PHYSICAL-CHEMICAL REMOVAL OF AMMONIA, IRON AND ZINC FROM SEMI-AEROBIC LANDFILL LEACHATE BY ZEOLITE AND LIMESTONE

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This dissertation is submitted to

UNIVERSITI SAINS MALAYSIA

As a partial fulfillment of the

requirement for the degree of

BACHELOR OF ENGINEERING (CIVIL ENGINEERING)

School of Civil Engineering

Universiti Sains Malaysia

April 2005

ACKNOWLEDGEMENT

I would like to take this opportunity to thank my supervisor, Prof. Madya Dr. Hamidi Abdul Aziz for his continuous advice and guidance throughout the duration of this thesis. I would like to thank him for the precious time he took to read my draft report, the effort for getting useful information and the suggestions that he given throughout this research project. His continuous enthusiasm and willingness to assist was greatly appreciated. The completion of this research would not be possible without his guidance and assistance.

In addition, I would like to thank Mr. Mohamed Shahrir Mohamed Zahari for providing me uninterrupted guidance and support throughout the course of this study. I would also like to thank Puan Nurul who has provided valuable help during laboratory work.

I would also like to thank my friends and others who involved in making this final year project a success. Lastly I would like to thank my parents for their moral and financial support.

ABSTRACT

This study investigates the removal of ammonia, iron and zinc using zeolite and limestone as adsorbents. Literature review indicated that zeolite and limestone are capable of removing heavy metal cations through batch process. Therefore, batch experiments were carried out in this research to determine the efficiency removal of ammonia, iron and zinc in leachate taken from Pulau Burung Landfill Site. Shaking and settling times, shaking speed, the optimum mixture of zeolite and limestone were pre-determinated, respectively. Result show that the shaking and settling times were 1 hour, respectively. The optimum shaking speed was 350 rpm and the optimum mixture between zeolite and limestone was 15 mL of zeolite and 25 mL of limestone. Mixing the limestone with zeolite could reduce the cost of treatment. Adsorption isotherm at the optimum mixture was determined using Freundlich and Langmuir principle. The value of $1/n$ and K_f for iron was 0.5845 and 0.00062, respectively and was 1.4131 and 0.1683, respectively for zinc. The breakthrough time for iron and zinc was 4.28 and 4344.33 days, respectively at flow rate $460 m^3$/day and 4.5 m^3 column volume. Adsorption kinetics determination showed that it followed the pseudo second order chemical adsorption of R^2 values for ammonia, iron and zinc was 0.9726, 0.9991 and 0.9958, respectively.

ABSTRAK

Penyelidikan ini mengkaji penyingkiran ammonia, ferum dan zink dengan menggunakan zeolite dan batu kapur sebagai bahan penjerap. Sorotan literatur menunjukkan bahawa zeolite dan batu kapur mampu menyingkirkan kation logam berat melalui ujian kelompok. Untuk itu ujian kelompok telah dijalankan untuk menilai keberkesanan penyingkiran ammonia, ferum dan zink dalam larut lesapan yang diambil dari Tapak Pelupusan Pulau Burung. Masa kocakan dan enapan, kelajuan kocakan serta campuran optimum di antara zeolite dan batu kapur ditentukan terlebih dahulu. Keputusan mendapati bahawa masa pengoncangan dan pengenapan yang diperolehi ialah 1 jam. Kelajuan pengoncangan optimum adalah 350 rpm, manakala campuran optimum adalah 15 mL untuk zeolite dan 25 mL untuk batu kapur. Percampuran batu kapur bersama zeolite dapat mengurangkan kos olahan. Penjerapan isoterma pada campuran optimum diperolehi dengan menggunakan model penjerapan Freundlich dan Langmuir. Nilai $1/n$ dan K_f untuk ferum ialah 0.5845 dan 0.00062. Untuk zink pula, nilai $1/n$ dan K_f ialah 1.4131 and 0.1683. Masa bulus untuk ferum dan zink masing-masing ialah 4.28 dan 4344.33 hari pada kadar alir $460 m^3$/hari dan isipadu column. Ujian jerapan kinetik menunjukkan bahawa jerapan yang berlaku adalah kinetik tertib kedua di mana nilai R^2 untuk ammonia, ferum dan zink masing-masing ialah 0.9726, 0.9991 dan 0.9958.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The quantities of solid waste are increasing daily and good management of solid waste is needed to provide us with a comfortable environment for living. Solid waste is mostly generated by residential, commercial, industrial, and so on. Before the solid waste is sent for disposal, the municipal solid waste separation is done at source, residential, commercial and industrial facilities. Some of the separated components are effectively reused and recovered. When come to the end of municipal solid waste separation, the remaining solid waste will be disposed.

