ANNALS of Faculty Engineering Hunedoara – International Journal of Engineering
ISSN: 1584 - 2665

A REVIEW OF HEAVY METAL POLLUTION AND POTENTIAL REMOVAL TECHNIQUES IN MALAYSIA

[1.] Abdelnaser OMRAN, [2.] Hamidi Abdul AZIZ

[1] School of Housing, Building and Planning, Minden, Universiti Sains MALAYSIA
[2] School of Civil Engineering, Nibong Tebal, Universiti Sains MALAYSIA

ABSTRACT
The objective of the paper is to present information concerning sources if heavy metals to waste, harmful effects of heavy metals, the problems posed by the disposal and recycling of heavy metals and heavy metal containing products, and to assess the options for substituting the heavy metals. In recent years, some heavy metals such as cadmium, lead, zinc, nickel, copper and chromium (III) or their compounds have been used extensively by various industries thus leading to sharp increase in the contamination especially of water. Because of their toxicity, the presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water. As a result, the standard B discharge limit of these metals under Environmental Quality Act 1974 of Malaysia, (Sewage and Industrial Effluents) 1979 are kept below 1.0 mg/l in which the standard for Cd is 0.02 mg/l, 0.50 mg/l for Pb, 1.0 mg/l each for Zn, Ni, Cu and Cr (III). Despite of their potential toxicity, many of these metals are widely used, particularly by industries, which rely on solutions of the metallic ions. This paper reviews heavy metals pollution in Malaysia and potential removal techniques, which may be suitable to overcome the problem.
Keywords:
Heavy metals, Pollution, Removal technique, Scheduled wastes, limestone

1. INTRODUCTION

Heavy metals are non-organic materials, which have high atomic weight. Examples of these heavy metals are mercury, lead, copper cadmium, chromium, nickel and zinc. At present, heavy metals are one of the important materials in our life. Heavy metals have been used extensively in steel industry, electroplating, battery, paint and pigment and other industries. Beside that, there are many products, which have been produced from heavy metals, or their compounds such as weapons, decorative materials and others. Extensive use of heavy metals may lead to sharp increase in the contamination, especially of water. Table 1 illustrates some of the heavy metals and the use.

Table 1: Heavy metals and the use

Heavy metals	Use
Cadmium	Alloy and solder manufacturing, plastic, electroplating, pigment, plastic material and battery stabilizer
Copper	Transformer, electrical conductor.
Chromium	Alloy crome manufacturing, plastic chrome, oxidation agent, pigment, textile, ceramic, photographic, glass
Nickel	Component in some alloy and electroplating, battery and some fungus poison.
Lead	Acid manufacturing, materials for gasoline, battery, pigment, bullets, cable insulator
Zinc	Battery, chemical material, ceramic, electroplating

2. SOURCE AND EFFECTS OF HEAVY METALS POLLUTION

Human is direct or indirectly exposed to heavy metal from various sources. Heavy metals can enter human body through foods and drinks, apart from pollution. Heavy metals may also enter ecosystem, water and land surface through industrial waste, agriculture, housing and poultry industries. There are many other sources of heavy metal pollution. For example, leaded petrol may cause lead pollution to soils. Mercury has been used in industry to produce basic material such as chlorine in plastic manufacturing and electrical element. Mercury has also been used to produce paint, fungus poison, thermometer and other raw material for timber industries. Mercury may also pollute the environment through fossil burning, pollution from oil and battery industries. Electroplating processes are the main industry that provides a range of goods for the electronics industry. The wastewater from these processes contains heavy metals, often as a mixture of metallic ions in acidic solution. Cadmium has been used extensively by various industries such as in battery manufacturing, electroplastic, plastic, pigment and alloy industries. Wastewater and fumes produced from industries will pollute air and water. This pollution will effect human in many ways.

3. EFFECTS OF HEAVY METALS ON HEALTH

Heavy metals such as chromium, cadmium, copper, zinc, nickel, mercury and lead are able to poison human organs. For example, non-organic lead will cause abdominal disease constipation, blue germs, anemia and *encephalopathy*. Organic lead especially leaded petrol, affects sleeping ability, trembling and *hyperexcitability*. Mercury can cause *gingivitis*, kidney disease and damage to neuro-systems. Cadmium can cause *itai-itai* disease, which attacks muscles and bones. Cadmium in human body effects kidneys, liver and bones. Cadmium can be dangerous to human body at low concentrations. Other dangerous metals include chromium, copper and zinc. These metals can be accumulated in human organs such as kidney and liver. It is reported that chromium can cause lung cancer and disturbance to respiratory system at higher concentrations. Zinc at higher concentration can effect metabolism process in body system. Table 2 gives the maximum concentration of heavy metals in drinking water and the associated health effects.

