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THESIS

REMOVAL OF HEAVY METALS FROM WASTEWATER BY EGG SHELL MEMBRANE

PINTIP KAEWKAMTHONG

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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This research was carried out to investigate the removal of heavy metals in synthetics wastewater by egg shell membrane (ESM). The effect of operating parameters, such as contact time, initial pH and initial concentrations in batch experiments were investigated.

The results from this work showed that the contact time of approximately 30 minutes was required for egg shell membrane (ESM) to reach the equilibrium for cadmium and zinc removal in synthetics wastewater. The optimum initial pH for adsorption of cadmium and zinc were 6.0 and 5.0, respectively. The kinetics of cadmium and zinc removal were studied using rate laws for chemical reaction. The results indicated that the initial removal rates of both cadmium and zinc were first-order with $K_L a$ values of 0.0031 and 0.0096 min^{-1}, respectively.

The removal efficiencies of both metals on ESM decreased with increasing the pH and concentration. The system equilibrium could be explained by Freundlich isotherm for cadmium and zinc.

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Student's signature Thesis Advisor's signature

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Pintip Kaewkamthong
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LIST OF ABBREVIATIONS

a = Empirical constant for Langmuir isotherm
b = Empirical constant for Langmuir isotherm
C_0 = Concentration of adsorbate at the begining, mg/L
C_e = Equilibrium concentration of adsorbate in solution after adsorption, mg/L
C_t = Concentration of adsorbate at time, mg/L
°C = degree Celsius
Cd^{2+} = Cadmium (II) ions
ESM = Egg shell membrane
$g\ l^{-1}$ = gram per litter
HNO_3 = nitric acid
K_f , n = Empirical constant
k_0 = zero-order reaction rate constant, concentration/time
k_1 = the first- order rate concentration, $time^{-1}$
K_La = min^{-1}
m = mass of adsorbent, g
$mg\ g^{-1}$ = milligram per gram
$mg\ l^{-1}$ = milligram per litter
µm = Micrometer
NaOH = sodium hydroxide
Q_e = $mg\ g^{-1}$
rpm = rotation per minute
R^2 = correlation coefficients
t = Time (minute)
v = volume of solution, mL
$\frac{x}{m}$ = Amount of adsorbate adsorbed per unit weight of adsorbent, $mg_{adsorbate}/mg_{adsorbent}$
Zn^{2+} = Zinc (II) ions

REMOVAL OF HEAVY METALS FROM WASTEWATER BY EGG SHELL MEMBRANE

INTRODUCTION

Nowadays, drainage, industrial and domestic effluents, agricultural run-off, acid rain, etc. have all contributed to some extent of metal loads in the water bodies. Metals are of special concern because they are non-degradable and therefore persistent. The effects of metals in water and wastewater could be dangerously toxic, depending on concentration. Cadmium and zinc are heavy metals, which are highly toxic to humans, plants and animals.

The efficient removal of toxic metals from wastewater is an important matter. A number of technologies have been developed over the years to remove toxic metals from wastewater. Physical treatment, such as filtration and adsorption, can be used to remove small concentrations of hazardous substances dissolved in water that would never settle out. Adsorption is one of the most commonly used techniques. The adsorption process can be described as the physical adhesion of chemicals onto the surface of a solid. The effectiveness of the adsorbent is directly related to the amount of surface area available to attract the molecules or particles of contaminant (Master, 1991). Adsorption processes using agricultural waste products or biosorption are becoming the new alternative for wastewater treatment.

Egg shell membrane (ESM) is an intricate lattice network of stable and water-insoluble fibers with high surface area. ESM accumulates and eliminates various heavy metal ions from dilute aqueous solution with high affinity and in short contact time, depending on pH and characteristics of the individual ion. ESM is promising to use for removal/recovery of metals and water pollution control (Suyama *et al*., 1994).

OBJECTIVES

1. To investigate the effectiveness of egg shell membrane for the adsorption of Cd^{2+} And Zn^{2+} from synthetic wastewater through:
   - adsorption isotherms study.
   - adsorption kinetics study.

2. To evaluate effects of the following factors on the removal of Cd^{2+} And Zn^{2+} by adsorption on egg shell membrane:
   - at pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0.
   - initial concentrations of heavy metals in the synthetic wastewater of 5,10, 20, 30, 40, and 50 mg/L.

LITERATURE REVIEW

1. Heavy metal in wastewater

Heavy metals are metals with densities higher than 5 g/cm^3. Heavy metals in wastewater come from industries and municipal sewage, and they are one of the main causes of water and soil pollution. Accumulation of these metals in wastewater depends on many local factors such as type of industries in region, people’s way of life and awareness of the impacts done to the environment by careless disposal of wastes. Therefore the presence of heavy metals in wastewater is not only of great environmental concern but also strongly reduces microbial activity, as a result, adversely affecting biological wastewater treatment processes. Moreover the toxicity of heavy metals in wastewater was shown to be dependent on factors like metal species and concentration, pH, pollution load, and solubility of the metal ions.

1.1 Cadmium : Cd

Cadmium (Cd) is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide). All soils and rocks, including coal and mineral fertilizers, contain some cadmium. Cadmium is a heavy metal posing severe risks to human health. It could not show that cadmium has any physiological function within the human body. Cadmium intoxication can lead to kidney, bone, and pulmonary damages. Cadmium is regularly found in ores together with zinc, copper and lead. Cadmium does not corrode easily and has many uses, including batteries, pigments, metal coatings, and plastics. Cadmium enters air from mining, industry, and burning coal and household wastes. Cadmium particles in air can travel long distances before falling to the ground or water. It enters water and soil from waste disposal and spills or leaks at hazardous waste sites. It binds strongly to soil particles. Some cadmium dissolves in water. Cadmium is a parameter of concern for water quality as it is a part of products produced by several industries. Cd^{2+} can accumulate and redistribute in some plant organs, resulting in plant injuries (Lagriffoul *et al.*, 1998; Reed et al., 1999), changes in plant protective enzymes (Chen *et al.*, 1998; Chien *et al.*, 2001), or changes in photosynthetic sensitivity of plants at different growth stages. It does not break down in the environment, but can change forms. Fish, plants, and animals take up cadmium from the environment. Cadmium stays in the body a very long time and can build up from many years of exposure to low levels.

The discovery of cadmium followed the discovery of zinc in 1746. Cadmium occurs in association with zinc ores, and is concentrated in flue dust from the extraction of zinc. Since World War I, significant production of cadmium has taken place for electroplating industries. Cadmium is concentrated in sulphide ores of zinc, mercury, lead and copper. The principal cadmium mineral is hexagonal CdS (greenockite). Rarer minerals, mostly of secondary origin, are cubic CdS (hawleyite), hexagonal CdSe (cadmoselite), CdO (monteponite), and $CdCO_3$ (otavite). Cadmium metacinnabar, or saukevite, is cubic (Hg, CdS) and may contain up to 11.7% cadmium.

a) Sources

(1) Production and Uses

Information provided in this subsection is summarized from Fergusson. Cadmium has a wide variety of industrial functions. The proportion of metal used in each industrial area varies from year to year. For example, electroplating and pigment uses are decreasing, whereas use in batteries is increasing. Cadmium coatings on metals are produced by electroplating from a Cd^{2+}/CN^- solution. The coatings are anticorrosive in marine, alkaline and tropical environments, are ductile and have a low efficiency of friction, and are readily soldered and retain their silver-white luster. Cadmium coated materials are used widely in automobile manufacturing (e.g., on bearings, bolts and disk brakes). Alloys containing cadmium are also used in bearings and for soldering. Fusible alloys with low melting points contain cadmium and are valuable in fire protection devices such as sprinklers.

Pigments containing cadmium are used in plastics, paints, printing inks and ceramics. They are resistant to heat and ultraviolet radiation, and are not darkened in an H_2S atmosphere, as are lead pigments. Cadmium lithopones are obtained by treating a mixture of $ZnSO_4$ and $CdSO_4$ with BaS to give a coprecipitated product, $ZnS/CdS/BaSO_4$. The pigments become darker as the proportion of cadmium to zinc increases. If the precipitation takes place in the presence of selenium, the incorporation of CdSe also produces darker shades. Organocadmium compounds are used in polyvinyl chloride (PVC) to increase the resistance of the polymer to heat, light and discolouration. However, environmental concerns are restricting its use in this way. Organocadmium compounds are also used as catalysts in organic hydrogenation and polymerization reactions.

(2) Natural Sources

Cadmium can be found in various natural sources, but is most abundant in zinc, lead and copper sulphide ores. Another source of cadmium is the ore tetrahedrite-tennartile $(Cu, Zn)_2(Sb)$ nitrate, which can be found in the upper water layer, and is influenced by the photic zone and phytoplankton productivity. The crustal abundance of cadmium is around 0.2 ppm. Low concentrations of cadmium occur in igneous rocks (<0.001 - 1.6 ppm). Higher concentrations occur in sedimentary rocks associated with organic material, such as shales, and in marine manganese nodules and phosphorite deposits. While cadmium is closely associated with zinc, the zinc/cadmium concentration ratio varies widely from 27 to 7000 (Fergusson, 1990). There is no clear association between cadmium and other elements in rocks, but there is some association between cadmium and organic material, as shown by higher relative cadmium concentrations in coal (0.01 – 22 ppm), peat (0.37 - 190 ppm) and crude oil (0.01 - 16 ppm) (Fergusson, 1990). Under natural conditions, metals are supplied to the sea by three processes: coastal supply, including input from rivers and from erosion by wave action and glaciers. Deep sea supply includes metals released by deep sea volcanism and those released from particles or sediments by chemical processes. Additional supply include those by-passes the near-shore environment and those transported in the atmosphere as dust particles and material, which is produced by glacial erosion in polar regions and is transported by floating ice. Rivers appear to be the most important source of heavy metals to the sea. The composition of river water includes the products of mechanical and chemical weathering of rocks, either in solution or as particles, and atmospheric deposition (rainfall) which may include components originally contained in salt particles of marine origin or in dust particles from land. Other natural sources of atmospheric cadmium include ocean sprays, forest fires, and the release of metal enriched particles from terrestrial vegetation. These sources are difficult to quantify, but only the release from vegetational sources is likely to be significant on a global scale.

(3) Anthropogenic Sources

Cadmium is used primarily in metal plating and the manufacture of pigments, batteries, and plastics. Cadmium is not often encountered at concentrations of concern in water, although it can be leached into water from pipes and solder or may enter water from chemical waste disposal sites. The largest source of cadmium to the environment is the combustion of fossil fuels (such as coal or oil) or the incineration of municipal waste materials. The main anthropogenic sources of cadmium are ore mines, metallurgical industries and sewage sludges. Cadmium concentrations in the fumes of copper, lead, nickel and zinc sulfide smelters can be relatively high due to the high volatility of the metal. Cadmium is extracted as a by-product during the refining of zinc ores. The two basic processes of zinc production (thermal smelting and electrolytic refining) produce different kinds of cadmium-rich discharges. Thermal smelters are responsible for much larger atmospheric emissions of cadmium than electrolytic refining and also produce liquid waste rich in cadmium which requires safe disposal. However, electrolytic refining has assumed an increasingly important share of the world's production of zinc and cadmium. Primary production of lead and copper also releases cadmium to the environment. Non-ferrous metal mines can be a significant source of local cadmium concentrations. Other anthropogenic sources releasing cadmium include high-temperature processes in steel and iron manufacturing, municipal and sewage sludge incineration and cement production. The estimated inputs of cadmium to the environment in the European

Community give an indication of emissions and disposals to land, but provide an incomplete account of aquatic inputs. An estimate of the generalized global anthropogenic input of cadmium to the ocean is calculated to be about 50% of the 9.25 x 10^3 tones/year (Simpson, 1981). Yeats and Bewer (1987) estimated that 2,600 t per year enter the world's oceans from atmospheric deposition, and a further 1,500 - 2,000 t per year enter via river runoff.

b) Behavior of Cadmium in the Aquatic Environment

(1) General Chemical Properties of Cadmium

The chemistry, but not the biochemistry, of cadmium closely follows that of zinc. Cadmium can form complexes with other ions and compounds. The four main species are: cadmium halides, cadmium sulphide, cadmium oxide and organocadmium compounds. All species have relatively high free energies of formation. Dependent on the pH, some of these compounds [CdO, CdS, $Cd(OH)_2$, $CdCO_3$, and $CdSiO_3$] have low solubilities in water. In salt waters of salinities 10 to 35 ppt, cadmium chloride complexes predominate.

(a) Cadmium halides: Four halides of cadmium are known, but of these the chloride is the only one of environmental importance. The structure of $CdCl_2$ is a cubic close-packing of chloride ions with cadmium occupying the octahedral cavities between pairs of layers. In seawater, the main species are $CdCl^+$, $CdCl_2$, and $CdCl^{3-}$, with approximately 2.5% of the total present as the free (hydrated) cadmium ion (Cd^{2+}). All halides are soluble in water and form complex ions.

(b) Cadmium sulphide: Cadmium sulphide is produced by passing H_2S with a solution of Cd(II). Cadmium has a strong affinity for sulphur, and the two ions Cd^{2+} and S^{2-} are naturally polarizing, which assists in the formation of a strong lattice. Two structural forms exist, a cubic (zinc blend) structure and a hexagonal (wurtzite) structure. These have a very low solubility in water, $\log K_{sp} = -27.2$. Cadmium sulphide is the most stable species in reducing environments.

(c) Cadmium oxide: Cadmium oxide is produced by the oxidation of cadmium, when the metal is tarnished in air. The color of the oxide, which varies from green/yellow to red and nearly black, is a function of the particle size and lattice defects. The oxide has a structure similar to that of NaCl and can be denatured when heated (loss of oxygen). The oxide is soluble in acids, forming the Cd^{+2} ion, but due to its basic properties, it has low solubility in water and alkaline solutions.

(d) Organocadmium compounds : Compounds of the organocadmium type are known and are prepared from the appropriate Grignard reagents. Dimethylcadmium boils at 105.7°C and diethylcadmium at 64°C at 19 mm-Hg pressure (Fergusson, 1990). The volatile compounds are only moderately reactive, do not normally catch fire in air, and do not react vigorously with water. The production of dimethylcadmium by biomethylation is not well documented, but it is presumed that if formed, it would decompose in an aqueous environment.