Sanitary landfill is the most widely used method for municipal solid waste disposal. It is used for treated as well as untreated waste (Isa, 2004). Landfill is a carefully engineered solid waste disposal facility. It is operated in an environmentally friendly manner with minimum public nuisances and does not threaten public health of safety (Isa, 2004). The purpose of landfill disposal is to stabilise the solid waste and to make it hygienic through proper storage of waste and use of natural metabolic functions. The reactions in a landfill are divided into biological, chemical and physical process (Isa, 2004).

One of the components that percolated through solid waste is leachate. Amount of contaminant in leachate is determined from the type of waste being dumped on site. However it decreases with time as the waste becomes more matured and stabilized.

Leachate may contain heavy metals, ammonia, BOD, COD, colour and other trace organics. Leachate can move to sub-surface aquifer and pollute ground water. Leachate production is highly variable in quality and depends on the soil type, waste composition, degree of compaction, rainfall, evaporation, landfill type and age (Isa, 2004). So, the leachate must first be treated before being released to the environment.

Leachate can be treated in many ways and the most efficient way is by integrating the treatment system. Integrated leachate management combines treatment in order to attain the most required effluent. Removal of ammonium by chemical precipitation has been reported by (Li *et. al,* 1999). The treatment of industrial landfill leachate using evaporation and reverse osmosis has been reported by Palma *et. al,* 2002. However, removal of metals from leachate is not well documented, especially in Malaysia. Removal of heavy metal like iron can be undertaken by aeration, softening, chlorination, ozonation and filtration (Aziz *et. al,* 1997). Aeration is the most common. For the filtration technique, the common media used are activated carbon and clay. The use of limestone for removing metals from water and industrial wastewater was found to be effective (Aziz *et. al,* 1997).

Other studies on leachate in Malaysia focuses on the leachate generated from Pulau Burung Landfill Site (Figure A.1.1), which is located in Penang, Malaysia. Pulau Burung Landfill Site has a semi-aerobic system and is under the management of Idaman Bersih Sendirian Berhad. Normally, Pulau Burung Landfill Site receives 1500 tons of solid waste daily. Leachate at the Pulau Burung Landfill Site is collected through collection pipes that feed into a detention pond (Figure A.1.2). The present study focuses on the removal of ammonia and heavy metals from semi-aerobic leachate using physical-chemical method with zeolite and limestone. The study also

aims to establish the Fe, zinc and ammonia isotherms and breakthrough time of the proposed limestone and zeolite filter for post-treatment of the migrating landfill leachate before its release to the environment. Table 1.1 revealed the characteristics of raw leachate from old detention pond at Pulau Burung Landfill Site.

Table 1.1 : The characteristics of raw leachate from old detention pond at Pulau Burung Landfill Site (Idaman Bersih Sendirian Berhad, 2003)

Parameter	Unit	Average value
BOD_5	mg/l	48 – 105
COD	mg/l	1533 – 2580
Suspended Solid	mg/l	159 – 233
Turbidity	mg/l	61 – 198
pH	mg/l	7.5 – 9.4
Zinc	mg/l	0.1
`Manganese	mg/l	15.5
Iron	mg/l	4.1 – 19.5
Copper	mg/l	4.6
Chromium (VI)	mg/l	0.6
Colour	Platinum unit, Pto	1000 – 4000

Based on 30 days monitoring.