Table 2: The maximum concentration of heavy metals in drinking water and associated health effects

Heavy Metal	Maximum Concentration (Mg/L) (WHO, 1971)	Health Effects
Cadmium	0	Lungs damage, headache, vomiting
Chromium	0	Kidneys damage, lung cancer, death if badly exposed.
Copper	1.5	Liver damage, muscle damage, hemolisis.
Nickel	0	Skin disease, *pneumonitis*, headache, bronchial disease
Lead	0.1	Nerves and kidney problem, *anemia*, tiredness, disturbs hemoglobin synthesis.
Zinc	15	Diarrhea, headache, mucus membrane damage

4. SOURCES OF HEAVY METALS TO WASTE

Heavy metals entering the techno-sphere will sooner or later be discharged to the environment or end up in waste. Heavy metals may end up in solid waste during all life cycle phases of the products as illustrated in the Figure below. This Figure shows the overall flows. In practice each step on the Figure may consist of several minor steps. Steps related to treatment of wastewater are e.g. not indicated on the Figure.

5. HEAVY METALS POLLUTION IN MALAYSIA

5.1 STATUS OF POLLUTION

Based on data from the Department of Environment, there are a total of 109,906 tons per year of wastewater, which contains heavy metals produced in Malaysia (NST, 20 Jan 1997). From this value, Federal Territory and Selangor produced a total 39,302 tons and 46,348 tons per year, respectively. Based on Environmental Quality Report (1993), water quality monitoring done at some river in Malaysia showed that the level of cadmium, arsenic mercury and lead has exceeded the Quality Standard (Class III) in Malaysia. Cadmium concentration was exceeded the standard of 0.01mg/l at 3 rivers, lead concentration exceeded the limited value of 0.02 mg/l at 34 rivers, mercury concentration exceeded the limited value of 0.004mg/l at 16 rivers out of 73 rivers and arsenic concentration exceeded the limited value of 0.4 mg/l at 5 rivers in Johor.

The reports also stated that, beaches in Sabah and Perak recorded the highest concentration of lead. Beaches in Sabah recorded high concentration of arsenic above the standard of 0.1 mg/l. High concentration of arsenic has been recorded at beaches in Johor. Environmental Quality Report 1995 reported that, a total of 11 metals were monitored in Malaysian rivers. The metals were nickel, lead, manganese, chromium, cadmium, zinc, iron, aluminum, mercury, copper and arsenic. Copper was recorded above the Water Quality Interim Standard for Class III (fisheries, water treatment and water for breeding) at all rivers monitored. In addition, mercury was also exceeded the same standard for all rivers except for Sg. Perai in Penang. Lead was exceeded the Standard level of 0.01 mg/l in all rivers monitored in Kelantan and Trengganu. Sg. Perai (Penang), Sg. Sepang and Sg. Buloh (Selangor), Sg. Muar (Johor) and Sg. Kuantan (Pahang) also exceeded the standard for lead. For iron, only 5 river followed the Standard Class III of 1 mg/l. The rivers were Sg. Pontian Besar, Sg. Tukang Batu and Sg. Skudai (Johor); Sg. Batang Kemena (Sarawak); and Sungai Padas (Sabah). Sg. Sepetang and Sg. Perak (Perak), Sg. Buluh and Sg. Sepang (Selangor) did not comply with the Standard Class III for cadmium (0.001 mg/l). However, nickel concentration was recorded within the Class III Standard (0.9 mg/l) in all rivers as for arsenic. For zinc, the Standard III level of 0.35 mg/l was complied, except for Sg. Kempas in Johor.

5.2 LEGISLATION

There is three set of regulation directly related to heavy metals in Environmental Quality Act 1974. These are Environmental Quality (Scheduled Wastes) Regulations 1989, Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Order 1989 and Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Regulations 1989. Most of the heavy metals are categorized as Scheduled Waste under the Regulation. Any waste falling within the categories of waste listed in the First Schedule of the Environmental Quality (Scheduled Wastes) Regulation 1989 is called Scheduled Wastes. There are a total of 107 sources of Scheduled Wastes under the Regulation, which are divided into 2 categories, i.e., Part I (Specific Sources-48 waste types) and Part II (Non-specific Sources-59 waste types). Please refer to the Regulation for details.