The transformation of inorganic forms of cadmium in seawater scarcely affects its solubility. Organic chelates, such as humates, are likely to liberate bound cadmium as a result of dilution and degradation in seawater. In sewage sludge, cadmium is held partly in combination with carbonates and sulfides, and partly in complex organic combinations. In the latter example, cadmium combines with the sulfur-rich fractions of organic matter of which there is great excess. Since most biogenic organocadmium complexes, including metallothioneins, are fairly easily biodegradable, there is a ready release of cadmium into aerobic waters and sediments under anaerobic conditions. Insoluble cadmium carbonates and sulphides may persist in sediment.

c) Distribution, Fate and Transport

(1) Distribution

Various forms of cadmium ions and compounds can be found in freshwater and seawater. The inorganic speciation of cadmium in water has similarities to that of lead, but is simplified in that the free cation (hydrated) exists at relatively low pH values (i.e., <7 to 8). Hence, it is a major component of freshwater, and a significant component of seawater. The hydroxy species only persist down to pH 8 - 9, below which the Cd2+ ion occurs. In seawater with a chloride ion concentration of 0.54 mol/L, the cadmium-chloro species ($CdCl_2$, $CdCl^{3+}$ and $CdCl^-$) are the major components at pH 7 to 9. In more dilute systems (i.e., $[Cl^-] = 0.01 - 0.03$ mol/L), the cadmium ion begins to dominate. The cadmium-chloro system is relatively stable, one reason being the strong Cd-Cl bond. Under oxidizing conditions cadmium is mobile and present as the hydrated cation, hence under normal environmental conditions the major species of cadmium in fresh to weakly saline water is the hydrated Cd^{2+} ion. Under reducing conditions, the soluble species of cadmium (when sulphur is present) is probably the bisulphide ion, $CdHS^-$. Cadmium carbonate ($CdCO_3$) is not as significant as the corresponding lead species. The amount of $CdCO_3$ will depend on the pH of the water the higher the alkalinity the greater the amount of $CdCO_3$ expected, In contaminated environments where other materials occur, different cadmium species may exist in solution, such as $CdSO_4$ and Cd-organic ligand complexes. Cadmium bonds well to sulphur donors such as cysteine, and also with amino acids, carboxylic acids, polysaccharides and organic pollutants. Whether or not organic complexes of cadmium occur will depend on the amount of organic material available, and the presence of competing cations. Estimates of the proportion of cadmium-organic complexes in freshwater and seawater range from 10 to 80% of the total cadmium. Cadmium-humic species are reported as minor (around 2.7%) in freshwater. Unless the organic content of the water is high, cadmium organic complexes appear of less importance than the free ion and inorganic species. Interestingly, in a study of the variation of cadmium concentrations and soluble organocadmium complexes with depth, it was found that when the salinity was at a minimum so also was the proportion of cadmium complexes.

(2) Fate

Cadmium in surface water is relatively mobile. Because cadmium exists only in the 2+ oxidation state, aqueous cadmium is not strongly influenced by the oxidizing or reducing potential of water. Sorption by clays and iron oxides is important for reducing cadmium in water. Cadmium is not reduced or methylated by microorganisms. Concentrations of heavy elements in ocean sediments vary considerably with geographical location, and depend on whether the sediments are from deep sea or coastal areas. Coastal metal concentrations are often significantly elevated because of nearby land-based pollution sources. The highest values are from nearest drains and outfalls. Deep sea sediments and sediments close to the coast may be similar or different in composition depending on whether or not an element is deposited rapidly on entering the ocean, or is carried further out into the ocean before deposition. An explanation of the different cadmium profiles in deep and surface waters is that concentrations in the surface water are depleted because the cadmium species are taken up by organisms or by sorption onto the organisms. In deeper water, sinking organic detritus and debris release cadmium. This corresponds to a minimum in the O_2 level, presumably because the dioxygen is being used in the decay. The ratio of cadmium concentrations in deep/surface (enriched/depleted) waters is 30, which is large. The higher cadmium concentration at greater depths is evident because of its elevated levels in upwelling water, compared with non-upwelling surface water [i.e., 0.009 and 0.001 μg/L, respectively. In most well-oxygenated freshwaters that are low in total organic carbon, free divalent cadmium will be the predominant form. Precipitation by carbonate or hydroxide and formation of soluble complexes by chloride, sulphate and carbonate should usually be of little importance. In salt waters with salinities ranging from 10 to 35 ppt, cadmium chloride complexes predominate. In both fresh and salt waters, particulate matter and dissolved organic material may bind a substantial portion of the cadmium.

(3) Transport

Cadmium can be transported to soil and water through wet or dry deposition. Cadmium in water comes from contaminated agricultural soils, mining wastes, mine waters, and the industrial use of cadmium. An important source is municipal sewage effluents and sludges, including those of domestic origin. It is released slowly into the environment from widespread sources. Cadmium enters the sea and ocean from the air mainly in particulate form and, to a lesser extent, dissolved in rain and snow. Highest concentrations of cadmium in air are observed in urban and industrialized areas, particularly near metal refining and processing plants. Airborne cadmium is a principal source of input to offshore and oceanic water. The transport of cadmium from freshwater to the sea occurs either in particulate or soluble form. The specific form depends on the state of the river, its mineralization and the sources of pollution, as well as on unidentified local factors. River sediments generally reflect neighbouring soils and mineral workings. Elevated cadmium levels are invariably accompanied by high levels of other trace metals. As a result of these inputs, there are enhanced levels of cadmium in near-shore sediments and sea waters.

1.2 Zinc : Zn

Zinc (Zn) is chemically active and alloys readily with other metals. These properties are utilized industrially in preparing a large number of zinc-containing alloys and compounds. The relatively high position of zinc in the electromotive series largely accounts for it extensive use to protect iron and steel products against corrosion (Nriagu, 1980). Zinc deficiency in humans in serious worldwide problem and outweighs the potential problem of accidental, self-imposed, or environmental exposure of zinc excess. Acute deficiency and chronic deficiency are well-known entities in human populations and are probably much more common than generally recognized. The industrial use of zinc affects the environmental distribution of this metal; zinc is frequently found in industrial waste sites. Zn^{2+} is a potently toxic cation involved in the neuronal injury observed in cerebral ischemia, epilepsy, and brain trauma. Toxic Zn^{2+} accumulation may result from either trans-synaptic Zn^{2+} movement and/or cation mobilization from intracellular sites.

a) Sources

(1) Production and Uses

Zinc is used most commonly as a protective coating for other metals. In addition, it is used in alloys (e.g., bronze and brass) for electrical uses, and in organic chemical extractions and reductions. Zinc chloride is a primary ingredient in smoke bombs. Salts of zinc are used as solubilizing agents in many drugs (e.g., insulin). Zinc and copper alloys are used in coinage. Zinc is used in a variety of other industries including the production of fungicides, rubber, paint, ceramics, glass and retrogress materials which are all potential sources of contamination of the environment during manufacturing and application.

(2) Natural Sources

The concentration of zinc in the earth's crust is relatively high. Zinc occurs in nature mainly as sulphides and sphalerite (Zn blende), as silix hemimorphite, and as carbonates in smithsonite. These minerals often contain cadmium and lead. The largest reserves of zinc are found in Australia, Canada, USA, USSR, Ireland, Peru and South Africa (Nriagu, 1980). It is estimated that zinc emissions into the atmosphere from natural sources amount to 43 x 106 kg. The majority (60%) of all emissions are from natural sources. About 20% of natural zinc emissions come from vegetation (as exudates, etc.) and about 5 to 15% may be attributed to forest fires or volcanogenic aerosols Erosion of soil particles containing zinc is the largest overall source of zinc to the aquatic environment but the effect on water quality at any one location is likely minor.

(3) Anthropogenic Sources

Zinc is the fourth most widely used metal in the world. Its major uses include galvanized steel for alloy production, and as an ingredient in rubber and paints. Zinc enrichment above 50 μg/L may usually be traced to industrial effluents with a large measure of certainty. The main sources are the galvanizing industry, viscous plants, candle and soap factories. Zinc is released to the air as dust and fumes from zinc production facilities, lead smelters, brass works, automobile emissions, fuel combustion, incineration, and soil erosion. Refuse incineration, coal combustion, smelter operations, and metallurgical industries are major sources of zinc in the air. More concentrated sources of zinc to aquatic environments include urban runoff, mine drainage, and municipal and industrial effluents. Metal corrosion and tire abrasion also contribute to urban runoff. Industries that directly discharge zinc to water include iron and steel foundries, zinc smelting, plastics, and electroplating. Municipal wastewaters are major contributors of zinc in estuarine environments. Zinc mining is a source of zinc released to marine environments.

b) Behavior of Zinc in the Aquatic Environment

(1) General Chemical Properties of Zinc

Zinc is often associated with cadmium and mercury. It exists in two stable oxidation states, the metallic element and oxidation state II. Metallic zinc is white, lustrous and tarnishable, and has a relatively low melting point of 41.9°C. Zn(II) is amphoteric, dissolving in acid to form hydrated Zn(II) cations and in strong bases to form zincate anions, usually $Zn(OH)_4^{2-}$. In aqueous solution, zinc exists in the +II oxidation state and may form complexes with ammonia, amines, halides, cyanides and other inorganic and organic ligands. In the absence of complexing or adsorbing agents, the zinc ion coordinates six water molecules to form the octahedral ion $(Zn(H2O)_6)^{2+}$.proposed that the main equilibrium species of dissolved zinc in seawater are Zn^{2+}, $ZnOH^+$, $ZnCO_3$, $ZnCl^+$, and $ZnSO_4$. Zirino and Yamamoto (1972) constructed a pH-dependent model for zinc in seawater. Their calculations showed that the major zinc species at pH 8.1 were: Zn^{2+} (17%), $Zn(OH)_2$ (62%), $ZnCl^+$ (6.4%), $ZnCO_3$ (5.8%), $ZnSO_4$ (4%), and $ZnCl_2$ (4%). At pH 7.0, the percentage of dissolved zinc present in seawater as the free ion increases to 50%. In the presence of dissolved organic materials, particularly humic substances, the major fraction of dissolved zinc is in the form of zinc-organic complexes. Under estuarine conditions, the proportion of aqua ion decreases and chloro complexes become increasingly important as salinity increases. Hydroxy and carbonate complexes constitute only a minor proportion of the total dissolved zinc species under the conditions outlined in Zirino and Yamamoto's (1972) model.

(2) Distribution, Fate and Transport

(a) Distribution

In the 1970s, it was generally believed that zinc concentrations in the oceans were on the order of 1 to 30 μg/L. Oceanic concentrations of zinc increase with depth, but concentrations in coastal areas and estuaries are often much higher. Similar concentrations were obtained using two different sampling methods and two different preconcentration procedures, and all collections and analyses were performed by ultra clean methods.

(b) Fate

Zinc occurs in many forms in natural waters and aquatic sediments. Zinc ions exist in seawater in a dissolved state, as solid precipitates, or absorbed to particle surfaces. The soluble species of zinc comprise three different forms: uncomplexed free (i.e., hydrated) ions, inorganic complexes, and organic complexes. In the open sea, the chemical form of trace metals in solution is largely determined by inorganic complexing, and is not appreciably influenced by complexing or chelation with natural organic compounds. In coastal waters, some zinc also exists in a soluble, firmly bound organic form which becomes extractable when seawater is treated to destroy organic matter. The tendency of zinc to be sorbed is also affected by pH and salinity. An increase in pH can increase sorption of zinc even if salinity increases. Zinc was completely removed from solution when pH exceeded 7, but little or no zinc was sorbed when pH was below 6. Above a pH of 6, zinc may be adsorbed by hydrous iron and manganese oxides, amorphous crystalline clays, humic materials and biogenic structures such as cell walls of phytoplankton, and be deposited in sediments by coprecipitation. In reducing environments, precipitation of sulphides is a possible mechanism for depletion of zinc from the water column. At high zinc concentrations and high pH values, the hydroxide and carbonate may also precipitate; an opposing factor may operate to solubilise zinc under reducing conditions, namely the reduction of iron and manganese hydroxides on which zinc can be adsorbed. Adsorption to sediments is the dominant fate of zinc in the aquatic environment. Zinc partitions to sediments or suspended solids in surface waters through adsorption onto hydrous iron and manganese oxides, clay minerals, and organic material. The tendency of zinc to be adsorbed is affected by the nature and concentration of the sorbent, and by the pH and salinity of the water. Zinc tends to sorb more readily at higher pH levels and desorption of zinc from sediments occurs as salinity increases. Zinc does not volatilize significantly from water. Although bioaccumulated by all organisms, zinc does not biomagnify in the food chain.

(c) Transport

Zinc introduced into the aquatic environment is partitioned into sediment by sorption onto hydrous iron and manganese oxides, clay minerals, and organic materials. Precipitation of the sulphide is an important control on the mobility of zinc in reducing environments, and precipitation of the hydroxide, carbonate, and basic sulphate salts can occur when zinc is present in high concentrations. Formation of complexes with organic and inorganic ligands can increase the solubility of zinc and might increase or decrease the tendency for zinc to be sorbed reported that sorption of zinc was also dependent on the organic carbon content of river sediments. Zinc is not easily removed from solution and is always readily available to aquatic animals. It is known that zinc is an essential metal that can be regulated within certain ranges of concentration. Zinc is one of the most ubiquitous and mobile of heavy metals and is transported in natural water systems to a great extent in the dissolved form in rivers, as well as being associated with particulate matter. In estuaries there are several factors which govern the transport of zinc between the dissolved and particulate states. In waters of low salinity (e.g., <2 ppt), up to 8 ppt of zinc may be desorbed from suspended particulate matter in the water column by microbial decomposition of organic matter to which zinc is adsorbed, and by displacement of adsorbed zinc by calcium, magnesium or other divalent metals (e.g., copper with stronger affinities for ligands than zinc). Increases in the oxidizing nature of sediments and the overlying water also tend to mobilize zinc. Helz *et al.* (1975) and Salomons (1980) found less sorption of zinc to particulate matter and sediment as salinity increased. This is due to displacement of sorbed zinc ions by alkali and alkaline earth cations, which are abundant in brackish and saline waters.

2. Treatment technologies for metals and hazardous waste.

Chemical, biological, and physical wastewater treatment processes are currently the most commonly used methods of treating aqueous hazardous waste. Chemical treatment transforms waste into less hazardous substances using such techniques as pH neutralization, oxidation or reduction, and reduction, and precipitation. Biological treatment uses microorganisms to degrade organic compounds in the waste stream. Physical treatment processes include gravity separation, phase change system, such as air and stream stripping of volatiles from liquid wastes, and various filtration operations, including adsorption (Grey *et al*., 1994). Most conventional wastewater treatment techniques such as filtration, flocculation, activated carbon, reverse osmosis, chemical precipitation or coagulation, ion-exchange, ultrafiltration and electrochemical deposition require high capital and operating costs and may produce large volumes of wastes.

a) Ion exchange

Ion exchange is a type of process to remove ions that is most often used for water treatment rather than wastewater treatment. Moreover, Ion exchange is explain by the reversible interchange of ions between a liquid and solid phase, which employs for the removal or exchange of dissolved organic substance in the water or wastewater (Kosayothin, 2002).

In practice the water being treated is passed through a filter bed of ion exchange material that releases the substitute ions for the ions adsorbed from the water. When the capacity for exchanging ions has been depleted, a regenerating solution with a high concentration of regeneration process displaces the contaminant ions and rejuvenates the exchange resin (Mark, 2001).

The equation used to described exchange reaction is shown below:

$$B^{+} \quad + \quad (R^{-})A^{+} \longrightarrow A^{+} \quad + \quad (R^{-})B^{+}$$

Where; A^{+} = initially counteraction of resin

B^{+} = initially counteraction in solution

R^{-} = the negatively charged functional group of the resin (James, 1985)

This was supported by Chayapiwat (1999) who studied an adsorption efficiency of palm pressed fibers for chromium removal from synthetic wastewater, using five levels of initial chromium concentration in wastewater, such as 1, 5, 10, 20 and 50 mg/l then adjusted pH to 2.5 to 3.5. And the results indicated an average efficiency at chromium concentration of 1, 5, 10, 20 and 50 mg/l with flow rate of 5 ml/min were 38.41, 43.61, 46.26, 33.97 and 43.36 % respectively; at flow rate 10 ml/min, percent removals were 52.25, 19.89, 41.79, 29.39 and 35.27 % respectively. And the average removal efficiencies at flow rate 5 and 10 ml/min were of 40.63 and 35.73 %.

b) Chemical precipitation

Chemical precipitation in wastewater treatment involves the addition of chemicals to alter the physical state of dissolved and suspended solids and to facilitate their removal by sedimentation. In some cases the alteration is slight, and removal is effected by entrapment within a voluminous precipitate consisting primarily of the coagulant itself. Another result of chemical addition is a net increase in the dissolved constituents in the wastewater. Chemical processes, in conjunction with various physical operations, have been developed for complete secondary treatment of untreated wastewater, including the removal, of heavy metals will be precipitated at varying pH levels, which depends on the solubility of metal ions. The choice of reactant is the first consideration in the precipitate with heavy metals. The second consideration is the solubility of heavy metals and the finally factor is the liquid or solid state of waste (Kosayothin, 2002 and Metcalf and Eddy, 2004).