1.2 OBJECTIVES OF THE STUDY

The main objectives of this study are:

a) To determine the optimum shaking and settling time for ammonia, iron and zinc removal from leachate.

b) To determine the optimum shaking speed in ammonia and iron and zinc removal from leachate.

c) To determine the optimum mixture ratio of zeolite and limestone that will provide maximum removal percentage of ammonia, iron and zinc for cost saving.

d) To determine the adsorption isotherms.

e) To determine the mechanism of removal by adsorption via adsorption kinetics study.

1.3 IMPORTANCE OF THE STUDY

The study is important in cost saving of leachate treatment. To reduce the cost of leachate treatment, the amount of zeolite may be reduced with addition of limestone.

1.4 SCOPE OF THE STUDY

Only batch study focuses on the capability of combination of limestone and zeolite in ammonia, iron and zinc removal. The scopes are as follow:

a) The actual leachate is used without being diluted.

b) Only zeolite and limestone used in the study

c) The limestone and zeolite used in the experiment is of constant size with 1.18 – 2mm and 2 – 4.75mm, respectively.

d) The study concern with removal of ammonia, iron and zinc

e) Adsorption studies involve only Freundlich and Langmuir isotherm.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

According to Section 75 of the Environmental Protection Agency, EPA (1990), solid wastes are defined as any substance which constitutes a scrap material or other unwanted surplus substances arising from the application of any process or any substance or article, which requires to be disposed of as being contaminated or otherwise, spoiled. The solid wastes are divided into seven categories; residential and commercial wastes, municipal solid waste, institutional wastes, construction and demolition waste, industrial waste, agricultural waste and special waste (hazardous waste). Improper management of solid wastes may contribute to ecological phenomena such as water and air pollution (Tchobanoglous *et. al,* 1993). Among the varying categories of waste, municipal solid waste is the most common waste generated. The most widely used method for municipal solid waste disposal is sanitary landfill. The reactions in landfill include biological, chemical and physical (Isa, 2004).

2.2 MUNICIPAL SOLID WASTE

Municipal solid waste comes from residential, commercial, institutional and industrial resources and includes durable goods, undurable goods, containers and packaging, food waste and miscellaneous inorganic wastes (Chen, 1995). The average amount of

municipal solid waste generated in Malaysia is 0.5-0.8 kg/ person/ day and has increased to 1.7 kg/ person/ day in major cities (Kathirvale *et. al,* 2003).

2.3 LANDFILL

The purpose of landfill disposal is to stabilise the solid waste. Besides that, it is also used to make it hygienic through proper storage of waste and use of natural metabolic function. Landfill performs two functions; treatment functions by which waste is decomposed and stabilised through natural processes, and storage function (storing waste). In the past landfills were nothing more than a place where one stored wastes. However, it has been realised that a landfill also performs purification function in the sense that it is the place where waste biodegrades and achieves a level of stability. The environment in which degradation occurs affects this process. When it occurs in the presence of oxygen (aerobic), the process is faster. In the broader context the functions of a sanitary landfill may be listed as follows (Sakai, 2004):

a) Storage of waste in hygienic condition

b) Environmental pollution control (second pollution)

c) To facilitate rapid decomposition / stabilization of waste

d) To alleviate the damage associated with explosive gas

To facilitate the above functions, the following facilities are necessary at a municipal solid waste landfill (Sakai, 2004).

a) Solid Waste Retaining Structure

b) Liner system to prevent leachate penetration into underground

c) Rainwater drainage facility which collects rainwater and drains it out from the landfill

d) Leachate collection and drainage facility

e) Leachate control pond

f) Leachate treatment facility

g) Gas venting facility

h) Access road

i) Transportation control equipment including weigh bridge

j) Monitoring equipment

k) Administrative office

l) Fencing to prevent waste scattering

2.3.1 CLASSIFICATION OF LANDFILL STRUCTURE

Landfill sites are categorised into 3 types in Malaysia. In terms of quality of leachate and gases generated from landfill site, semi-aerobic, aerobic or anaerobic landfill method is desirous (Isa, 2004).