6. SCHEDULE WASTE

Many big industries in our country have their own in-house treatment facilities for metallic industrial waste. Unfortunately, many others are not, especially for the Small and Medium Industries. The heavy metals could not be discharged freely as some of them are categorized as a Scheduled Wastes under Table 1 of the Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Order and Regulation 1989. Treatment facility normally ends up with by-product of the treatment, i.e., sludge.

The sludge also needs proper treatment as it contains concentrated metals. For those industries that do not have treatment facilities, the sludges are kept in containers prior the completion of the centralized treatment facility in Bukit Nenas. Industries need to get permission from the Department of Environment for installation of on-site treatment facilities. If they were to send the waste to off-site facilities, permission are also needed for the transportation of waste. In 1996, a total of 165 licenses for the setting up of scheduled waste facilities and transportation were issued by the Department of Environment.

In 1995, the government has signed an agreement with Kualiti Alam Sdn. Bhd., a concession company appointed to centrally handle industrial waste in the country for 15 years. The construction of the Integrated Scheduled Waste Disposal and Treatment Facility at Bukit Nanas progressed according to plan for 1996. Three Task Force Committees were formed to monitor and facilitate its progress to deal with an estimated amount of 331,000 tons of scheduled wastes. The Bukit Nenas site has been operational since March 1997 with secured landfill facility. Amongst the facilities available are treatment of wastes in form of organics, inorganics, innocuous, and sludges via secured landfill, incinerator, physico-chemical treatment and solidification. In general, treatment of heavy metals may be done via physico-chemical treatment plus neutralization process.

7. WASTEWATER TREATMENT TECHNOLOGY FOR HEAVY METALS

There are a few available methods for removing heavy metals from water and wastewater. These include precipitation of metal hydroxide, ion exchange, reverse osmosis, electrodialysis, oxidation and reduction, carbon adsorption and removal by limestone. However, current heavy metal removal generally requires the use of chemical reagents for precipitation of these metals from the solution. Some of the options available are discussed below.

7.1 PRECIPITATION OF METAL HYDROXIDE

Precipitation is a famous method for removing heavy metals from the solution. In this method, heavy metals will be removed via precipitation in hydroxide form at higher pH values. Lime (calcium hydroxide) is the common chemical used to increase the pH. Ionic hydroxide that is added will react with the heavy metals ion such as Cu^{2+} to form insoluble hydroxide metals in precipitation. For example, the solubility product (K_{sp}) of zinc hydroxide is $3x10^{-17}$ and zinc hydroxide $1x10^{-20}$, (Barnes *et al.*, 1987). The precipitates are then removed via settling and filtration. This precipitated metal hydroxide (called sludge) can be withdrawn and further dewatered, for example in a filter press. The dewatered sludge requires safe disposal, such as chemical fixation process. The chemical reaction involved in copper removal is as follows:

$$Cu^{2+}(aq) + 2OH^{-}(aq) \rightarrow Cu(OH)_2\ (ppt)$$

7.2 ION-EXCHANGE

Ion exchange is a phenomenon that uses a kind of resin that allows metals to be exchanged and then precipitated. Ion exchange can be used for the removal of undesirable anions and cations from wastewater. Cations will be used to remove heavy metals ions such as Cr^{3+}, Zn^{2+}, Cu^{2+} and others. Ion exchange resins consist of an organic or inorganic structure with attached functional groups. Most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerization of organic compounds. Ion exchange resins are called cations, if they exchange positive ions and called anions if they exchange to negative ions. Cation exchange resins have acidic functional groups, such as sulfonic, whereas anion exchange resins contain basic functional groups such as amine. In the reaction, hydroxyl ion (H^{+}) in acid group will be replaced by heavy metals such as Cu^{2+}.

7.3 MEMBRANE TECHNOLOGY

7.3.1 REVERSE OSMOSIS

Reverse osmosis is a natural phenomenon that occurs when dilute and concentrated liquids are separated by a semi-permeable membrane such as diaphragm, which selectively permits only one type of molecule to pass through. Under normal conditions, pure water would diffuse through the membrane into adjacent higher concentration liquid, but by the application of pressure to the concentration solution, the flow moves back to an opposite direction. The process is called reverse osmosis. Concentrated wastewater, which is rich in ionic metals molecule, will then be removed. Cellulose acetate is the generally type of membrane used. Reverse osmosis is generally used in the electroplating industry to recover both metals and water.