Many studies on the chemical precipitation of heavy metals have been carried out. Moolthongnoi (2000) who studied on the possibility of employing chemical precipitation for instance Na_2CO_3, $Ca(OH)_2$ and Na_2SiO_3 for treatment of wastewater from an environmental laboratory, resulting at pH 9.0, the most of heavy metals removal of the water sample could be maximized up to 99 % except for mercury, while the other metals fell below standard levels for effluent water. Work done by Pradit (2001) also supported the precipitation and coagulation process. Sodium hydroxide was used to precipitate heavy metals from the laboratory wastewater, indicating the optimum pH were 7 and 11. And the efficiency of precipitation of heavy metal ions were above 95 % averagely.

c) Coagulation

Coagulation is a process for combination small particles into larger aggregates. This very small particles called “colloidal particles” that causes the problems in waterworks can not rapidly precipitate by itself.

The process that makes these colloidal particles to aggregate and is easy to precipitate, which is called “floc”, names coagulation process. Actually, there are 2 steps in coagulation process, they are rapid mixing and slow mixing. Coagulation is the addition of chemicals to water in order to induce suspended solid agglomeration. The most widely used coagulants are aluminum salts, iron salts and organic polymers.

The coagulant which is widely used, nowadays, are alum which occurs in aluminum compound named aluminum sulfate and ferric compound name ferric chloride. At the same time, the coagulant aid widely used are polymer or polyelectrolyte which is high molecular weight organic compound.

Coagulant aids may be used to enhance the process of flocculation. For example, organic polymers provide bridging between particles by attaching themselves to the absorbent surfaces of colloids, building larger flocculated masses.

Removal of turbidity by coagulation depends on the type of colloids in suspension, the temperature, pH and chemical composition of the water, the type and dosage of coagulants and coagulants aids; and the degree and time of mixing provided for chemical dispersion and floc formation.

The disadvantage of the coagulation process is the generation of a large amount of the chemical sludge which increases in the treatment cost (Tipprasertsin, 2003, Iamtrakoon, 1999 and Mark, 2001).

This was supported by Kochakijjarak (1999) who studied the effect of ferric chloride or anionic polymers, i.e., Qmafloc 985, FA 40, Kurita C-3310 and Kurita C-0320S as a coagulant an coagulant aids to remove heavy metals (copper, lead and nickel) from the integrated circuit industrial wastewater. The results indicated that Kurita C-0320S was found to be the suitable anionic polymer in treating equalizing wastewater. The optimal condition was at the pH 10 and polymer dose 0.1 mg/l. After coagulation, heavy metals in treating wastewater were less than the standard limits.

d) Adsorption

Adsorption, in general, is the process of collecting soluble substances that are in solution on a suitable interface. The interface can be between two phases. In any solid or liquid, atoms at the surface are subjected to unbalanced forces of attraction normal to the surface plane. The molecule that is accumulated or adsorbed at the interface, is called adsorbate and the solid phase is called adsorbent.

There are various kind of adsorbents that commonly used in wastewater treatment for instance activated carbon, ion exchange resins, adsorbent resins, metal oxides, metal hydroxides, activated alumina and clays. The major advantages of the adsorption process are low capital cost, simple design, ease of operation, no toxic by product generation and excellent effectiveness. The activated carbon and polymer resins are the best adsorbents for organic removal from wastewater, but are expensive and difficult to regenerate (Tipprasertsin, 2003 and Metcalf and Eddy, 2004).

e) Reverse osmosis

Reverse osmosis is a solvent flows through a semipermeable membrane from a less concentrated to a more concentrated solution by osmotic pressure. The pressure applied exceeds osmotic pressure of the salt solution against a semipermeable membrane, thereby forcing pure water through membrane and leaving salts behind (Kosayothin, 2002).

However, these traditional technologies are often in effective as mentioned above. Thus, new technologies for the required to decreased metal ion concentrations to environmentally acceptable levels and also at affordable costs.

3. Adsorption

In general, adsorption is the process of collecting soluble substances (adsorbate) that are in a solution, on a suitable interface (with adsorbent). The interface can be between the liquid and gas, a solid, or another liquid. Adsorption at the liquid-solid interface was used in this study.

a) Adsorptive process

The adsorption process can be divided into three steps:

1) Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterized first by surface properties such as surface area and polarity.

2) A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large members of small sized pores between adsorption surfaces. The size of the micropores determines the accessibility of adsorbete molecules to the internal adsorption surface , so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents. Especially materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation.

3) Surface polarity corresponds to affinity with polar substances suchas water or alcohols. Polar adsorbents are thus called “hydrophilic” and aluminosilicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type. On the other hand, nopolar adsorbents are generally “hydrophobic”. Carbonaceous adsorbents, polymer adsorbents and silicalite are typical nonpolar adsorbents. These adsorbents have more affinity with oil or hydrocarbons than water.

b) Adsorptive mechanism

The removal of heavy metal using adsorptive process involves a number of steps, each of which can affect the rate of removal:

1) Bulk solution transport: Adsorbates must be transported from bulk solution to the boundary layer of water surrounding the adsorbent particle. The transport occurs by diffusion if the adsorbent is suspended in quiescent water, such as in a sedimentation basin, or by turbulent mixing, such as during turbulent flow through a packed bed of GAC, or when PAC is being mixed in a rapid mix or flocculator.

2) Film diffusion transport: Adsorbates must be transported by molecular diffusion through the layer of water, which surrounds the adsorbent particles when water is flowing past them.

3) Pore diffusion transport: The adsorbent has many pores in the particles. After passing through the film of water, the adsorbates are transported through the adsorbent's pore to available adsorptive sites.

4) Adsorptive Process: The adsorptive bond is formed between the adsorbate and adsorbent, after transport to available site. This reaction is occurred by physical adsorption, which is very rapid. However, it can be occurred by chemical reaction, which is slower than the diffusion reaction (Kosayothin, 2002 and Uaychinda, 2002).

The primary driving force between the adsorbate and the adsorbent is the electrostatic attraction and repulsion which can be either physical or chemical. The adsorption processes may be classified as physical or chemical, depending on the nature of the forces involved.

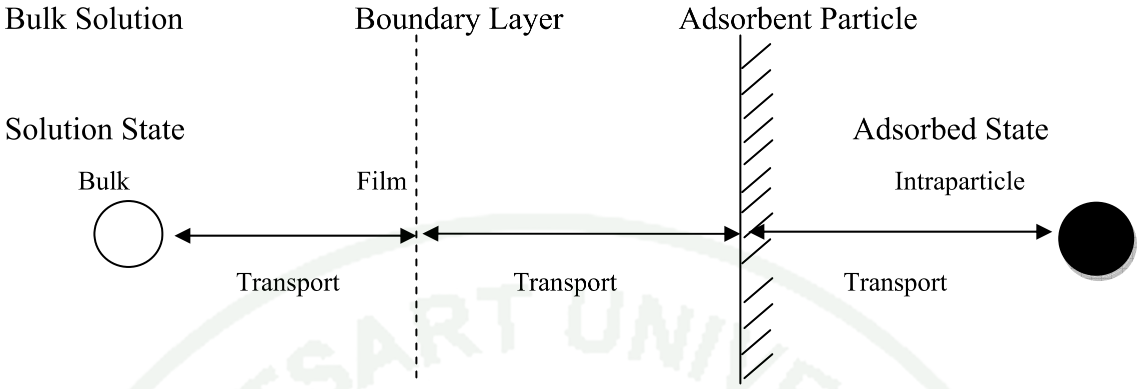

Figure 1 The step of adsorptive process by adsorbent

Source: Tipprasertsin (2003)

(a) Physical adsorption: Physical adsorption is the intermolecular forces that interact between the adsorbate and the adsorbent. These forces include the van der waals forces and hydrogen bonding. In liquid phase, the van der waals force is the primary physical driving force. Physical adsorption is a reversible reaction and includes mono and multilayer coverage because it does not involve the sharing of electrons. Generally, this forces has a low energy of adsorption and is not site specific.

(b) Chemical adsorption: Chemical adsorption is based on the electrostatic force and has the mechanism similar to physical adsorption. Chemical adsorption involves the transfer of electrons and the formation of chemical bonds between the adsorbate and the adsorbent. It is irreversible reaction and has high energy of adsorption. Chemical adsorption involves monolayer coverage and the reaction occurs at specific sites.

c) Factors affecting adsorption

The efficiency of the adsorptive process depends on these factors. In this work in considerable the effect of pH, particle size, and contact time, as following below:

1) Solubility of adsorbate

The formation of material substance influence to the solubility of adsorbate. Solubility is one of the most important factor affecting the adsorptive capacity. In general, a higher solubility indicates low adsorptive capacity because the bond between the solute and the solvent breaks before the adsorption can occur.

The polarity of adsorbent has a similar effect on adsorption as solubility; higher polarity results in less adsorption ability. For example, the polar substances (soluble or ionized), such as cadmium (Cd). Chromium (Cr), iron (Fe), manganese (Mn), silver (Ag), and mercury (Hg), etc., are expected to increase solubility higher than non-polar substance.

2) pH of solution

The adsorption of weak electrolytes, both acids and bases, by clay from aqueous system is affected by the solution pH. This is because it changes in the characteristics of the adsorbent and the solute molecules. The pH of solution related to the molecular.

At pH values greater than the pKa of a weak organic acid, the adsorptive capacity is greatly reduced. If increases with a decrease in pH and a maximum adsorption capacity occurs when the pH is equal to pKa. At pH values lower than the pKa, the adsorptive capacity usually decreases with decreasing pH.

3) Surface area and particle size

In fact, it has generally been known that the adsorptive efficiency of adsorbent is proportional to the surface area is one of the factors affecting the adsorptive capacity of an adsorbent. The adsorption of solutes increases with increasing surface area. In term of the particle size, the surface area of nonporous adsorbents increases with decreasing particle size and so does the adsorptive capacity.

For highly porous adsorbents such as activated carbon, most of the surface area is in the internal pore structure. As a result, the adsorptive capacity is independent of the particle size. there are numerous work reported on the effect of surface area and particle size on adsorption capacity (Boonpanaid, 1998).

4) Molecular weight and size of adsorbate molecule

It is clearly to say that the molecular weight and size of adsorbate molecule affect the adsorptive capacity. Higher molecular weights are usually associated with large molecular sizes (longer lengths of molecular chain) and low solubility. Therefore, adsorbates with higher molecular weights and larger molecular sizes tend to have more adsorptive capacity.

5) Mixing of solution

It has been known that the efficiency of heavy metal adsorption relates to the film diffusion and pore diffusion. The column experiment that uses low mixing, so the film diffusion determines the adsorptive efficiency. On the other hand, high mixing is used for the bath experiment, so the adsorptive efficiency is determined by pore diffusion.

6) Temperature

There are also the influence of the temperature to the adsorption efficiency. An increasing of temperature effects to the increasing efficiency of heavy metal adsorption, until it will be in an equilibrium adsorptive capacity because the adsorption process is always exothermic.

7) Contact time

There are various documents have mentioned about the effect of contact time to adsorption capacity. Kosayothin (2002), Tipprasertsin (2003) and

Boonpanaid (1998) Increasing contact time effects to the increasing efficiency of heavy metal adsorption until it will be in an equilibrium. Many studies found that the effects of contact time to removal heavy metals by adsorption, such as Lopez et al. (1998) who studied the feasibility of using red mud (RM), a residue from bauxite refining, for phosphorous (P) adsorption wastewater treatment, using contact times of 3, 6, 24, and 48 hr and the results indicated that adsorption occurred by both fast and slow reaction. The RM aggregates had maximum adsorption capacities. As well as the study of Viraraghavan (1991) on the removal of chromium from wastewater by ash, has indicated that the optimum contact time was 3 hr and removal efficiency was 44 %.

d) Adsorption equilibrium

Adsorption from aqueous solutions involves concentration of the solute on the solid surface. As the adsorption process proceeds, the sorbed solute tnds to desorb into the solution. Equal amounts of solute eventually are being adsorbed and desorbd simultaneously. Consequently, the rates of adsorption and desorption will attain an equilibrium state, called adsorption equilibrium. At equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution. The position of equilibrium is characteristic of the entire system, the solute, adsorbent, solvent, temperature, pH, and so on. Adsorbed quantities at equilibrium usually increase with an increase in the solute concentration. The presentation of the amount of solute adsorbed per unit of adsorbent as a function of the equilibrium concentration in bulk solution, at constant temperature, is termed the adsorption isotherm (Samuel *et al*., 1987).

e) Adsorption isotherms

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an adsorption isotherm. Two equations that are often used to describe the experimental isotherm data was developed by two scientists Fruendlich and Langmuir (Metcalf and Eddy, 2004). The empirically derived Freundlich isotherm is defined as follows.

$$\frac{x}{m} = K_f C_e^{1/n} \quad , \quad n > 1$$

Where, $\frac{x}{m}$ = amount of adsorbate adsorbed per unit weight of adsorbent ($mg_{adsorbate}/mg_{adsorbent}$)

C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L)

K_f, n = empirical constant

The constant in the Freundlich isotherm can be determined by plotting (x/m) versus C_e (as shown in Figure 1) and using the following equation.

$$Log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e$$

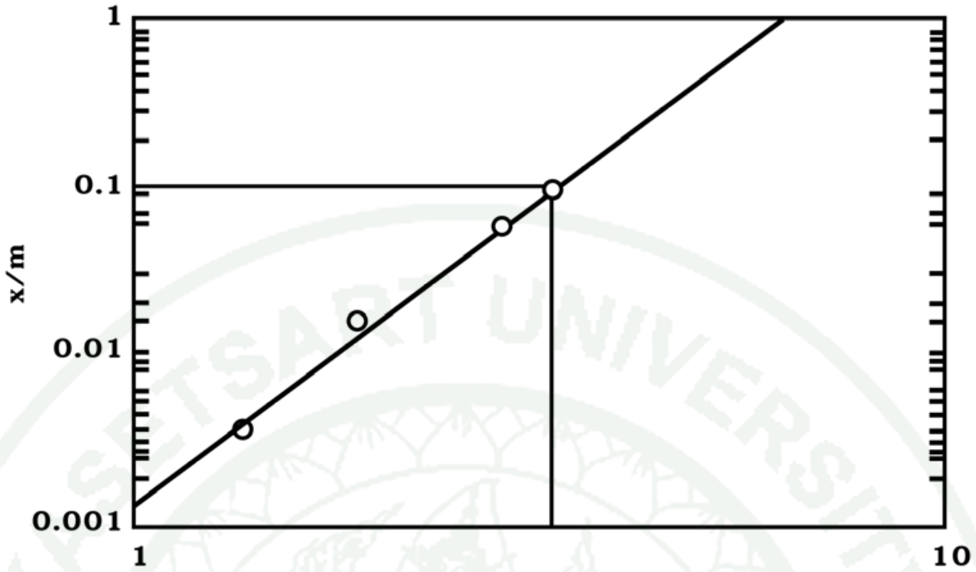

Figure 2 Freundlich isotherms

Source: Metcalf and Eddy (2004)

The Langmuir adsorption isotherm is defined as:

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e}$$

Where, $\frac{x}{m}$ = amount of adsorbate adsorbed per unit weight of adsorbent ($mg_{adsorbate}/mg_{adsorbent}$)

a, b = empirical constant

C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L)

The Langmuir adsorption isotherm was developed by assuming that:

1) A fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy and that

2) Adsorption is reversible

Equilibrium is reached when the rate of adsorption of molecules onto the surface is the same as the rate of desorption of molecules from the surface. The rate at which adsorption proceeds is proportional to the driving force, which is the difference between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At the equilibrium concentration, this difference is zero. The constant in Langmuir isotherm can be determined by plotting $C_e/(x/m)$ versus C_e (as shown in figure 2) and making use of the following equation (Metcalf and Eddy, 2004).

$$\frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{1}{a}(C_e)$$

Isothermal data can be used to calculate the ultimate sorption capacity of the adsorbent by substituting the required equilibrium concentration in Freundlich and/ or Langmuir equations.