Semi-aerobic landfill

Leachate collection duct is bigger compared to the sanitary landfill. The opening of the duct is surrounded by air and the duct is covered with small crushed stones. Moisture content in solid waste is small. Oxygen is supplied naturally to solid waste from leachate collection duct.

Aerobic landfill

In addition to the leachate collection pipe, air supply pipes are attached and air is forced to enter the solid waste by which condition becomes more aerobic than semi-aerobic landfill.

Anaerobic landfill

Solid wastes are filled in digged area of plane field or valley. Wastes are filled with water and in anaerobic condition.

2.3.2 REACTIONS IN LANDFILL

There are 3 types of reactions occurring in landfills which are biological, chemical and physical reactions (Isa, 2004).

2.3.2.1 BIOLOGICAL REACTIONS

Biological reactions in landfills involve the organic material of municipal solid waste that produce landfill gases and liquids (leachate). Initially the reactions are aerobic and gradually turn to anaerobic as the available oxygen is depleted. The principal gas produced in aerobic decomposition is CO_2. In anaerobic decomposition, CO_2, CH_4 and trace amounts of NH_3 and H_2S are produced (Isa, 2004).

2.3.2.2 CHEMICAL REACTIONS

Chemical reactions that occur within the landfill are the dissolution and suspension of landfill materials and biological conversion products in the liquid that percolating through the waste. There is adsorption of organic compounds onto landfill material. The organic compounds are dehalogenated and the redox reactions affecting metal and salt solubilities. The organic compounds will react with clay liners to alter their structure and permeability. Due to methane gas generated in landfill, they pose combustion or explosion hazard (Isa, 2004).

2.3.2.3 PHYSICAL REACTIONS

Physical reactions that occur within the landfill are the lateral diffusion of gases in the landfill and emission of landfill gases to environment. There are cracks and leak in landfill cover due to internal gas pressure. Escaping landfill gas may carry trace amounts of carcinogens to the environment. Combustion and explosion may occur because landfill gas has high methane content. Leachate in landfill will migrate within landfill and underlying soil. The leachate has the potential to cause severe ground water pollution (Isa, 2004).

2.4 LEACHATE

Leachate is defined as the water percolating out of the landfill area (Oygard and Gjengedal, 2003). It has its origin either as rainwater or surface water that flows into the landfill area, or as water contained within the deposited waste. The leachate is usually defined as being polluted due to the contact with deposited waste. In addition

to methane gas emission, the leachate represents an important source of the environmental problems connected with landfilling of waste (Oygard and Gjengedal, 2003). Landfill leachate has been perceived to be a severe source of pollutants by the general public. The assumption is that the levels of pollutants such as nitrogen, chemical oxygen demand (COD)-driving compounds, heavy metals, persistent and other anthropogenic organic pollutants are high in the leachate. Landfill leachate treatment has been given significant attention in recent years especially for municipal areas. The composition of landfill leachates can vary depending on the nature of the landfilled solid wastes, the active microbial flora, characteristics of the soil, the rainfall patterns and the age of the landfill. Young landfill leachates are usually treated more easily than old ones (Oygard and Gjengedal, 2003).

2.4.1 PROCESS IN LANDFILL LEACHATE

A variety of microbiological processes take place inside a municipal solid waste landfill. In a well-constructed landfill with top layer, there will be no oxygen below the top layer. This will promote the growth of anaerobic bacteria (Manahan, 1994). Growth of anaerobic bacteria will in general, lead to a reducing chemical environment (Manahan, 1994). Among the many microbiological processes that take place in a landfill, some of the anaerobic bacteria produced methane as a result of metabolism of organic carbon compounds. Available oxygen in such an environment will stop this reaction and lead to oxidation of sulfide to sulfate. In addition such a reaction will decrease the pH (Flyghammar and Hakanson, 1999).

