.47	0.46	**0.45**	0.46	0.41	0.42	**0.43**	0.33	0.38	0.39	**0.37**	0.33	0.28	0.32	**0.31**
2	150	1500		0.42	0.43	0.39	**0.41**	0.29	0.30	0.31	**0.30**	0.23	0.27	0.26	**0.25**	0.24	0.28	0.28	**0.27**
3	200	2000		0.37	0.36	0.42	**0.38**	0.28	0.24	0.26	**0.26**	0.17	0.16	0.18	**0.17**	0.15	0.12	0.12	**0.13**
4	400	4000		0.26	0.29	0.24	**0.26**	0.22	0.19	0.20	**0.20**	0.12	0.17	0.16	**0.15**	0.10	0.10	0.04	**0.08**

Table 4: Result On Zinc Concentration Using Dates Seed as Adsorbent at 1 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
				1			Average	3			Average	6			Average	24			Average
1	100	1000	105.00	96.00	107.00	103.00	**102.00**	99.00	103.00	102.00	**101.33**	101.00	102.00	101.00	**101.33**	99.00	101.00	100.00	**100.00**
2	150	1500		99.00	97.00	101.00	**99.00**	97.00	95.00	99.00	**97.00**	95.00	96.00	95.00	**95.33**	88.00	88.00	104.00	**93.33**
3	200	2000		97.00	98.00	93.00	**96.00**	95.00	96.00	90.00	**93.67**	90.00	95.00	85.00	**90.00**	81.00	89.00	96.00	**88.67**
4	400	4000		93.00	88.00	93.00	**91.33**	91.00	86.00	92.00	**89.67**	78.00	90.00	99.00	**89.00**	86.00	77.00	88.00	**83.67**

Table 5: Result On Zinc Concentration Using Bunga Lawang as Adsorbent at 100 ppm

Sr. NO.	Wt.of Adsorbent	Conc.of Adsorbent	Final metal ion Concentration, Ce (mg/L) at time (hr)																
				1			Average	3			Average	6			Average	24			Average
1	100	1000	10.20	10.04	10.25	10.20	**10.16**	9.80	10.08	10.25	**10.04**	9.76	9.69	9.79	**9.75**	9.64	9.55	9.65	**9.61**
2	150	1500		9.76	9.69	9.79	**9.75**	9.50	9.60	9.35	**9.48**	9.30	8.95	9.31	**9.19**	9.00	8.75	9.10	**8.95**
3	200	2000		9.41	9.45	9.35	**9.40**	9.30	8.60	9.25	**9.12**	8.69	8.40	8.67	**8.59**	8.60	7.90	8.55	**8.35**
4	400	4000		8.79	8.76	9.12	**8.89**	8.67	8.55	8.62	**8.61**	8.45	8.30	8.52	**8.42**	7.71	7.81	7.78	**7.77**

Table 6: Result On Zinc Concentration Using Bunga Lawang as Adsorbent at 10.20 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
				1			Average	3			Average	6			Average	24			Average
1	100	1000	1.00	0.99	0.98	0.96	**0.98**	0.93	0.89	0.90	**0.91**	0.58	0.62	0.59	**0.60**	0.60	0.58	0.54	**0.57**
2	150	1500		0.81	0.82	0.85	**0.83**	0.71	0.73	0.74	**0.73**	0.56	0.56	0.60	**0.57**	0.49	0.55	0.49	**0.51**
3	200	2000		0.72	0.75	0.76	**0.74**	0.65	0.68	0.66	**0.66**	0.46	0.41	0.48	**0.45**	0.29	0.31	0.35	**0.32**
4	400	4000		0.66	0.69	0.58	**0.64**	0.49	0.50	0.51	**0.50**	0.36	0.36	0.36	**0.36**	0.19	0.17	0.18	**0.18**

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
			0	1			Average	3			Average	6			Average	24			Average
1	100	1000	1.00	0.45	0.50	0.44	**0.46**	0.45	0.42	0.42	**0.43**	0.46	0.34	0.40	**0.40**	0.22	0.26	0.23	**0.24**
2	150	1500		0.42	0.42	0.38	**0.41**	0.30	0.32	0.30	**0.31**	0.24	0.29	0.21	**0.25**	0.21	0.22	0.21	**0.21**
3	200	2000		0.38	0.40	0.41	**0.40**	0.25	0.26	0.28	**0.26**	0.18	0.17	0.18	**0.18**	0.13	0.12	0.14	**0.13**
4	400	4000		0.25	0.28	0.23	**0.25**	0.23	0.18	0.20	**0.20**	0.19	0.11	0.16	**0.15**	0.07	0.11	0.09	**0.09**