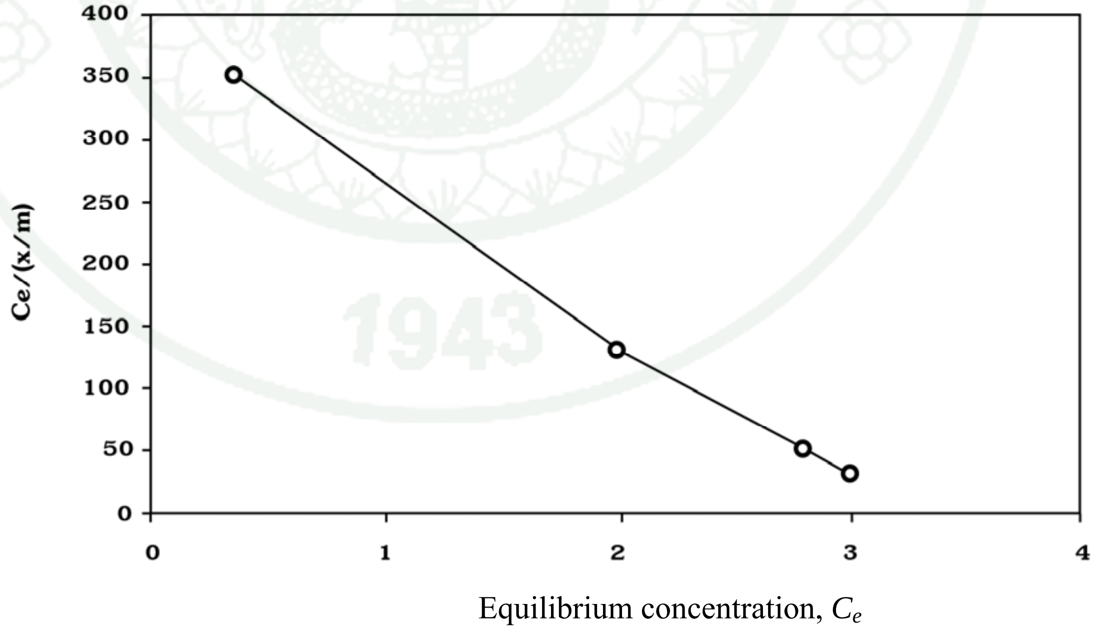

Figure 3 Langmuir isotherms

Source: Metcalf and Eddy (2004)

f) Adsorption kinetics

Two important physicochemical aspects for evaluation of the sorption process as a unit operation are the kinetics and the equilibrium of sorption. Adsorption kinetics are studied to estimate the time required for obtaining equilibrium concentration of adsorbate for the adsorption of heavy metals on an adsorbent.

The adsorption kinetics of an adsorbent can be determined by plotting sorbed heavy metal concentration (C_t) versus time (t) as shown in figures 3-4 for zero-order and first-order reactions rates, respectively.

1) A zero-order reaction

Differential form

$$\frac{dC}{dt} = k_0$$

Solution

$$C_t = C_0 + k_0 t$$

Where, k_0 = zero-order reaction rate constant (concentration/time)

A plot of C_t versus t will yield a straight line for a zero order reaction.

The rate constant can be determined directly from the slope of this line (Sawyer *et al*.,2003).

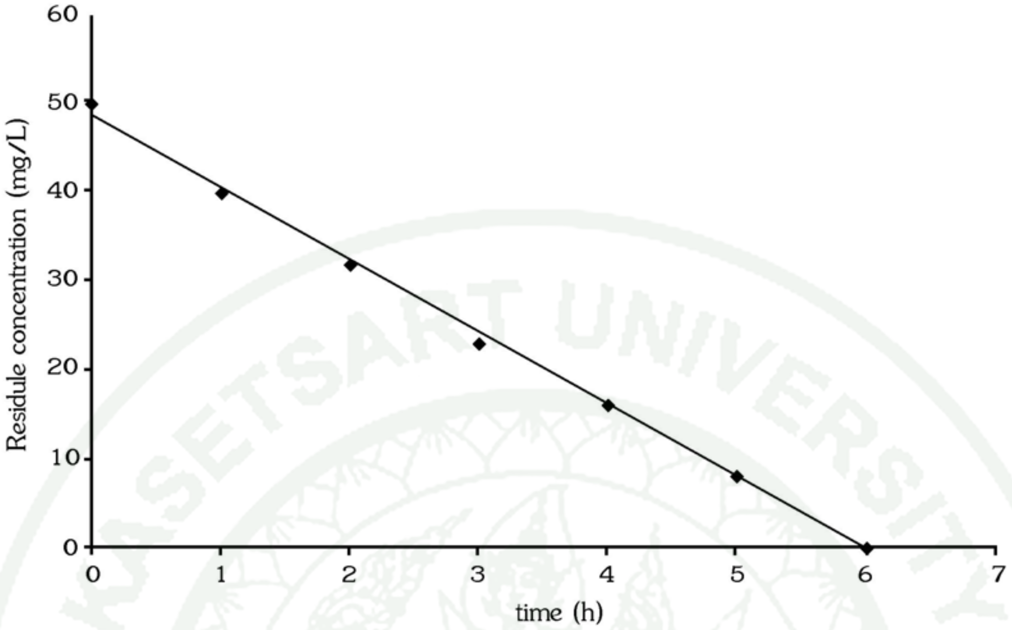

Figure 4 Example of zero-order reaction rate for adsorption

Source: Sawyer *et al*. (2003)

2) A first-order reaction

Differential form

$$\frac{-dC}{dt} = k_1 C$$

Solution
$$C = C_0 e^{-k_1 t}$$

$$ln(C/C_0) = -k_1 t$$

where, C_t = concentration of adsorbate at time t (mg/L)

C_0 = concentration of adsorbate at the beginning (mg/L)

k_1 = the first-order rate constant (time^{-1})

t = time (minute)

A plot of *ln*(C/C_0) versus t will yield a straight line for a first-order reaction.

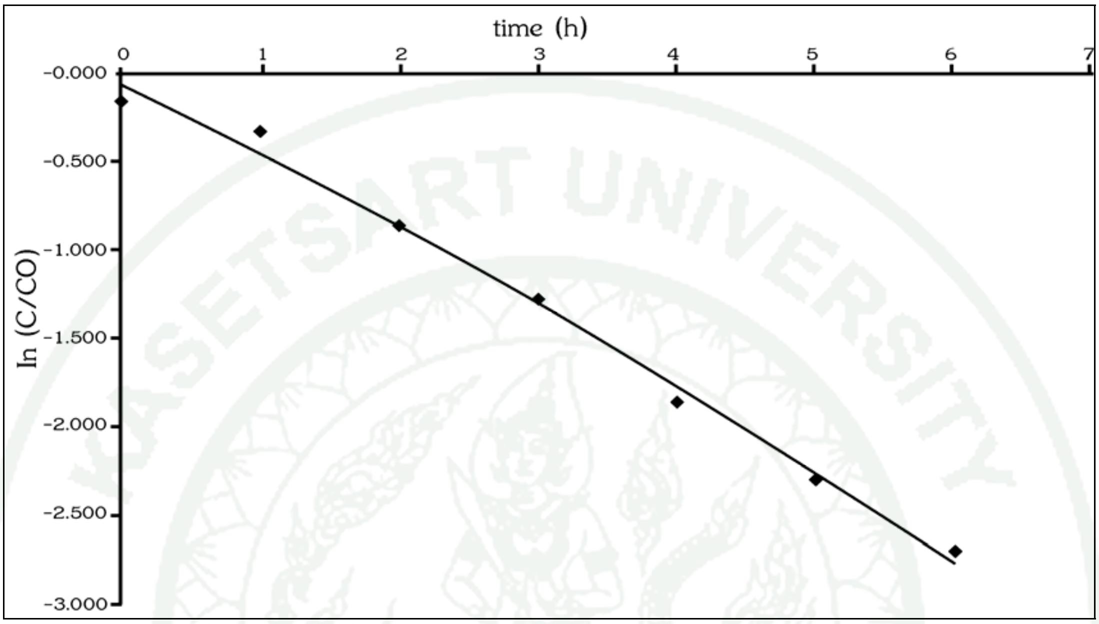

Figure 5 Example of first-order reaction rate for adsorption

Source: Sawyer *et al*. (2003)

3. Egg Shell Membrane (ESM)

Egg shell membrane (ESM) is an intricate lattice network of stable and water-insoluble fibers with high surface area. ESM accumulates and eliminates various heavy metal ions from dilute aqueous solution with high affinity and in short contact time, depending on pH and characteristics of the individual ion. Suyama *et al*. (1994) reported that under certain conditions, the level of precious ions, Au, Pt, and Pd accumulation approaches 55, 25, and 22% of dry wt. of ESM, respectively. Also uranium uptake is 30% of dry wt. of ESM. The experiments results suggested that ESM is promising to use for removal/recovery of metals and water pollution control.

4. Previous studies

Ishikawa *et al*. (1999) conducted a study of removal of radioactive elements from the effluent and waste aqueous solutions. Batch laboratory pH profile, time dependency, and capacity experiments were performed to determine the binding of uranium (U) and thorium (Th) to ESM. Batch pH profile experiments indicated that the optimum pH for binding these actinides was approximately 6.0 for U and 3.0 for Th. The adsorption isotherms were developed at pH 5.0 (U) or 3.0 (Th) at 25°C, and the adsorption equilibrium data fitted both Langmuir and Freundlich models. The maximum uptakes by the Langmuir model were about 240 mg U/g and 60 mg Th/g dry weight ESM. In addition, their adsorption capacities increased as salt concentration increased. ESM could also accumulate uranium from dilute aqueous solution by adjusting to the optimum pH. These results showed that ESM was effective for removing actinides from solution and would be useful in filtration technology to remove actinides from aqueous solution.

Ishikawa *et al*. (2000) conducted a study of the animal byproduct, hen eggshell membrane (ESM), was evaluated for its ability to sorb gold ions dicyanoaurate(I) and tetrachloroaurate(III) from solutions and electroplating wastewater. The gold uptake was dependent on pH, temperature and co-ions present in the solutions, with pH 3.0 being the optimum value. The equilibrium data followed the Langmuir isotherm model with maximum capacities of 147 mg Au^+/g dry weight and 618 mg Au^{3+}/g, respectively. Desorption of sorbed gold(I) with 0.1 mol/l NaOH resulted in no changes of the biosorbent gold uptake capacity through five consecutive sorption/desorption cycles. The affinity of metal sorption was in the order Au>Ag>Co>Cu>Pb>Ni>Zn.

Surasen (2002) studied the efficiency and suitable conditions of cadmium removal in synthetic wastewater by egg shell filter. The pH level, size of egg shell granul, filter rate, type of egg shell, the height of filter media and concentration of cadmium in synthetic wastewater were tested. The results showed that the suitable pH range for cadmium removal by hen egg shell and duck egg shell filter were 4-6 and 5-

6 respectively. The size of egg shell granul was 0.300-0.850 mm. in diameter. And the filter rate was 1.5 m^3/m^2-hr. The best type of egg shell was hen egg shell and the average efficiency of hen egg shell and duck egg shell were 89.85% and 73.62% respectively. The height of filter media increased the efficiency of cadmium removal in creased, that the waste egg shell 50 cm. height was higher efficiency than 20 cm. and the efficiency of cadmium removal decreased as the cadmium concentration in synthetic wastewater increased. The highest efficiency, more than 99.99% of cadmium removal for this study was at the 50 cm. height of hen egg shell, cadmium concentration of 5 mg/L for 24 hours of filtration time.

Boontha (2002) investigated the adsorption ability of cadmium (II), chromium (III) and arsenic (V) from synthetic wastewater by diatomaceous earth in a batch experiment. The results indicated that concentration of heavy metal, amount of diatomaceous earth, pH and contact time affected the heavy metal removal efficiency. The appropriate conditions for this study were as follow : for cadmium, 40 ppm. of Cd at pH 5, 2.0 grams of diatomaceous earth, 100 rpm. of shaking rate and contact time for 10 hours., and for chromium, 40 ppm. of Cr at pH 4, 1.0 gram of diatomaceous earth, 100 rpm. of shaking rate and contact time for 10 hours. As the results, the removal efficiency was 99.92% and 99.82%, respectively. For arsenic, the calcined diatomaceous earth was used, and the condition was as follow : 40 ppm. of As at pH 4, 1.0 gram of calcined diatomaceous earth, 100 rpm. of shaking rate and contact time for 6 hours. The result showed that the removal efficiency was 99.96% The adsorption isotherm of cadmium can be described by the Freundlich isotherm. For chromium, the equilibrium was not followed the adsorption isotherm because the removal of chromium was based on the precipitation, and for arsenic, the adsorption isotherm could be described by the Langmuir isotherm. The results from leaching test showed that concentration of cadmium and chromium in the solution were less than those values of the Ministry of Industry's standard but concentration of arsenic in the solution was higher than the standard. In the case of battery factory's wastewater containing chromium, arsenic and lead at 0.23, 0.42 and 5.89 ppm., respectively, more than 99% of all heavy metals could be removed by diatomaceous earth.

Misra *et al*. (2002) conducted a study of Keratin protein fiber (AKFTM), a renewable source of biosorbent that can be used for filtration of heavy metal and nanosize contaminants. The major composition of keratin fiber is the structured protein micofibril, consisting of numerous nanosized pores. The combination of nanostructure and metal binding capacity protein sites made it an ideal material for removal of heavy metals from solutions. The mechanism of heavy metal uptake onto keratin protein involved a combination of several steps such as adsorption, precipitation, and ion exchange. Keratin protein had good tensile strength and was stable over a wide pH range.

Tsai *et al*. (2004) conducted a study of the chemical and physical characterization of eggshell and eggshell membrane particles prepared from the hen eggshell waste. Under the characterization measurements investigated, it was found that the pore structures of the two biomaterials belong to a typical Type II, indicating that they should be basically characteristic of nonporous materials or materials with macropores or open voids. Further, the chemical composition of the resulting eggshell particle was strongly associated with the presence of carbonate minerals from the Fourier transform infrared (FTIR) spectra. In contrast to the resulting eggshell membrane particle, the presence of functional groups of amines and amides was observable because of its chemical composition of fibrous proteins. From the isotherm data of methylene blue at 25 °C, the Freundlich model yielded a somewhat better fit than the Langmuir model. The adsorption isotherms revealed the eggshell biosorbents could only uptake the basic dye of less than 1.0 mg/g in aqueous medium, which was attributed to their poor pore properties.