The sulfide generated in a landfill will influence the mobility of most heavy metals. Sulfide compounds like PbS, CdS and HgS have a relatively low solubility. Many of the potentially harmful heavy metals will to a large extent to be precipitated and thus immobilized within the landfill when reacting with sulfides (Reinhart and Grosh, 1998). Fe will also form sulfide compounds, which have a low solubility. It has been reported that only low levels of the metals precipitated as sulfides will subsequently be dissolved and discharged in the leachate (Reinhart and Grosh, 1998), unless reducing conditions change or acidic conditions occur. Water treatment by the addition of sulfide and successive precipitation of metals is a well-known process for the remediation of heavy metal rich effluent water from metallurgic or other heavy industry (Feng *et. al,* 2000). In landfills, this process is naturally present as part of the biodegradation processes of the wastes deposited. Out of the heavy metals, only chromium will not react with sulfides to produce weakly soluble compounds. However, precipitation of chromium will occur since the neutral/weakly basic environment in the landfill will lead to the generation of chromium-hydroxide, which has a relatively low solubility (Reinhart and Grosh, 1998).

2.4.2 LEACHATE TREATMENT

Usually in leachate treatment, the combination of physical, chemical, and biological methods are used for effective treatment of landfill leachate (Kargi and Pamukoglu, 2003) since it is difficult to obtain satisfactory effluent water quality by using anyone of those methods alone. Sedimentation, air-stripping, adsorption, and membrane filtration are the major physical methods used for leachate treatment. Major chemical methods used for landfill leachate treatment are coagulation-flocculation, chemical

precipitation, and chemical-electrochemical oxidations. Biological treatment methods used for the leachate treatment can be classified into aerobic, anaerobic, and anoxic processes which are widely used for the removal of biodegradable compounds. Physical-chemical methods are used along with the biological methods mainly to remove non-biodegradable compounds from the leachate (Kargi and Pamukoglu, 2003).

2.5 ADSORPTION

Adsorption is the process of collecting soluble substances that are in solution on a suitable interface. The interface can be between the liquid and a gas, a solid, or another liquid. Although adsorption is used at the air-liquid interface in the flotation process, only the case of adsorption at the liquid-solid interface will be considered in this discussion.

Adsorption is currently being used in leachate treatment for removal of ammonia and heavy metals. The kinetics of adsorption depends on the adsorbate concentration and the physical and chemical characteristics of the adsorbent (Gupta *et. al,* 2003). Adsorption mechanisms are generally categorised as either physical adsorption, chemisorptions, or intra-particle diffusion. Weak molecular forces, such as Van der Waals forces, provide the driving force for physical adsorption, while a chemical reaction forms a chemical bond between the compound and the surface of the solid in chemisorptions. In liquids, interactions between the solute and the solvent also play an important role in establishing the degree of adsorption.

2.5.1   ANALYSIS OF THE ADSORPTION PROCESS

The adsorption process takes place in three steps: macrotransport, microtransport, and sorption. Macrotransports involves the movement of the organic material through the water to the liquid-solid interface by advection and diffusion. Microtransport involves the diffusion of the organic material through the macropore system of the adsorbent to the adsorption sites in the micropores and submicropores of the adsorbent. Adsorption occurs on the surface of the granule and in the macropores and mesopores, but the surface area of these parts of the adsorbent are so small compared with the surface area of the micropores and submicropores that the amount of material adsorbed there is usually considered negligible. Sorption is the term used to describe the attachment of the organic material to the adsorbent. The term sorption is used because it is difficult to differentiate between chemical and physical adsorption. When the rate of sorption equals the rate of desorption, equilibrium has been achieved and the capacity of the carbon has been reached. The theoretical adsorption capacity of the carbon for a particular contaminant can be determined by calculating its adsorption isotherm (Metcalf and Eddy, 1991).

The quantity of adsorbate that can be taken 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 adsorption isotherm. Equations that are often used to describe the experimental isotherm data were developed by Freundlich, by Langmuir, and by Brunauer, Emmet, and Teller (BET isotherm). Of the three, the Freundlich isotherm is used most commonly to describe

the adsorption characteristic of the activated carbon used in water and wastewater treatment (Metcalf and Eddy, 1991).