7.3.2 ELECTRODIALYSIS

Electricity is used for electrodialysis methods. It uses cathode and anode, which are submerged in wastewater, separated by semi-permeable membrane and connected, to an electricity source. The membrane allows either positively or negatively charged ions to pass through. When the circuit is switch on, metallic heavy metals with positive valence such as copper ion Cu^{2+} will be attracted towards anode and the negative ions will be attracted towards cathode. In this way, concentrated metallic ions are separated from negatively charge ions and then pumped to clean water and wastewater tanks. Electrodialysis is used in the electroplating industry for the recycling of metals and for water purification. Because a single pass through, an electrodialysis cell usually removes only 30 to 60% of the metal, (LaGrega, 1994).

7.3.3 ULTRAFILTRATION

Ultrafiltration separates solutes from a solvent on the basis of molecular size and shape by passing the solution through a membrane module where a pressure difference is maintained across a membrane. Water and small molecules move through the membrane to the lower pressure side, while the membrane retains the larger molecules. In ultrafiltration, solutes of molecular weight greater than about 500 and less than 500,000 can be separated from a solution, (LaGrega, 1994). It can be operated as a batch, single-stage continuous or feed-and-bleed, and multi-stage continuous operation.

7.4 OXIDATION AND REDUCTION

Oxidation and reduction method is suitable to remove heavy metals with different valence such as chromium metals from Cr^{6+} to Cr^{3+}. Chromium presents as hexavalent chromium (Cr^{6+}) does not precipitate under normal high pH conditions. It is necessary to reduce the hexavalent chromium to trivalent chromium (Cr^{3+}), which form an insoluble hydroxide (solubility value, $K_{sp}=1x10^{-30}$). Therefore, reduction agent such as Fe^{2+}, sulphur dioxide and sodium bisulphate will need to be added in order to allow reduction process from Cr^{6+} to Cr^{3+} to occur as shown below.

$$Cr^{6+}(aq) + 3Fe^{2+}(aq) \rightarrow Cr^{3+}(aq) + 3Fe^{3+}(aq)$$

7.5 CARBON ADSORPTION

Adsorption is a process in which a soluble contaminant (the adsorbate) is removed from water by contact with a solid surface (the adsorbent). The adsorbent most widely used in environmental applications is carbon that has been processed to significantly increase the internal surface area (called activated carbon). Activated carbon is a good adsorption media and can be used to remove heavy metals from wastewater.

It is also used as catalyst in chemical reactions during wastewater treatment. There are two types of activated carbon, powder and granulated. The application depends on the type of waste to be treated. Granular activated carbon (GAC) is most commonly used for removal of a wide range of toxic organic compounds from groundwater and industrial waste streams. Powder activated carbon is often used in biological treatment systems. Activated carbon is able to produce a very high-quality effluent, and is utilized in drinking water systems as well as for pollution control. Activated carbon can also be produced from carbonaceous local waste materials such as coconut husk, palm oil shell, lignin, nut shell, sawdust, bones, etc. The properties of final product will be different, depending on the nature of the raw materials, activating agent, carbonization and activation processes. Much of the surface area available for adsorption is finding in pores within the material during the activation process.

In Malaysia, there are four known plants using charcoal from palm and coconut shells to produce granulated activated carbon and only one plant produces powdered activated carbon from saw dust. Specific surface area of activated carbon produced ranges from 800 to 1,200 m^2/gram by which all the plants use steam as the activating agent, (Ku Halim, 1994). As activated carbon can be locally produced, therefore, there is a high potential in using this material in water and wastewater industries.

7.6 HEAVY METALS REMOVAL USING LIMESTONE

Aziz (1989, 1992, 1993) and Aziz & Smith (1992, 1996) have studied the use of limestone in removing manganese from water. In their study, a manganese solution of 1 mg/l was shaken with limestone (containing 53.9% $CaCO_3$ and 5.2% $MgCO_3$), gravel, and crushed brick or with no solid media at various pH values. At a final pH value of 8.5, limestone gave 95% removal of Mn, crushed brick gave 82% removal, gravel gave about 60% removal and the removal for aeration and settlement with no solid media was less than 15%. Their results indicated that rough solid media and the presence of carbonate are beneficial in the precipitation of Mn in water.