Chojnacka (2004) carried out sorption studies of Cr^{3+} from aqueous solutions by eggshells as a low-cost sorbent. It was found that crushed eggshells posses relatively high sorption capacity, when comparing with other sorbents. The sorption capacity was calculated to be 21–160 mg/g. The effect of process parameters: pH, temperature, initial concentration of Cr^{3+} on the process kinetics was studied. It was found that the equilibrium of the process was reached after 60 min. Mathematical models describing kinetics and equilibrium of sorption were proposed. The process kinetics was described with pseudo-second-order pattern and equilibrium was described with Langmuir-type equation, and the influence of sorbate concentration, with an empirical dependence. The models were positively verified. Eggshells were able to remove the concentration of Cr^{3+} below the acceptable level at 40 °C, at the initial concentration of metal ions 100 mg/kg, and at sorbent concentration 15 g/L.

Vijayaraghavan *et al*. (2004) investigated ability of ESM to remove copper from aqueous solution in an up-flow packed column. The sorption performance of eggshell in the column was examined by varying the bed height (15–25 cm) and flow rate (5–20 ml/min). The column was regenerated using 0.01 M EDTA solution and sorption–desorption studies were carried out for five cycles.

Rattanatraicharoen *et al*. (2004) investigated the adsorption of Potassium and Zinc ions from solution by rice husk ash was studied. The extent of adsorption studied as a function of burning temperature, adsorbent size, pH value of solution and solution temperature. The maximum adsorption of zinc(II) occurred at pH 6.5, solution temperature 45 ˚C by rice husk burned at 400 ˚C with their size smaller than 180 micrometer. In contrast, Potassium did show a capacity of adsorption but it can be released into solution 1.15 mg/g from the husk. In study of adsorption behavior of Zn on untreated(R), Sodium Chloride-treated rice husk(NRH), Potassium Hydroxide-treated rice husk(KRH) and Acetic acid-treated rice husk(ARH), it was found out that KRH had the best performance for adsorbing Zinc, while both ARH and NRH reduced the capacity of adsorption. The sorption process conformed to the Langmuir Isotherm. The maximum amount of adsorption (v) of Zn(II) is 11.56 mg/g.

Michael *et al*. (2005) investigated of the effect of temperature on the removal of Pb^{2+} and Cd^{2+} in aqueous effluent using *C. bicolor* biomass in a batch sorption process. The result showed that the most suitable sorption temperature was 40ºC with maximum sorption capacities of 49.02 mg/g and 52.63 mg/g for Pb^{2+} and Cd^{2+} respectively. Various thermodynamic parameters, such as ΔG^o, ΔH^o, ΔS^o and E_a have been calculated. The data showed that the sorption process was spontaneous and exothermic in nature and that lower solution temperatures favours metal ion removal by the biomass. The findings of this investigation suggest that physical sorption plays a role in controlling the sorption rate. The sticking probability model was further employed to assess the applicability of the *C. bicolor* biomass as an alternative adsorbent for metal ion contaminants in aqueous system.

Sushree *et al*. (2005) investigated the adsorption of Cd^{2+} onto amorphous hydrous manganese dioxide (δ-MnO_2) has been studied in (a) 0.5 M NaCl solution and (b) major ion seawater. The adsorption experiments were carried out in two methods: isotherms at constant pH in the presence of a buffer solution over a wide range of initial Cd^{2+} concentrations (0.0089 to 0.5357 mM) and varied pH (2–7.5) in the absence of a buffer solution at 0.0911 mM Cd^{2+} concentration. In order to describe the isotherm mathematically, the experimental data of the adsorption equilibrium were correlated by either the Langmuir or Freundlich equations. Results indicated that the Langmuir-type model gave a better fit to the experimental data than the Freundlich type in both electrolyte media. The proton stoichiometry derived from isotherms at two close pH values vary between 0.22 to 0.42 for the 0.5 M NaCl solution. The variation of fractional adsorption with pH could be modeled either with the formation of a $SOCd^+$ complex or with a combination of $SOCd^+$ and SOCdOH complex, depending upon the electrolyte medium. The equilibrium constants obtained from Kurbatov-type plots were found to be the most suitable for these model calculations.

Yamkate *et al*. (2005) investigated the removal of nickel and cadmium ions by husk and *Bacillus subtilis*, in 50 mg/l of Ni^{2+} and Cd^{2+} solutions at pH 5, pH 6 and pH 7. The highest removal by husk ash at pH 7 of Ni^{2+} was 30.957% and Cd^{2+} was 52.847% and by husk ash and bacteria at pH 7 of Ni^{2+} was 39.383% and Cd^{2+} was 67.986%.

Zheng *et al*. (2006) conducted a study of carbonate hydroxylapatite (CHAP), synthesized by using eggshell waste as raw material, as metal adsorption for Cd^{2+} and Cu^{2+} from aqueous solutions. The effect of various parameters on adsorption process such as contact time, solution pH, amount of CHAP and initial concentration of metal ions was studied at room temperature to optimize the conditions for maximum adsorption. The results showed that the removal efficiency of Cd^{2+} and Cu^{2+} by CHAP could reach 94 and 93.17%, respectively, when the initial Cd^{2+} concentration 80 mg/L and Cu^{2+} 60 mg/L and the liquid/solid ratio was 2.5 g/L. The equilibrium sorption data for single metal systems at room temperature could be described by the Langmuir and Freundlich isotherm models. The highest value of Langmuir maximum uptake, *b*, was found for cadmium (111.1 mg/g) and copper (142.86 mg/g). Similar Freundlich empirical constants, *K*, were obtained for cadmium (2.224) and copper (7.925). Ion exchange and surface adsorption might be involved in the adsorption process of cadmium and copper. Desorption experiments showed that $CaCl_2$, NaCl, acetic acid and ultrasonic were not efficient enough to desorb substantial amount of metal ions from the CHAP. The results obtained show that CHAP has a high affinity to cadmium and copper.

Yeddou and Bensmaili (2006) investigate the sorption of Fe^{3+} onto eggshells. The batch sorption was studied with respect to solute concentration, contact time, adsorbent dose and temperature. The results showed that the sorption capacity decreases with an increase in temperature from 20 to 50°C at the initial Fe^{3+} solution concentration of 5 mg/L. Pseudo-second order model can be used to describe the kinetics of Fe^{3+} sorption. The constants obtained from the pseudo-second order kinetic model at different temperatures were evaluated and the activation energy was found to be –13.40 kJ/mol. Thermodynamic parameters such as enthalpy, entropy and Gibb's free energy changes were also calculated. The Freundlich and Langmuir adsorption models were applied to experimental equilibrium data and the isotherm constants were calculated using linear regression analysis.

Arami *et al*. (2006) investigated the adsorption isotherms of Direct Red 80 (DR80) and Acid Blue 25 (AB25) on the egg shell membrane (ESM) at 20+/-1 degrees C. Physical characteristics of ESM such as surface area and presence of functional groups were verified. The Fourier transform infra-red (FTIR) spectra proved the presence of functional groups such as hydroxyl, amine and carbonyl groups in ESM. The surface area of ESM was found to be 2.2098 m^2/g. The effects of operational parameters such as initial dye concentration, pH, contact time, particle size and ESM doses were studied. The Langmuir, Freundlich, BET, Redlich-Peterson and Temkin adsorption models were applied to describe the equilibrium isotherms. The pseudo-first-order and pseudo-second-order kinetics models were examined to evaluate the kinetics data at different pH values and the rate constants were calculated. Maximum desorption of 81.8% was achieved for both dyes in aqueous solution at pH 12. Also scanning electron micrographs (SEM) of the treated and untreated adsorbent were performed. Results indicate that ESM could be employed as a natural and Eco-Friendly adsorbent material for the removal of trace organics in solutions.

Maria *et al*. (2006) investigated the ion-exchange equilibrium of Pb^{2+} and Cd^{2+} on clinoptilolite from different deposits. The Langmuir isotherm fitted the ion-exchange equilibrium data of both ions better than the Freundlich isotherm. The capacity of the natural zeolite to exchange Cd^{2+} and Pb^{2+} increased, augmenting the solution pH. This behaviour was attributed to the interactions between the ions in solution and the surface charge of the zeolite. Moreover, the capacity of the natural zeolite to exchange Cd^{2+} and Pb^{2+} was increased when the temperature was raised from 15 to 35 °C. This tendency was explained by assuming that the ion exchange was an endothermic reaction. The selectivity of the zeolite for the metal cations decreased in the following order: $Pb^{2+} > Cd^{2+}$. This order was not modified while reducing the solution pH, but the zeolite selectivity was increased. At pH 2 the selectivity of the zeolite for Pb^{2+} was nearly three times larger than at pH 4.

Ibrahim *et al*. (2006) investigated the ability of sugarcane bagasse to adsorb Cd^{2+} from aqueous solutions through batch experiments. The highest Cd^{2+} adsorption was achieved at agitation rate of 150 rpm. The adsorption process was relatively fast and equilibrium was achieved after about 90 min of contact. The optimum adsorption of cadmium occurred at pH range 5-7. The kinetic process of Cd^{2+} adsorption onto sugarcane bagasse was tested by applying pseudo-first order, pseudo-second-order and intraparticle diffusion rate equations. The equilibrium data fitted the Langmuir isotherm model. The maximum adsorption capacity determined from the Langmuir isotherm was found to be 6.79 mg/g at 30 °C.

Park *et al*. (2007) conducted a study of the removal capacity of toxic heavy metals by the reused eggshell. As a pretreatment process for the preparation of reused material from waste eggshell, calcination was performed in the furnace at 800°C for 2 h after crushing the dried waste eggshell. Calcination behavior, qualitative and quantitative elemental information, mineral type and surface characteristics before and after calcination of eggshell were examined by thermal gravimetric analysis (TGA), X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. After calcination, the major inorganic composition was identified as Ca (lime, 99.63%) and K, P and Sr were identified as minor components. When calcined eggshell was applied in the treatment of synthetic wastewater containing heavy metals, a complete removal of Cd as well as above 99% removal of Cr was observed after 10 min. Although the natural eggshell had some removal capacity of Cd and Cr, a complete removal was not accomplished even after 60 min due to quite slower removal rate. However, in contrast to Cd and Cr, an efficient removal of Pb was observed with the natural eggshell rather than the calcined eggshell. From the application of the calcined eggshell in the treatment of real electroplating wastewater, the calcined eggshell showed a promising removal capacity of heavy metal ions as well as had a good neutralization capacity in the treatment of strong acidic wastewater.

Tungtakanpoung *et al*. (2007) investigated the passion fruit *(Passionflora Edulis)* peel was used to study its efficiency as sorbent for the removal of cadmium, nickel and zinc from aqueous solution. Batch experiments were performed as a function of contact time, pH, initial metals concentration and temperature. The results show that, the sorption process was relatively fast and equilibrium was reached after about 60 min of contact. The optimum pH for cadmium and nickel sorption was 7 while for zinc it was 5. The Langmuir isotherm model was found to be suitable for describing the sorption equilibrium.

Erol *et al*. (2007) conducted the removal of trace amounts of heavy metals can be achieved by means of selective ion-exchange processes. The newly developed resins offered a high resin capacity and faster sorption kinetics for the metal ions such as Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions. Experimental investigations were undertaken using the ion-exchange resin Lewatit CNP 80 (weakly acidic) and were compared with Lewatit TP 207 (weakly acidic and chelating). The optimum pH range for the ion-exchange of the above mentioned metal ions on Lewatit CNP 80 and Lewatit TP 207 were 7.0-9.0 and 4.5-5.5, respectively. The obtained sorption affinity sequence in the presented work was $Ni^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$. The metal ion concentrations were measured by AAS methods. The distribution coefficient values for metal ions of 10^{-3} M initial concentration at 0.1 mol/L ionic strength show that the Lewatit CNP 80 was more selective for Ni^{2+}, Cu^{2+} than it was for Cd^{2+}, Zn^{2+} and Pb^{2+}. Langmuir isotherm was applicable to the ion-exchange process and its contents were calculated. The uptake of metal ions by the ion-exchange resins was reversible and thus has good potential for the removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} from aqueous solutions. The amount of sorbed metal ion per gram dry were calculated as 4.1, 4.6, 4.7, 4.8, and 4.7 meq./g dry resin for Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+}, respectively. Selectivity increased in the series: $Cd^{2+} > Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$. The results obtained showed that Lewatit CNP 80 weakly acidic resin had shown better performance than Lewatit TP 207 resin for the removal of metals. The change of the ionic strength of the solution exerts a slight influence on the removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+}. The presence of low ionic strength or low concentration of $NaNO_3$ does not have a significant effect on the ion-exchange of these metals by the resins. We conclude that Lewatit CNP 80 can be used for the efficient removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} from aqueous solutions.

Buasri *et al*. (2008) investigated the potential of adsorption of heavy metal ions by natural zeolite, the effect of initial concentration and pH of heavy metal ions solutions in respective ranges of 100-1,500 ppm and 2.0 to 7.0 on adsorption efficiency. The optimum initial pH for lead and cadmium adsorption by the natural zeolite was 7.0. The adsorption of lead and cadmium ions solution was 59.98 and 24.78 mg metal/g zeolite, respectively.

Table 1 The summary of previous studies

Type of Metal	pH	Technology	Material adsorption	Reference
Cd^{2+}	4.0-6.0	adsorption	Egg shell	Surasen (2002)
	5.0	adsorption	Diatomaceous earth	Boontha (2002)
	5.0	adsorption	C. *bicolor* biomass	Michael *et al*. (2005)
	2.0-7.5	adsorption	Amorphous hydrous manganese dioxide	Sushree *et al*. (2005)
	5.0-7.0	adsorption	Husk and Bacillus subtilis	Yamkate *et al*. (2005)
	-	adsorption	Egg shell	Zheng *et al*. (2006)
	2.0-4.0	ion-exchange	Zeolite	Maria *et al*. (2006)
	5.0-7.0	adsorption	Sugarcane bagasse	Ibrahim *et al*. (2006)
	7.0-9.0	ion-exchange	Resin	Erol *et al*. (2007)
	2.0-7.0	adsorption	Zeolite	Buasri *et al*. (2008)
Zn^{2+}	5.0	adsorption	Rice husk	Rattanatraicharoen *et al*. (2004)
	2.0-9.0	adsorption	Passion fruit peel	Tungtakanpoung *et al*. (2007)
	7.0-9.0	ion-exchange	Resin	Erol *et al*. (2007)

MATERIALS AND METHODS

Materials

1. Analytical balance (4 digits)	(Satorius model RP210S)
2. Atomic adsorption spectrophotometer (AAS)	(Perkin – Elmer model 3110)
3. Hot air oven	(Memmert model ULE 500)
4. Water shaker bath	(Hettich model EBA 20)
5. Sieve mesh no.35,40	(RETSCH model AS2000)
6. pH meter pen type	(Tecpel Co., Ltd. model PH703)
7. Erlenmeyer flask	(Pyrex)
8. Blender	(Toastess model TB-50GS)
9. $Zn(NO_3)_2.6H_2O$	Analytical grade, Riedel-de Haen
10. $Cd(NO_3)_2.3H_2O$	Analytical grade, Riedel-de Haen
11. HCl	Analytical grade, Merck
12. 0.1 M HNO_3	Analytical grade, Merck
13. 0.1 M NaOH	Analytical grade, Merck
14. de-ionized water	-

Methods

1. Adsorption Rate Experiment

The rapid initial was a common behavior found in adsorption of organic contaminants to soils or colloidal particle. The initial rapid adsorption could be described by the surface phenomenon. The mass transfer (or in this case, adsorption rate) can be modeled as a function of (Eq.1) the difference between the phase equilibrium condition and the actual condition and the interfacial area as described by following equation.

$$\frac{dC_w}{dt} = K_L a\left(C_w - C_w^*\right) \qquad \text{(Eq.1)}$$

Where $\frac{dC_w}{dt}$ = rate of mass transfer or adsorption rate, mg/L min^{-1}

K_La = adsorption rate constant, min^{-1} (the product of mass transfer coefficient, K_L (m min^{-1}) and interfacial area per unit volume, a (m^2 m^{-3})

C_w = Cd^{2+} and Zn^{2+} concentration in water, mg/L

C_w^* = concentration of Cd^{2+} and Zn^{2+} that is equilibrium with concentration in the solids, mg/L

In this study, the initial adsorption rates were analyzed, i.e., the adsorbed Cd^{2+} and Zn^{2+} concentration was taken as zero and consequently, C_w^* is equal to zero. Thus Eq.1 was written as;

$$\frac{dC_{w,i}}{dt} = K_L a C_{w,i} \qquad \text{(Eq.2)}$$

Where $C_{w,i}$ = initial Cd^{2+} and Zn^{2+} concentration in water, mg/L

In the analyzes, the initial adsorption rates for each set of experiment were calculated from initial concentration at time zero and the subsequent concentration.