2.5.1.1 FREUNDLICH ISOTHERM

The empirically derived Freundlich isotherm is defined as follows (Metcalf and Eddy, 1991):

$$\frac{x}{m} = K_f C_e^{1/n} \qquad\qquad (2\text{-}1)$$

Where $\dfrac{x}{m}$ = amount adsorbate adsorbed per unit weight of absorbent (mg/g)

C_e = equilibrium concentration of solute in the bulk solution (mg/L)

K_f = Freundlich constant; an indicative adsorption capacity of the adsorbent (mg/g)

1/n = constant

The constants in the Freundlich isotherm determined by plotting $\log(x/m)$ versus $\log C_e$ and making use of Equation 2-1 rewritten as

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \qquad\qquad (2\text{-}2)$$

Table 2.1 : Freundlich adsorption equations and constants (log *k* and *n*) for metal

cations on natural zeolite (Hasany *et. al*, 2002)

Metal	logk_f (mg/g)	1/*n*
Cu^{2+}	0.13	0.30
Co^{2+}	0.28	0.36
Zn^{2+}	0.19	0.43
Mn^{2+}	0.81	0.50

Table2.1 revealed the constants of log *k* and *n* for metal cations on natural zeolite. The numerical value of 1/*n* less than 1 indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface (Hasany *et. al*, 2002).

2.5.1.2 LANGMUIR ISOTHERM

The Langmuir equation is commonly written as follows (Metcalf and Eddy, 1991):

$$q = \frac{a_L b_L C_e}{1 + a_L C_e} \qquad \text{(non-linear)} \qquad (2\text{-}3)$$

$$\frac{C_e}{q} = \frac{1}{a_L b_L} + \frac{1}{b_L} C_e \quad \text{(linear)} \qquad (2\text{-}4)$$

Where q = amount of solute adsorbed per unit weight of adsorbent (mg/g)

C_e = equilibrium concentration of solute in the bulk solution (mg/L)

a_L = Langmuir isotherm constant, related to the energy of adsorption (L/g)

b_L = maximum monolayer adsorption capacity (mg/g)

The validity of this isotherm is regulated by the following rules:

(a) The equilibrium is obtained when there is a formation of a monolayer on the adsorbent

(b) All the sorption sires are equivalent and the surface is uniform

(c) The capacity of a molecule to be adsorbed on a specific is independent of the occupation of the other near sites

Conformation to Langmuir isotherm by particular adsorption indicates monolayer coverage of metal ions on the outer surface of the adsorbent due to chemisorption. High value of maximum adsorption capacity b_L, implies strong bonding of metal ions to the adsorption.

2.5.1.3 BREAKTHROUGH ADSORPTION CAPACITY

In the field, the breakthrough adsorption capacity, $(x/m)_b$ in a full-scale colume is some percentage of the theoretical adsorption capacity found from the isotherm. The $(x/m)_b$ of a single column can be assumed to be approximately 25 to 50 percent of the theoretical capacity $(x/m)_o$. Once $(x/m)_b$ is known, the time to breakthrough can be calculated by solving the following equation for t_b(Metcalf and Eddy, 1991).

$$\left(\frac{x}{m}\right)_b = Q\left(C_i - \frac{C_b}{2}\right)\frac{t_b}{M_c}\left[8.34 Ib/Mgal.(mg/L)\right] \qquad (2\text{-}5)$$

Where $(x/m)_b$ = field breakthrough adsorption capacity (g/g)

M_c = mass of adsorbent in the column (g)

Q = flow rate (Mgal/day)

C_i = influent organic concentration (mg/L)

C_b = breakthrough organic concentration (mg/L)

t_i = time to breakthrough (day)

Equation 2-5 was developed assuming that C_i is constant and that the effluent concentration increases linearly with time from 0 to C_b. Rearranging equation 2-5, the time to breakthrough can be calculated using the following relationship (Metcalf and Eddy, 1991).

$$t_b = \frac{(x/m)_b M_c}{Q[C_i - (C_b/2)][8.34 Ib/Mgal.(mg/L)]}$$

(2-6)

2.5.2 ADSORPTION KINETICS

Many attempts have been made to formulate a general expression describing the kinetics of adsorption on solid surfaces for liquid-solid phase sorption systems. Kinetic models are, therefore, often used to test experimental data. These kinetic models include the pseudo first order model and pseudo second order model. The kinetic data generally used to elucidate the adsorption mechanism and to understand the dynamics of the sorption reaction in terms of the rate constant (Aw, 2004).