Their batch studies were continued by conducting a laboratory scale filtration technique to prove that limestone particle could be used as a media for removing manganese from water (Aziz and Smith, 1996). The filtration results indicated that at an input pH of 7 with Mn concentration of 1 mg/l, 1.35 hour's retention time, 500-mm media depth and 20 ml/min, a good removal (above 90%) was observed in the limestone media as compared to the gravel media (Aziz and Smith, 1996). This validates the batch results obtained by Aziz and Smith (1992). One of the results of this filtration experiments is given in Aziz and Smith, 1996. Aziz & Rashid (1994), Aziz & Mohd (1996), Aziz (1997) and Aziz & Mohd (1996, 1998) extended the studies on the use of limestone with different metals. They proven that in general the removal for copper, cadmium, chromium, nickel, lead, zinc were above 90% at initial metal concentration of 12 mg/l. Result of filtration experiment for lead removal is given in Table 1. The results indicate that a rough solid media and the presence of carbonate are beneficial in the precipitation of heavy metals from water. Limestone offers the potential for a low cost filtration technique for the removal of heavy metals from water, (Aziz, 1992). However, current application of this treatment may suitable for a low concentration metallic wastewater up to concentration of 12 mg/l. Apart from that, maintenance work needs to be done at intervals for the replacement of the filter media.

Studies show that if the wastewater can be regulated and the influent flow is controlled, the filter model is expected to last at least a month. Spare filter columns may help to continue the treatment system once maintenance needs to be undertaken. Backwashed water could be recycled back to the filter model. Even though the model might not solve all the problems of treating metallic wastewater in wastewater; it may help to provide cheap alternatives for Small and Medium Industries in Malaysia. It is mostly suitable for lower concentration of metals, especially at the polishing end of wastewater treatment.

REFERENCES

[1] *Aziz. H. A. Removal of Manganese from Water: Batch Study with Limestone. Thesis Master of Science, University of Strathclyde, 1989.*

[2] *Aziz, H. A. A study on the removal of manganese from water in the presence of coarse media. Ph.D. thesis, Dept. of Civil Engineering, Univ. of Strathclyde, Glasgow, UK. (Unpublished), 1992.*

[3] *Aziz, H.A. and Smith, P.G. The influence of pH and coarse media on manganese precipitation from water, Water Research, 26, 853-855, 1992.*

[4] *Aziz, H.A. Removal of manganese from water using low cost filtration technique. Proceedings National Seminar on Advances in Environmental Control Technology, ENVIROTECH '93, 18-19 August, Kuala Lumpur, 1993.*

[5] *Aziz, H.A., Rashid, R. Batch study on the removal of a few heavy metals (Zn, Pb, Cd, Cu, Ni and Mn) from water using limestone particle, Proceedings of the International Conference on Environment, ENVIRO MAL'94, Kuala Lumpur, vol. 1, 99-108, 1994.*

[6] *Aziz, H.A. and Smith, P.G. Removal of manganese from water using crushed dolomite filtration technique. Water Research, vol. 2, 489-492, 1996.*

[7] *Aziz, H.A and Mohd. M. 'Study on the removal of selected heavy metals (Pb, Cd, Cu, Ni, Cr (III) and Zn) from an artificial acidic wastewater using limestone particle', Proceedings International Symposium on Limestone, Holiday Villa, Subang, Malaysia, pp, 13-15 November, 1996.*

[8] *Aziz, H.A. and Mohd., M. 'Potential use of low cost filtration technique for removing selected heavy metals from wastewater at pH less ha 5', Indian Journal of Engineering and Material Sciences, Vol.5, April, pp 300-000, 1998.*

[9] *Barnes, D., Bliss, P.J., Gould, B.W. and Vallentine, H.R. 'Water and Wastewater Engineering Systems', Longman Scientific Technical, UK, 1986.*

[10] *Department of Environment Malaysia. 'Environmental Quality Report 1993', 1994.*

[11] *Department of Environment Malaysia. 'Environmental Quality Report 1995', 1996.*

[12] *Ku Halim Bin Ku Hamid and Azzudin Bin Shebli. The use of activated carbon in industrial waste treatment, (In Malay), Paper presented at the National Energy Seminar, UKM, Bangi, (17-19 May), 1995.*

[13] *LaGrega, M.D.; Buckingham, P.L; and Evans, J.C. The Environmental Resources Management Group. 'Hazardous Waste Management, McGraw-Hill International Editions, Singapore, 1994.*

[14] *MDC Sdn. Bhd. Laws of Malaysia - Environmental Quality Act 1974 and Regulations, 4th edition, Kuala Lumpur.*

ANNALS OF FACULTY ENGINEERING HUNEDOARA – INTERNATIONAL JOURNAL OF ENGINEERING

Faculty of Engineering Hunedoara,
5, Revolutiei, 331128, Hunedoara,
ROMANIA
http://annals.fih.upt.ro