2. Experimental Preparation

2.1 Synthetic wastewater preparation

A synthetic wastewater was prepared from zinc(II) nitrate ($Zn(NO_3)_2.6H_2O$), cadmium(II) nitrate ($Cd(NO_3)_2.3H_2O$) the initial concentration of all are 5.0, 10.0, 20.0, 30.0, 40.0, 50.0 mg heavy metals/L. Also HCl, and de-ionized water were used in this study. All synthetic wastewater pH were adjusted with 0.1 M HNO_3 and/or 0.1 M NaOH.

2.2 Equipments preparation

All equipments used in this study were rinsed with 0.1 M HNO_3 and de-ionized water.

2.3 Egg shell membrane (ESM) preparation

Egg shell membrane (ESM) was removed from crushed hen-egg shell waste that was thoroughly washed and dried in hot air oven at 60 °C for 1 hour. After that, ESM was blended in a domestic blender that have glass body with stainless steel blade for 3 minutes. The blended ESM was sieved to obtain particle size between 32-35 mesh or about 0.425-0.500 μm. After completed the sieve, about 85.92 % of all blended ESM was recovered.

2.4 Control experiment

The control experiment was carried out under the same conditions except without adding ESM. The flasks were put on water bath shaker controlled at the 25°C and the rotation speed of 80 rpm. at all time during the experiments.

3. Adsorption experiments

In order to evaluate adsorption performance of ESM for the removal of Zn^{2+} and Cd^{2+} from the synthetic wastewater, following steps will be involved.

3.1 Determination of optimum pH for adsorption

The optimum pH for adsorption of Zn^{2+} and Cd^{2+} by ESM was determined experimentally. The concentrations of Zn^{2+} and Cd^{2+} solutions were prepared at 5 mg/L. Samples of 50 mL of these solutions were transferred into the acid rinsed erlenmeyer flasks. The initial pH of the samples were adjusted to 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and

10.0 by 0.1 M HNO_3 acid and 0.1 M NaOH when needed. Subsequently, 50 mg of blended ESM was added to each flask. The flasks were placed on a shaker water bath maintained at 25 °C and 80 rpm. Samples were centrifuge and withdrawn from supernatant after equilibrium was achieved and heavy metal concentrations were analyzed by using atomic adsorption spectrophotometer apparatus by Perkin – Elmer model 3110. The optimum pH for Cd^{2+} and Zn^{2+} adsorption were ascertained from maximum metal adsorption by ESM. A step by step methodology of this study is shown in Figure 6.

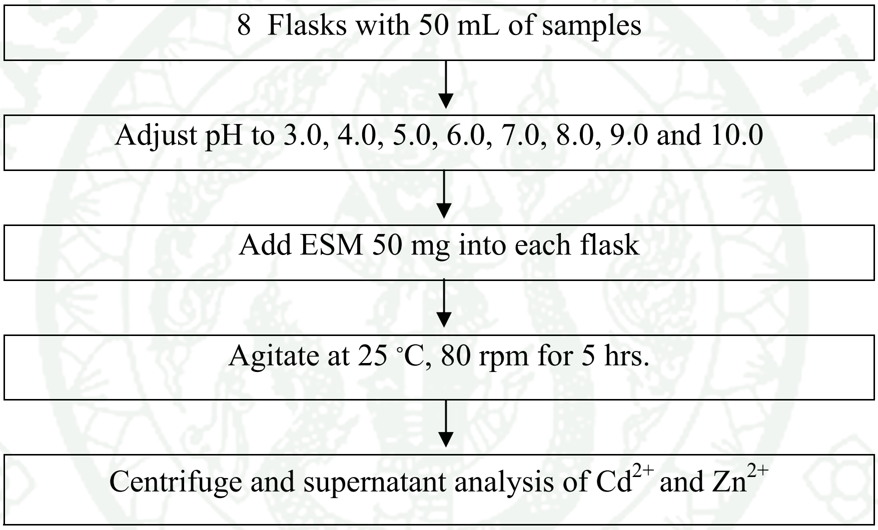

Figure 6 Experimental steps for determination of optimum pH for adsorption.

The adsorption capacity of ESM will be estimated by following equation:

$$\frac{x}{m} = \frac{V(C_0 - C_{eq})}{m}$$

Where, V = volume of solution (mL)

m = mass of adsorbent (g)

C_0 = initial metal concentration (mg/L)

C_{eq} = metal concentration at equilibrium (mg/L)

$\frac{x}{m}$ = the adsorbate concentration or sorption capacity of ESM (mg/g)

3.2 Determination of adsorption kinetics

Solutions with an initial heavy metal concentration of 5 mg/L were prepared from the standard solutions and then adjusted to optimum adsorption pH for each metal. Samples of 50 mL from these solutions were poured into 8 acid rinsed erlenmeyer flasks and then 50 mg of ESM particles were added to each flask. All flasks were placed on shaker water bath maintained at the temperature of 25 °C and the rotation speed of 80 rpm. Each flask was removed from water bath shaker at predetermined time interval, which were 5 min, 10 min, 15 min, 30 min, 1 hr, 2 hr, 3 hr, 4 hr and 5 hr. Flask contents were centrifuged to remove ESM particles at 80 rpm (Hettich model EBA 20) and the amount of heavy metal contents in the supernatant were analyzed using atomic adsorption spectrophotometer (Perkin – Elmer model 3110). A step by step methodology of this study was shown in Figure 7.

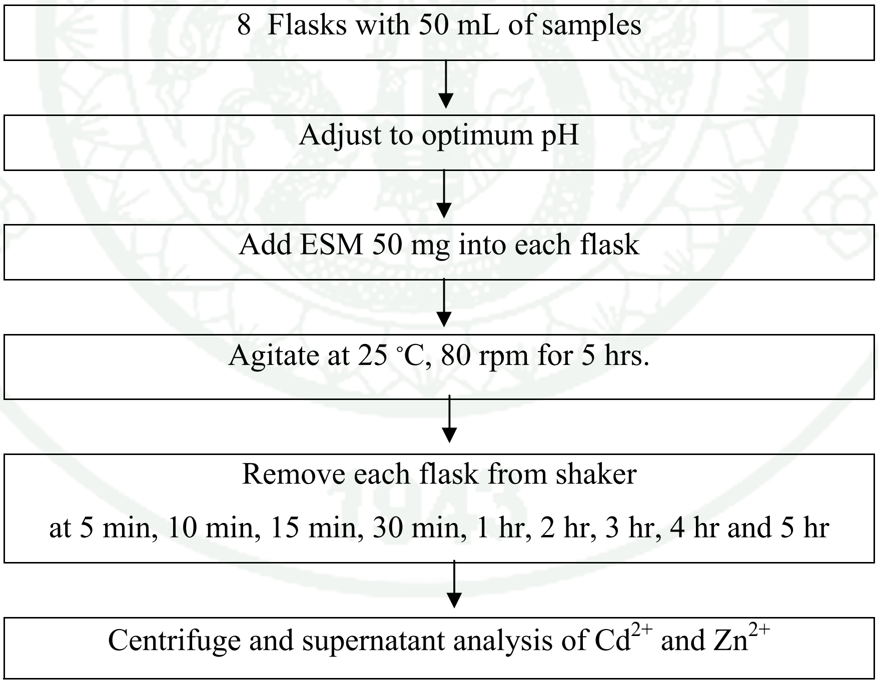

Figure 7 Experimental steps for adsorption kinetics studies.

3.3 Determination of adsorption isotherms

Isotherm studies were conducted to estimate the adsorption capacity of ESM for heavy metals removal from synthetic wastewater. Cadmium and zinc solutions with various concentrations were prepared from standard solutions. Samples of 50 mL from these solutions were poured into 6 erlenmeyer flasks and the initial pH were adjusted to the optimum adsorption pH for each metal. Subsequently, 50 mg of ESM were added to each flask. The content of the flasks were agitated using water bath shaker controlled at the 25 °C and the rotation speed of 80 rpm. After 4 hours, content of each flask were centrifuge to remove ESM particles and the amount of heavy metal content in the supernatant were analyzed by using atomic adsorption spectrophotometer apparatus by Perkin – Elmer model 3110. A step by step methodology of this study is shown in Figure 8.

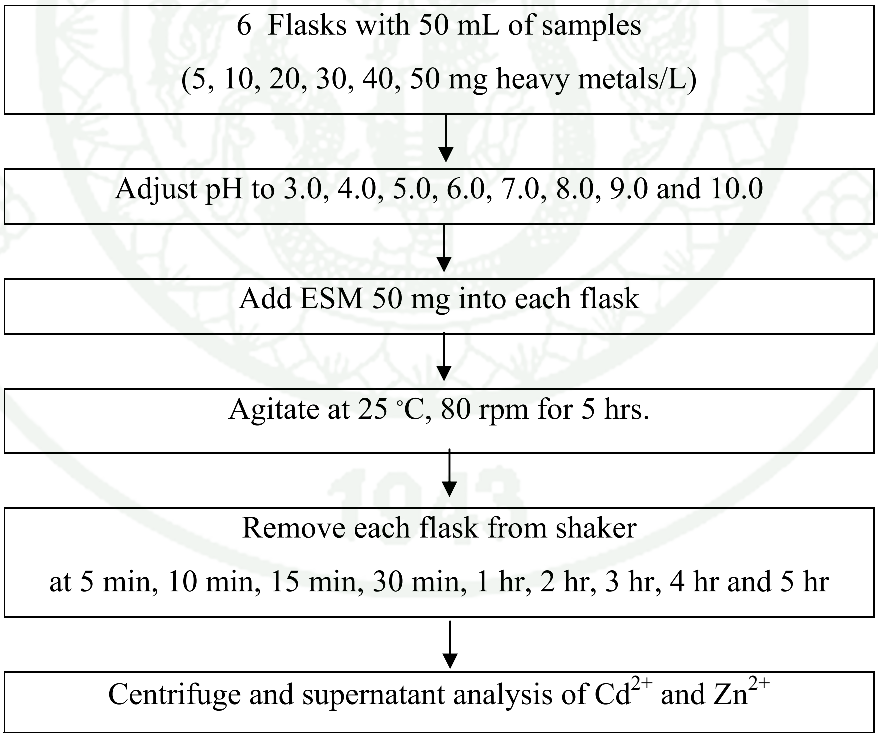

Figure 8 Experimental steps for adsorption isotherm studies.

RESULTS AND DISCUSSION

In this study, the experiments were set up in laboratory and were divided into 5 parts which consisted of the study on adsorption isotherm, adsorption kinetic, effect of pH and effect of contact time on cadmium and zinc adsorption by egg shell membrane (ESM).

1. Effect of contact time on cadmium and zinc adsorption by egg shell membrane (ESM)

The effect of contact time on cadmium and zinc adsorption. The contact time 0-300 min. The adsorption data (at pH 5, 6 respectively) for initial Cd^{2+} and Zn^{2+} concentration of 5 mg/L was show in Figure 9. Experiments conducted with different contact times show that the amounts of Cd^{2+} and Zn^{2+} ions adsorbed per unit mass of egg shell membrane (ESM) increase with the adsorption time of metal ions. The slopes of the lines joining the data points in the figure reflect the adsorption rates. As it was seen, high adsorption rates were observed at the beginning and then plateau values were reached within 120 min. The mechanism can be explained that active site is caught by heavy metal ion, when the time passing, active site for adsorbing ion is reduced affecting the decreasing of adsorption rate. This results was supported by work done by Sriketphet (2002) who reported that the equilibrium time to adsorb lead, zinc, cadmium and chromium by clay could be reached at about 1-2 hr. As well as the study of Ibrahim et al. (2006), who studied o the equilibrium time to removal Cd^{2+} from aqueous solutions by sugarcane bagasse, and the results showed that the necessary contact time to be reaches equilibrium was about 90 min.

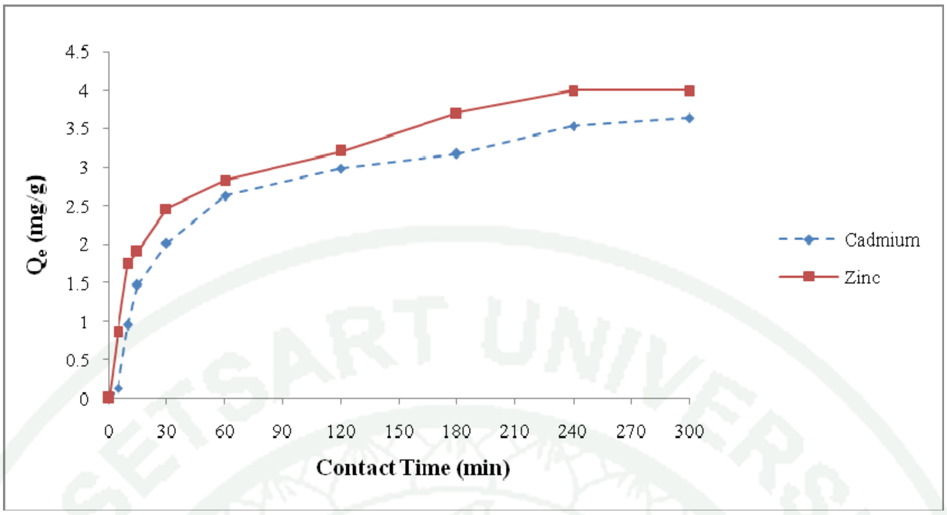

Figure 9 Effect of contact time on the removal of Cd^{2+} and Zn^{2+} by egg shell membrane. (Initial Cd^{2+} and Zn^{2+} concentration 4.79 mg/L, pH 5.0 for cadmium and 6.0 for zinc, adsorbent 1 g/L, adsorption time 0-300 minutes)

2. Effect of initial pH on cadmium and zinc adsorption by egg shell membrane (ESM)

pH is one of the most important controlling parameters in all adsorption processes. The effect of pH on cadmium and zinc adsorption by egg shell membrane (ESM) was studied for pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0. Efficiency of metal sorption depends on the pH level of aqueous solution. The pH dependence of Cd^{2+} and Zn^{2+} adsorption onto egg shell membrane is shown in Figure 10. As it is seen in figure, q_e was low at low pH values. Cd^{2+} and Zn^{2+} adsorption was found to increase with increasing pH of the solution. Cd^{2+} adsorption was only 2.17 mg/g at pH 3.0 but increased to 3.64 mg/g at pH 6.0. For Zn^{2+} adsorption was only 3.85 mg/g at pH 3.0 but increased to 3.99 mg/g at pH 5.0. And when using solutions the pH values over 6.0 the adsorption the value of Q_e was decreased.