2.5.2.1 PSEUDO FIRST ORDER KINETIC

The pseudo first order equation generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

(2-3)

where q_e = amount of heavy metals sorbed at equilibrium (mg/g)

q_t = amount of heavy metals sorbed at time t (mg/g)

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k_1 = rate constant of pseudo first order sorption (L/min)

The linear form of this equation can be represented as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (2\text{-}4)$$

Compliance to pseudo first order kinetics indicates that the adsorption is predominantly due to physisorption-type mechanism. Several studies have shown that adsorption of heavy metals conform to pseudo first order kinetics (Table 2.2) (Aw, 2004).

Table 2.2 : Selected studies of metals adsorption that conform to pseudo first order kinetic model

Adsorbent	Adsorbate
Activated carbon	Cd, Zn, Cu
Calcined Mg-Al-CO$_3$ hydrotalcite	Cr(VI)
cassava	Cd, Zn
Fly ash	Cu, Ni, Zn
Moss	Cr(III), Cr(VI)
Red mud	Cd, ZN
zeolite	Co(II)

2.5.2.2 PSEUDO SECOND ORDER KINETIC

The pseudo second order equation can be expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2\text{-}5)$$

where q_e = amount of heavy metals sorbed at equilibrium (mg/g)

q_t = amount of heavy metals sorbed at time t (mg/g)

k_2= rate constant of pseudo second order sorption (g/mg per min)

The linear plot of pseudo second order kinetic model can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad\qquad (2\text{-}6)$$

The adsorption of heavy metals on several adsorbents has also been shown to conform to pseudo second order (Table 2.3). Compliance to pseudo second order kinetics strongly suggests chemical adsorption or chemisorption (Aw, 2004).

Table 2.3 : Selected adsorption studies that conform to pseudo second order kinetic model

Adsorbent	Adsorbate
Activated carbon	Cd, Co, Hg, Pb
Bone char	Cd
Chitin and chitosan	Cr, Cu
Fly ash	Cr
Grafted silica	Cu, Pb
Sphagnum moss peat	Cu, Ni, Pb

2.5.2.3 INTRA-PARTICLE DIFFUSION

The kinetic data of an adsorption experiment can also be used to elucidate whether the adsorption process involves intra-particle diffusion mechanism. Intra-particle

diffusion generally characterized by a relationship between solid phase concentration (q) and the square root of time (Aw, 2004):

$$q = k_i \sqrt{t} \qquad\qquad (2\text{-}7)$$

Where k_i = intra-particle diffusion rate constant (mg/g per $min^{1/2}$)

A linear plot of q and $\sqrt{t}$ indicated the adsorption can also be attributed to intra-particle diffusion. Stidues have shown that the adsorption of metal on several adsorbents can involve intra-particle diffusion (Table 2.4).

Table 2.4 : Selected adsorption studies that conform to intra-particle diffusion

Adsorbent	Adsorbate
Activated carbon	Cu
Cassava	Cd, Zn
Chitosan-based crab shells	Cd
Fly ash	Ni
Groundnut husks	Cd,Pb

2.6 RESEARCH REVIEWS

A SIDERITE / LIMESTONE REACTOR TO REMOVE ARSERNIC AND CADMIUM FROM WASTEWATER

Since leakage of the liner system usually occurs (Jayawickrama *et. al*, 1988), much effort has been devoted to find simple and inexpensive treatment technologies to

entrain or remove undesirable elements from solid waste leachate. In the communication, geomaterials — siderite and limestone — are demonstrated to effectively remove As and Cd from wastewaters. Although this technology is developed for a pump-and-treat remediation design, the particular reactions would proceed unattended in the unsaturated zone situation or with air sparging in a reactive wall setting below the water table (Reardon and Wang, 2001).