Table 8: Result On Zinc Concentration Using Bunga Cengkih as Adsorbent at 1 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
			0	1			Average	3			Average	6			Average	24			Average
1	100	1000	10.00	7.42	7.91	7.49	**7.61**	6.95	7.47	7.47	**7.30**	6.87	7.13	7.27	**7.09**	6.56	6.96	7.21	**6.91**
2	150	1500		7.47	7.02	7.16	**7.22**	6.82	7.20	6.64	**6.88**	6.73	6.76	6.75	**6.75**	6.59	6.68	6.66	**6.64**
3	200	2000		6.89	7.09	6.65	**6.88**	6.77	6.69	6.35	**6.60**	6.45	6.13	6.35	**6.31**	6.17	5.71	6.28	**6.05**
4	400	4000		6.59	6.62	6.39	**6.53**	6.21	5.98	6.64	**6.28**	5.91	5.92	6.53	**6.12**	5.52	5.83	6.35	**5.90**

Table 9: Result On Zinc Concentration Using Bunga Cengkih as Adsorbent at 10 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
			0	1			Average	3			Average	6			Average	24			Average
1	100	1000	100.00	80.00	82.00	78.00	**80.00**	72.00	78.00	78.00	**76.00**	71.00	75.00	76.00	**74.00**	70.00	74.00	77.00	**73.67**
2	150	1500		78.00	73.00	75.00	**75.33**	72.00	76.00	70.00	**72.67**	71.00	74.00	72.00	**72.33**	70.00	73.00	73.00	**72.00**
3	200	2000		72.00	74.00	69.00	**71.67**	72.00	71.00	67.00	**70.00**	69.00	66.00	68.00	**67.67**	66.00	61.00	67.00	**64.67**
4	400	4000		70.00	70.00	68.00	**69.33**	66.00	64.00	71.00	**67.00**	63.00	64.00	70.00	**65.67**	60.00	63.00	69.00	**64.00**

Table 10: Result On Zinc Concentration Using Bunga Cengkih as Adsorbent at 100 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
			0	1			Average	3			Average	6			Average	24			Average
1	100	1000	100.00	89.00	91.00	88.00	**89.33**	82.00	81.00	80.00	**81.00**	85.00	78.00	80.00	**81.00**	77.00	81.00	82.00	**80.00**
2	150	1500		82.00	83.00	81.00	**82.00**	77.00	86.00	73.00	**78.67**	79.00	81.00	75.00	**78.33**	81.00	75.00	79.00	**78.33**
3	200	2000		76.00	85.00	75.00	**78.67**	78.00	80.00	74.00	**77.33**	77.00	77.00	77.00	**77.00**	79.00	80.00	70.00	**76.33**
4	400	4000		78.00	79.00	75.00	**77.33**	74.00	69.00	70.00	**71.00**	72.00	67.00	70.00	**69.67**	71.00	64.00	69.00	**68.00**

Table 11: Result On Zinc Concentration Using Kayu Manis as Adsorbent at 100 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
			0	1			Average	3			Average	6			Average	24			Average
1	100	1000	10.00	8.52	8.81	8.41	**8.58**	7.87	7.76	7.73	**7.79**	8.10	7.41	7.64	**7.72**	7.32	7.60	7.73	**7.55**
2	150	1500		7.88	7.96	7.75	**7.86**	7.37	8.17	7.02	**7.52**	7.45	7.65	7.07	**7.39**	7.58	7.03	7.44	**7.35**
3	200	2000		7.33	8.13	7.21	**7.55**	7.54	7.64	6.97	**7.38**	7.32	7.26	7.22	**7.27**	7.36	7.43	6.55	**7.12**
4	400	4000		7.43	7.49	7.16	**7.36**	6.96	6.55	6.67	**6.73**	6.73	6.28	6.59	**6.53**	6.58	5.91	6.42	**6.30**

Table 12: Result On Zinc Concentration Using Kayu Manis as Adsorbent at 10 ppm

Sr. NO.	Wt.of Adsorbent (mg)	Conc.of Adsorbent (mg/L)	Final metal ion Concentration, Ce (mg/L) at time (hr)																
			0	1			Average	3			Average	6			Average	24			Average
1	100	1000	1.00	0.47	0.59	0.45	**0.50**	0.46	0.44	0.50	**0.47**	0.41	0.35	0.40	**0.39**	0.35	0.26	0.30	**0.30**
2	150	1500		0.47	0.46	0.42	**0.45**	0.41	0.39	0.42	**0.41**	0.29	0.32	0.28	**0.30**	0.24	0.23	0.28	**0.25**
3	200	2000		0.46	0.44	0.43	**0.44**	0.49	0.40	0.27	**0.39**	0.35	0.29	0.24	**0.29**	0.20	0.17	0.21	**0.19**
4	400	4000		0.37	0.34	0.38	**0.36**	0.26	0.31	0.34	**0.30**	0.20	0.21	0.25	**0.22**	0.14	0.10	0.16	**0.13**

Table 13: Result On Zinc Concentration Using Kayu Manis as Adsorbent at 1 ppm