In fact the effect of pH on heavy metal adsorption capacity of soil are depending on several mechanisms in soil. In addition, the pH is also affected by cation adsorption site of soil particle, metal species and type of charge at soil surface. The importance of pH to adsorption capacity has also mentioned by Tungtakanpoung *et al.* (2007), who work to removal of cadmium, nickel and zinc by passion fruit peel and started that the pH of synthetic solution is an important variable which controls adsorption of the metal at the passion fruit peel-water interfaces. In case of decreasing of the heavy metal adsorption, it is probably during to a reduction of negative surface charges on the passion fruit peel. As the pH level very much affected to the hydrogen ion (H^+) on the surface of egg shell membrane. Whenever, the low pH has been applied in the adsorption process, the large amount hydrogen ion (H^+) will be released and presented in the solution. Therefore, it is unable to adsorb the heavy metal as good as the solvent with high pH level, during to competition with ion of heavy metal to achieve areas of the adsorption (Methongmool, 2002).

As we can see from results of this work that the egg shell membrane has high adsorption efficiency for heavy metal. Moreover, we also found that after the dissolvent contacts with egg shell membrane, the pH level will be rising up until it becomes precipitated. Since egg shell membrane (ESM) is an alkaline that cause to dispersion of the hydroxyl group (OH^-) on the surface of egg shell membrane. The dispersed hydroxyl group (OH^-) combined with heavy metal ion in the solvent which cause heavy metal precipitation. Otherwise, it is as a result of positive ion of which is interchanged on the surface of passion fruit peel with high pH level. The interchange of positive ion and hydrogen ion (H^+) which dispersed from H_2O, cause the hydroxyl group (OH^-) will then combine with ion of heavy metal which also cause precipitation in heavy metal. Thus the adsorption efficiency of heavy metal in synthetic wastewater occurred by egg shell membrane (Tungtakanpoung *et al.*, 2007). Generally. Adsorption and precipitation process are occurred at the same time when heavy metal solution and egg shell membrane (ESM) are combined at particular pH level. However, the obtainable pH level that suitable for adsorption of Cd^{2+} and Zn^{2+} are 6.0 and 5.0 respectively.

These results are in agreement with the result conducted by Tungtakanpoung *et al.* (2007), who indicated the efficiency of passion fruit peel in removing cadmium, nickel and zinc, and also the maximum efficiency to cadmium and zinc removal at pH 7.0 while for zinc it was 5.0. This work is also consistent to work done by Yamkate *et al.* (2005), who reported that the maximum efficiency of husk and *Baillus subtilis* in removing Ni^{2+} and Cd^{2+} solutions at pH 5.0-7.0. Moreover, work done by Surasen (2002) have also reported on adsorption efficiency of cadmium by hen egg shell, showing that at the pH 4.0-6.0 the adsorption efficiency of solutes would be increased.

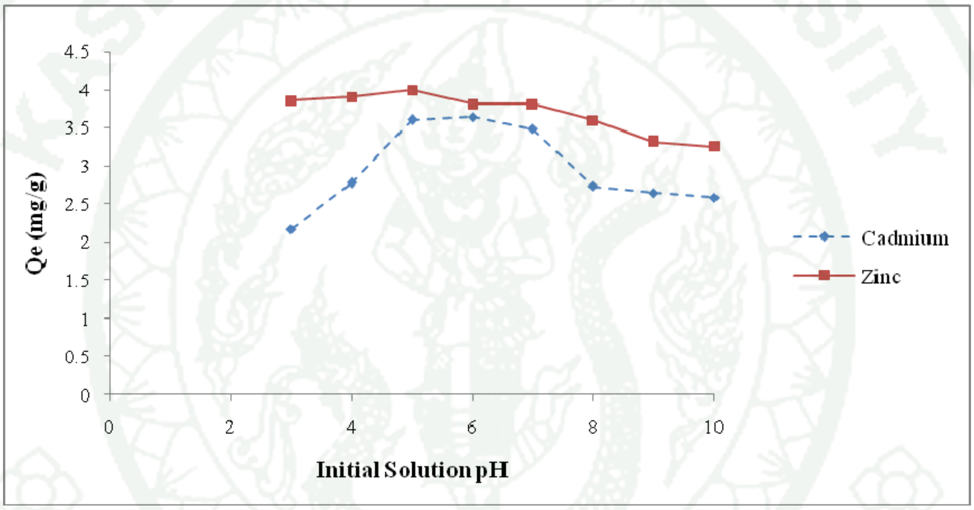

Figure 10 Effect of initial solution pH on the removal of Cd^{2+} and Zn^{2+} by egg shell membrane. (Initial Cd^{2+} and Zn^{2+} concentration 4.79 mg/L, pH 3.0-10.0, adsorbent 1 g/L, contact time 300 minutes)

3. Effect of initial concentration of heavy metal ion solution

Figure 11 illustrates the adsorption of Cd^{2+} and Zn^{2+} ions by egg shell membrane (ESM) as a function of initial metal ion concentration. This increase continues up to 20 mg/L for Cd^{2+} and 40 mg/L for Zn^{2+} and beyond value, there is not a significant change at the amount of adsorbed metal ions. This plateau represents saturation of the active sites available on the egg shell membrane (ESM) samples for interaction with metal ions. It can be concluded that the amount of metal ions adsorbed into unit mass of the egg shell membrane (ESM) at equilibrium (the adsorption capacity) rapidly increased at the low initial metal ions concentration and then it began to a slight increase with increasing metal concentration in aqueous solutions in a range between 20 and 50 mg/L for cadmium, but 40 and 50 mg/L for zinc.

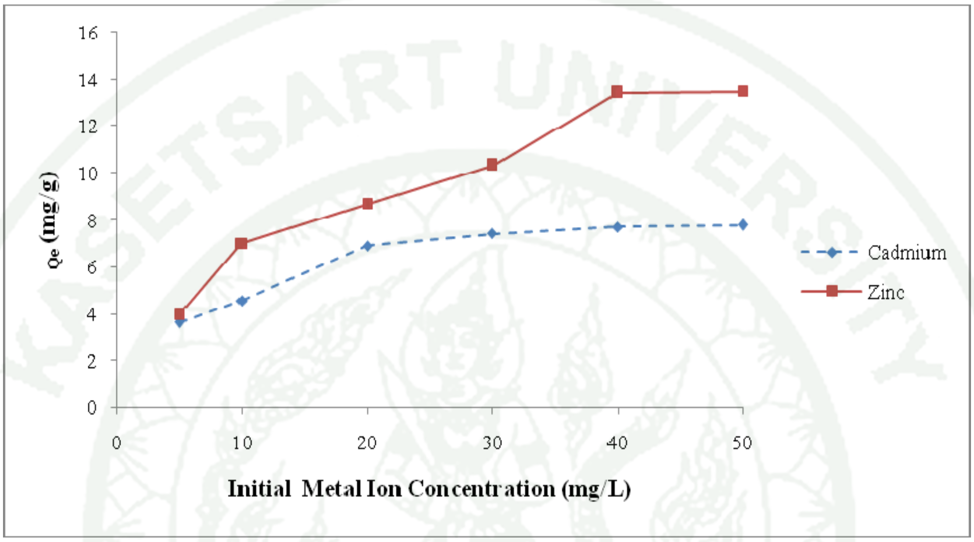

Figure 11 Effect of initial concentration on the removal of Cd^{2+} and Zn^{2+} by egg shell membrane. (Initial Cd^{2+} and Zn^{2+} concentration 5-50 mg/L, pH 5.0 for cadmium and 6.0 for zinc, adsorbent 1 g/L, adsorption time 300 minutes)

4. Adsorption isotherms

Experiments were conducted for finding the adsorption isotherm of cadmium and zinc on egg shell membrane by adding 50 mg of adsorbent to initial heavy metal concentration approximately from 5-50 mg/L. The pH of each heavy metal solution was adjusted to the every heavy metal concentration to equal the highest concentration (50 mg/L), because the ESM has an alkaline property it can lead to high pH value affecting heavy metal precipitation. Adjust pH value of the heavy metal solution to low range is necessary for this experiments.

The resulting data of heavy metal solutiion were calculated to carried out the adsorption isotherm using the Langmuir and Freundlich isotherm. In this work, both models were applied to describe the relationship between the amount of heavy metal adsorbed and its equilibrium concentration in solution. The Langmuir isotherm has assumption that the equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent. While Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverafe (Uaychinda, 2002). As the results from Appendix Table 5, all residual concentration (C_e) of cadmium and zinc after adsorbed by ESM was ploted of C_e/Q_e versus C_e for Langmuir isotherm as shown in Figure 12, whereas the Freundlich isotherm was ploted of log C_e versus log Q_e as shown in Figure 13, and values of the contants for each heavy metal were determined after linearizing the equations through linear regression analysis.

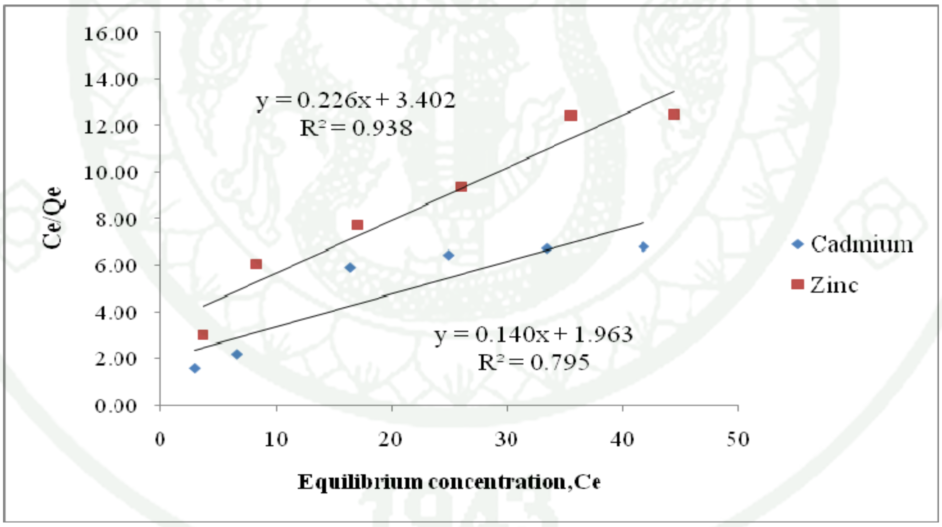

Figure 12 Langmuir isotherm (Initial Cd^{2+} and Zn^{2+} concentration 5-50 mg/L, pH 5.0 for cadmium and 6.0 for zinc, adsorbent 1 g/L, adsorption time 300 minutes)

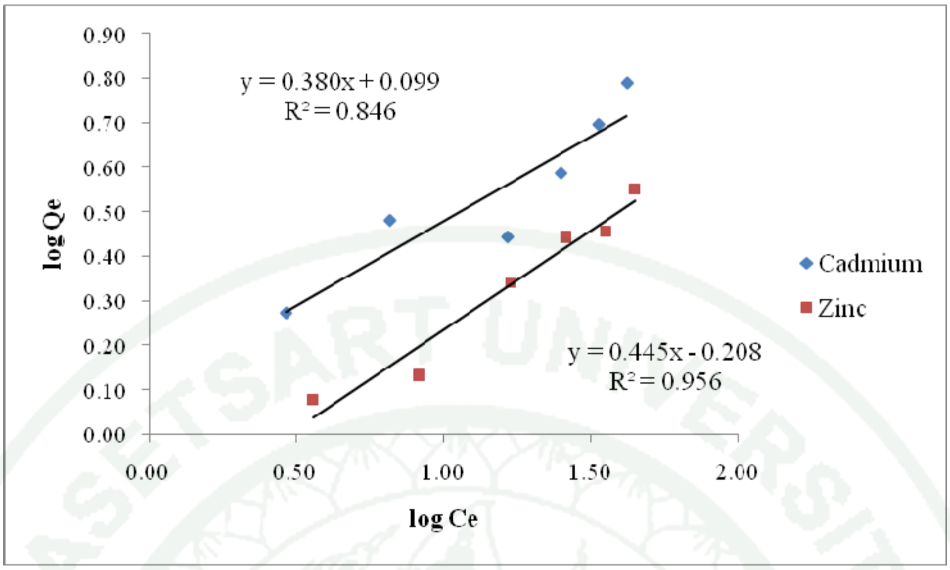

Figure 13 Freundlich isotherm (Initial Cd^{2+} and Zn^{2+} concentration 5-50 mg/L, pH 5.0 for cadmium and 6.0 for zinc, , adsorbent 1 g/L, adsorption time 300 minutes)

Table 2 Constants and Correlation coefficients by heavy metal adsorption

Heavy metal	Langmuir isotherm			Freundlich isotherm		
	a	b	R^2	K_f	1/n	R^2
Cadmium	7.14	0.0901	0.795	1.3368	0.380	0.846
Zinc	4.42	0.0710	0.938	0.6220	0.445	0.956

According to the results shown in Table 2, it can be seen that the Langmuir equation were fitted to the data with the Least square fit (R^2) of cadmium and zinc were 0.795 and 0.938, respectively. For the Freundlich equation the value of R^2 of cadmium and zinc were 0.846 and 0.956, respectively. A constant values of Langmuir (a, b) and Freundlich (K_f, 1/n) equations were also presented in Table 2.

The experimental data of these two metals on ESM was well described by the Freundlich isotherm, because the regression line obtained from the Freundlich curve were obviously fit better than the Langmuir curve. The constant value (K_f) that the Frundlich equation for cadmium and zinc were 1.3368 and 0.6220, respectively. The value of 1/n from the Freundlich equation of cadmium and zinc were 0.380 and 0.455, respectively. The value of 1/n is usually between 0.2 to 0.7 and the value of n 2 to 10 shows good adsorption (Naseem and Tahir, 2001). The results of n constants for cadmium and zinc were 2.63 and 2.24, respectively and the maximum of n constant was of cadmium.

The calculated n value was qualitatively related to the distribution of site bonding energies. The n values for all the studied were higher than 1, which may indicated that the energies of adsorption were decreased with the increase in surface area of ESM covered the heavy metal ion (Sheta et al., 2003). And 1/n values were lower than 1 indicate that the adsorption capacity is on slightly reduced at the lower equilibrium concentration (Samuel and Osman, 1987).

5. Adsorption kinetic

In the analyses, the initial adsorption rates for each set of experiment were calculated from initial concentration at time zero and the subsequent concentration, i.e. at 30 min. In case of Cd^{2+} and Zn^{2+} adsorption onto ESM, the values of K_La obtained from linear regression analyses at different pH values were, Cd^{2+} i.e. 0.0031, 0.0041, 0.0051, and 0.0031, min^{-1} at pH 3.0, 4.0, 5.0, and 6.0 respectively. In cases of Zn^{2+} adsorption onto ESM particle, the values of K_La at different pH showed more variation, i.e. 0.0079, 0.0086, 0.0096, and 0.0077 min^{-1} at pH 3.0, 4.0, 5.0, and 6.0 respectively. The values of K_La were shown in Table 3. In general, pH would be important in the sorption of chemicals onto surface of sediments; especially in case of clay particles, since the net surface charges on clay particle surface can change with pH (Kim et al., 2004).