In the present study, the possibility was examined by passing a fly ash leachate feedwater, spiked to increase the concentrations of several trace metals (As, Cr, Se, and Cd), through this two-column limestone reactor. The experimental results for metal oxyanions were not encouraging. Borate, molybdate and chromate showed no concentration reduction; and arsenate and selenate, modest reductions. Cd, however, was reduced to below detection (<0.01 mg/L). In later testing of the Cd removal efficiency of the reactor where 120 pore volumes of a $CdCl_2$ solution (30 mg/l Cd) were passed through the reactor, effluent Cd concentrations were always below detection. Substantial amounts of otavite and Cd-containing calcite precipitated in the second column of the reactor. The Ca decrease was typically 150 mg/L (Reardon and Wang, 2001).

Column 1 of the reactor was filled with crushed siderite and column 2 with crushed limestone. During upward flow in the first column, siderite and ankerite dissolution occurs, resulting in an increase in dissolved Fe(II). Upon exiting the column, the feedwater is directed into the top of a second, aerated column of crushed limestone, where it passes by unsaturated flow. Fe(II) oxidizes quickly to Fe(III) and precipitates as Fe(III) oxyhydroxides. Thus this second column is designed to remove AsO_4^{3-}, SeO_4^{2-} and CrO_4^{2-} by sorption onto the constantly accumulating Fe(III)

oxyhydroxides. The air stream also promotes the degassing of dissolved CO_2 from the infiltrating water and generates a supersaturated state with respect to carbonate minerals, which results in the removal of Cd by direct precipitation as otavite ($CdCO_3$) and co-precipitation with calcite (Reardon and Wang, 2001).

The As concentration of the effluent from the second column was always below detection (0.005 mg/L). Although it was designed that As be removed in the second column by sorption onto a continuously accumulating mass of Fe(III) oxyhydroxide, most of the As was actually removed in the first column. The reason for this is that Fe(III) oxyhydroxide also formed in the first column. The feedwater concentration of Cd(II) does not change during flow through the siderite column. However, its concentration is brought below detection in the second column of crushed limestone. This is due to either direct precipitation of $CdCO_3$ (otavite) or co-precipitation with calcite (Reardon and Wang, 2001).

EFFECT OF ZEOLITE FOR THE TREATMENT OF TEXTILE WASTEWATER IN BIOLOGICAL AERATED FILTER

The effluents from the textile industry are one of those wastewaters that are hard to treat satisfactorily because they are highly variable in composition (Hamza and Hamoda, 1980). The most notorious characteristic of the textile wastewater is strong colour. If not properly dealt with, the colour would cause a significantly negative impact on the aquatic environment due to the increment of turbidity and high polluting strength. In recent years, several technologies using biological aerated filter (BAF) were developed to treat wastewater from slaughterhouses, and from pulp and mill industries (Kantardjieff and Jones, 1996).

The chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solid (SS), total Kjeldahl nitrogen (TKN), and nitrite nitrogen (NO_2-N) plus nitrate nitrogen (NO_3-N) were analysed according to standard methods. The temperature, dissolved oxygen (DO) and pH were routinely monitored during the experimental period (Won *et. al*., 2001).

The results obtained from the operation of a pilot-scale BAF indicate that natural zeolite is a superior media for textile wastewater treatment. Reductions for COD (86–92%), BOD (99%) and colour (77–79%) were not significantly dependent of hydraulic load. A temperature range of 4–10 °C could be considered as the main effect causing a lower total nitrogen removal at a higher hydraulic load (Won *et. al*., 2001).

REMOVAL OF AMMONIUM FROM MUNICIPAL WASTEWATER USING ZEOLITE

Removal of ammonium from municipal wastewater concerns the removal of ammonium ions from wastewater using a naturally occurring zeolite from Dogantepe region in Turkey. Complete removal of ammonium is required due to its toxicity to most fish species. For fish life, ammonium nitrogen concentration must not be more than 1.5 mg NH_4^+-N l^{-1}(Metcalf and Eddy, 1991). It is stated in Water Pollution Control Regulation in Turkey that the permissible NH_4^+-N (ammonium nitrogen) concentration for first and second class surface water sources should not exceed 0.2 and 1 mg NH_4^+-N l^{-1}, respectively (National Newspaper, 1988).