Table 3 Values of K_La from regression analyses

	K_La,min^{-1} (R^2)	
	Cd^{2+}	Zn^{2+}
pH=3.0	0.0031 (0.8931)	0.0079 (0.9345)
pH=4.0	0.0041 (0.8436)	0.0086 (0.9451)
pH=5.0	0.0051 (0.9512)	0.0096 (0.9754)
pH=6.0	0.0031 (0.9729)	0.0077 (0.9551)

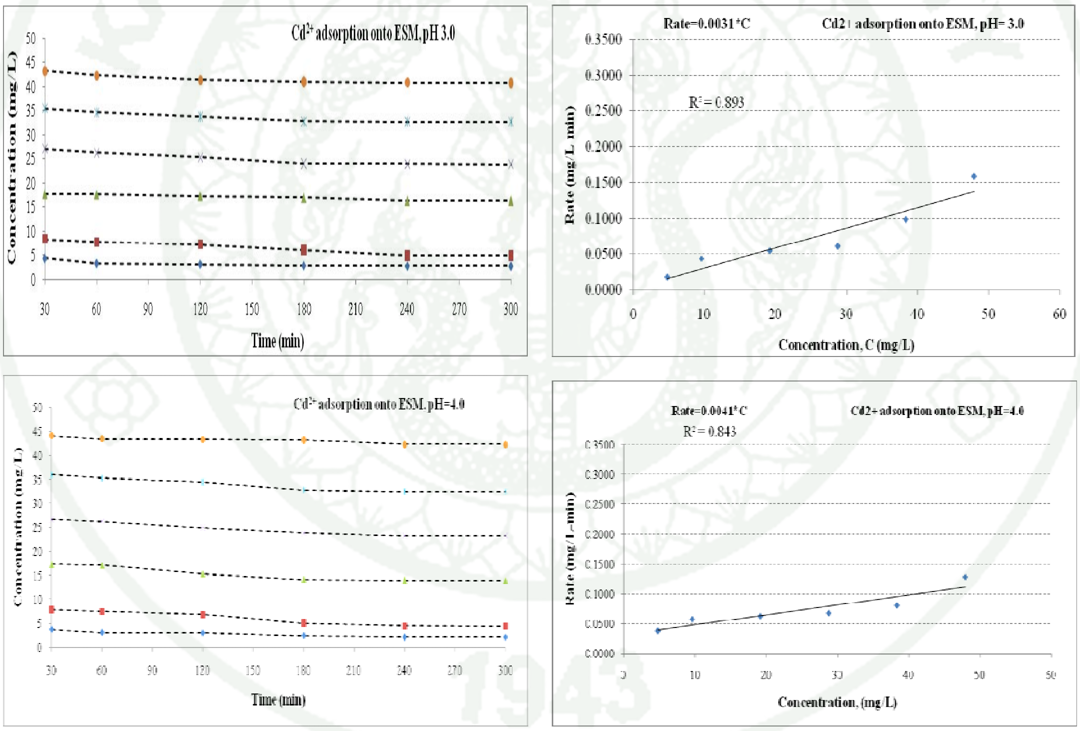

Figure 14 Cd^{2+} concentration variation with time during adsorption experiments for ESM particle and relationship between initial adsorption rate for Cd^{2+} and initial concentrations for ESM particle at pH 3.0 to 6.0.

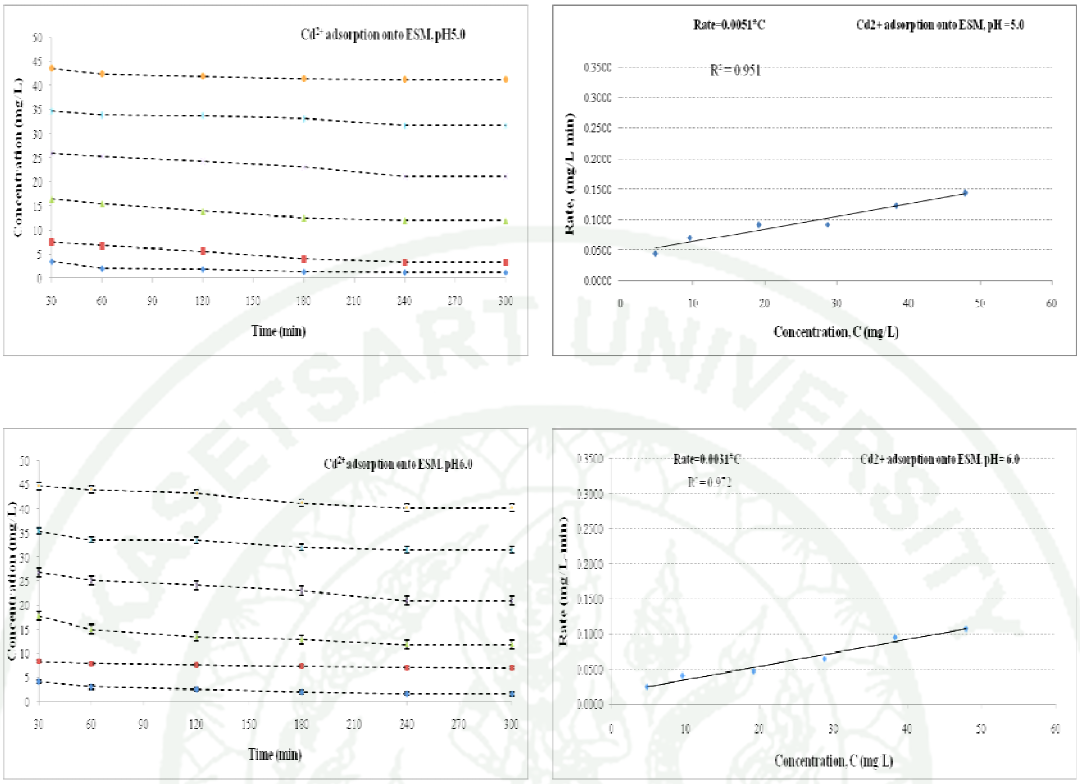

Figure 14 (Continued)

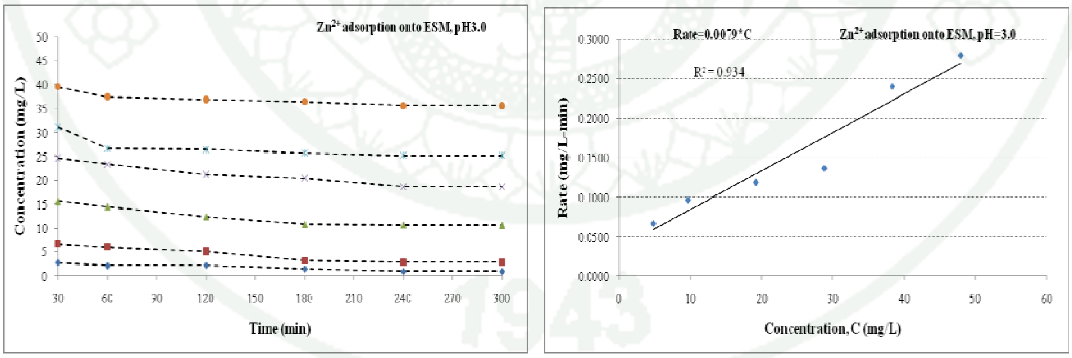

Figure 15 Zn^{2+} concentration variation with time during adsorption experiments for ESM particle and relationship between initial adsorption rate for Zn^{2+} and initial concentrations for ESM particle at pH 3.0 to 6.0.

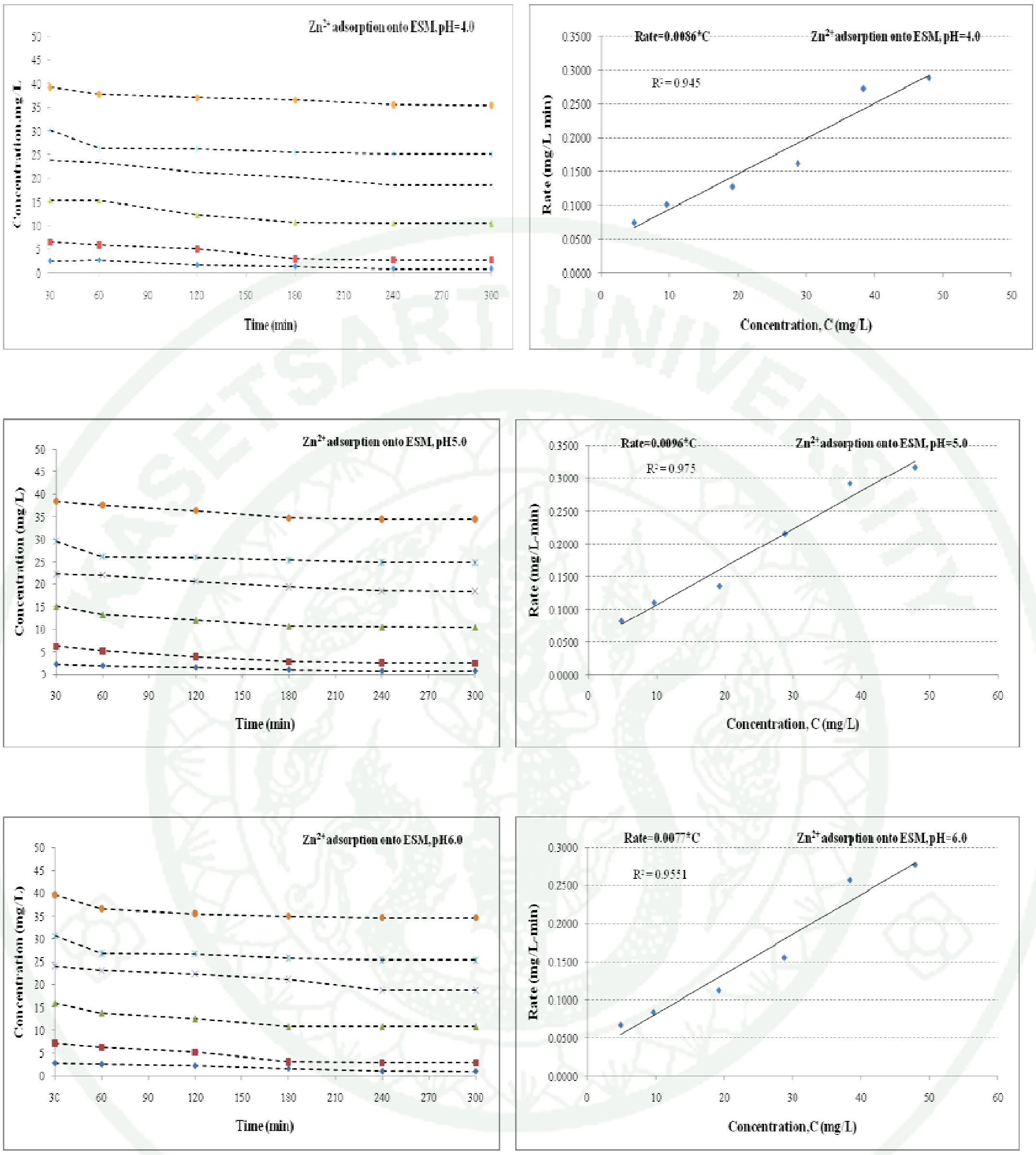

Figure 15 (Continued)

CONCLUSION AND RECOMMENDATIONS

Conclusion

The results from this work showed that the contact time of approximately 30 min was required on egg shell membrane (ESM) to reach the equilibrium to removal cadmium and zinc in synthetic wastewater. The optimum initial pH for adsorption of cadmium and zinc were pH values of 6.0 and 5.0, respectively and the adsorption kinetic of cadmium and zinc the K_La values obtained from linear regression analyses at different pH values were 0.0031 and 0.0096 min^{-1}, respectively.

The removal efficiencies of heavy metals on egg shell membrane (ESM) decrease with increasing the pH and concentration. Considering both predicting models of this experiments, the adsorption isotherm data fit well with the Freundlich isotherm for cadmium and zinc.

The utilization of egg shell membrane (ESM) to removal heavy metals will help in alternative method for the treatment of heavy metals in wastewater and health hazard problem.

Recommendations

1. The experiments to removal heavy metals in wastewater by adsorption on egg shell membrane (ESM) should be further conducted in experimental column using egg shell membrane (ESM) on the pilot scale operation.
2. The comparative study should be conducted concerning the adsorption capacity of heavy metals with the other adsorbents.
3. An investigation of leaching is recommended for further study.
4. The regeneration of adsorbent should be further investigated.

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APPENDIX

Adsorption results

Appendix Table 1 Effect of pH on cadmium adsorption (25 °C, 80 rpm)
(Initial concentration = 4.79 mg/L)

pH	Final concentration (mg/L)	Cd^{2+} sorbed (mg/g)
3.0	2.62	2.17
4.0	2.11	2.77
5.0	1.15	3.64
6.0	1.61	3.16
7.0	1.19	3.60
8.0	1.31	3.48
9.0	1.40	3.39
10.0	1.60	3.19

Appendix Table 2 Effect of pH on zinc adsorption (25 °C, 80 rpm)
(Initial concentration = 4.79 mg/L)

pH	Final concentration (mg/L)	Zn^{2+} sorbed (mg/g)
3.0	0.94	3.85
4.0	0.89	3.90
5.0	0.80	3.99
6.0	0.98	3.81
7.0	0.98	3.81
8.0	1.20	3.59
9.0	1.48	3.31
10.0	1.54	3.25

Appendix Table 3 Effect of contact time on cadmium adsorption (25 °C, 80 rpm) (Initial concentration = 4.79 mg/L, pH=5.0)

Time (min)	Final concentration (mg/L)	Cd^{2+} sorbed (mg/g)
0	4.79	0
5	4.76	0.03
10	4.70	0.09
15	4.62	0.17
30	4.06	0.73
60	3.94	0.85
120	3.67	1.12
180	3.55	1.24
240	3.49	1.30
300	3.47	1.32

Appendix Table 4 Effect of contact time on zinc adsorption (25 °C, 80 rpm) (Initial concentration = 4.79 mg/L, pH=6.0)

Time (min)	Final concentration (mg/L)	Zn^{2+} sorbed (mg/g)
0	4.79	0
5	3.92	0.87
10	3.04	1.75
15	2.89	1.90
30	2.33	2.46
60	1.96	2.83
120	1.59	3.20

Appendix Table 4 (Continued)

Time (min)	Final concentration (mg/L)	Zn^{2+} sorbed (mg/g)
180	1.09	3.70
240	1.02	3.77
300	1.04	3.75

Appendix Table 5 The final concentration of heavy metal at various concentration and adsorption capacity for adsorption isotherm.

Heavy metal	Initial conc. (mg/L), C_o	Final conc. (mg/L), C_e	Adsorption capacity (Q_e, x/m)	C_e/Q_e	Log C_e	Log Q_e
Cadmium	4.79	2.91	1.88	1.5479	0.4639	0.2742
	9.58	6.55	3.03	2.1617	0.8162	0.4814
	19.16	16.38	2.78	5.8921	1.2143	0.4440
	28.74	24.87	3.87	6.4264	1.3957	0.5877
	32.32	33.35	4.97	6.7103	1.5231	0.6964
	47.9	41.74	6.16	6.7760	1.6206	0.7896
Zinc	4.79	3.59	1.20	2.9917	0.5551	0.0792
	9.58	8.22	1.36	6.0441	0.9149	0.1335
	19.16	16.96	2.2	7.7091	1.2294	0.3424
	28.74	25.96	2.78	9.3381	1.4143	0.4440
	32.32	35.46	2.86	12.3986	1.5497	0.4564
	47.9	44.34	3.56	12.4551	1.6468	0.5514

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