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Industrial Discharge and Their Effect to the Environment

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1. Introduction

Industrialization has become an important factor to the development of a country's economy, through the establishment of plants and factories. However, the waste or by-products discharged from them are severely disastrous to the environment consists various kind of contaminant which contaminate the surface water, ground water and soil. There are a number of reasons the waste are not safely treated. One of the reasons is mainly due to the lacking of highly efficient and economic treatment technology. The focus of this chapter is to give a detail illustration at the effect of industrial discharge and on the environment and human health. Some corrective actions shall also be illustrated in the later part of this chapter, to overcome the contamination of industrial discharge. The content of this chapter will be as follows:-

In section 2, there is an illustration of the source and types of industrial contaminants in many parts of the world. It is essential to understand the characteristic of industrial discharge in order to have an idea for ways to reduce or remove the contaminants for a sustainable tomorrow.

It is required to understand the impacts of industrial waste to the environment (freshwater, seawater, land) in order to design highly efficient treatment and developing effective remedial methods. Section 3-5 explains how such contamination is going to affect living organism, as well as, abiotic compartment such as sediment through case studies.

Section 6 depicts the possible health problem which caused by the contaminant from industrial discharge. Some of the contaminants merely cause mild discomfort to human being, while others might be detrimental to human health. The latter is usually caused by carcinogenic contaminants.

Section 7 discusses the treatments to the contaminant. Corrective actions that can be taken to solve the current environmental issue caused by industrial discharge are discussed as well. Currently, many researchers all over the world use remediation which is a method using biological agent in treating the contaminant in surface water, groundwater and land. Hence, various bioremediation and phytoremediation case studies are also outlined in this section.

Suggestion of some future work can be done on the industrial discharge is included in section 8 as part of the summary to this book chapter.

2. Industrial discharge

The contaminant from the discharge is directly related to the nature of the industry. For example, in textile industry, the discharge is usually high chemical oxygen demand (COD), biochemical oxygen demand (BOD) and colour point; tannery industry is on the other hand, produces discharges which have high concentration of metal such as cadmium, and etc. Table 1 presents a summary of the types of contaminants discharged from the industries at different parts of the world by random case studies.

Location	Contaminant	Type of industry	Reference
Malaysia, to Juru River	**Metalloid** Arsenic (As) **Metal** Chromium (Cr), Cadmium (Cd), Zinc (Zn), Copper (Cu), Lead (Pb), Mercury (Hg) **Organic/ inorganic matter and parameter** Phosphate (PO_4^{3-}) Ammonia (NH_3) Nitrate (NO_3^-) Sulphates (SO_4^{2-}) Chloride (Cl^-) Aluminium (Al)	Chemical products Papers and printings Batteries Electroplating Textile and leathers Fertilizers, pesticides, insecticides Plastic-based products Rubber-based products Wood based products Electric and electronic industries Cosmetics Fungicides Fluorescent lights Dental amalgams Art supplies Mining and siltation Cement and cement products Iron, steel and tin workshops Welding fumes Medical equipment Smelting plants Metal fabrications Oil refineries Quarries Beverages and food	DOE, 1998 Salman A. Al-Shami et al., 2010
Bangladesh, to lagoon	**Metalloid** As **Metal** Zn, Cu, Strontium (Sr), Pb, Nickel (Ni), Cr, Lithium (Li), Vandadium (V), Silver (Ag), Cobalt (Co), Selenium (Se) **Organic/inorganic matter and parameter** Biochemical oxygen demand (BOD), chemical	300 industries included textile, dyeing to plastics, metal fabrications, semiconductor goods, lather tanning etc.	Ahmed et al., 2011

Location	Contaminant	Type of industry	Reference
	oxygen demand (COD), electrical conductivity, pH, total alkalinity, total hardness, total organic carbon (TOC), Turbidity (Cl^-), total suspended solids (TSS) and total dissolved solids (TDS).		
Japan, to Nishitakase River	2-[2-(acetylamino)-4-[bis(2-methoxyethyl)amino -5-methoxyphenyl]-5-amino-7-bromo-4-chloro-2-H-benzotriazole (PBTA-1)	Textile industry	Shiozawa et al., 1999
Germany, to three rivers of North Rhine-Westphalia	**Organic/ inorganic matter and parameter** (i) Chemical process site 1 Dichloroaniline Tetramethylbutanedinitrile Tributylphosphate Triethylphosphate Diisopropylnaphthalenes Benzoic acid 2,2,4-Trimethyl-1,3 pentanedioldiisobutyrat (TXIB) (ii) Meat production site and chemical site N, N-dibenzylamine 1-methyl-2-indolinone N,N-Dibenzylamine Triethyl phosphate (TEP) Trimethyl- and 4-tert-butylbenzoic 2-(Chloromethyl)-1,3-dioxolan 1-Methyl-2-indolinon Trimethylbenzoic acid Tris(chloro-propyl) phosphat (TCPP) (iii) Oil production sites and chemical complex Tributylamine Dimethylpyridine Dimethylpyrazine Indole Methylindole 1-Ethylpyrrolidone Thioanisole Methylphenyl sulfone TCPP, Isomer 1 TCPP, Isomer 2 C1 Benzoic acid C2 Benzoic acid 2,4,6-Trimethylbenzoic acid	Petrochemical site, paper production, meat production	Botalova & Schwarzbaue et al., 2011

Location	Contaminant	Type of industry	Reference
Kingdom of Saudi Arabia, to Red Sea	**Metal** Cd, Cr, Cu, Iron (Fe), Ni, Pb, Zn, Aluminium (Al), Barium (Ba), Molybdenum (Mo), Sr **Organic/ inorganic matter and parameter** Benzene, styrene, toluene, indene, Naphthalene, 1, 4-dioxane, Ethyl Benzene, Xylene, O&G	Two petrochemicals, three refineries	Ahmad et al., 2008
India, to agriculture field	**Metal** Cd, Cu, Fe, Ni, Pb, Zn **Organic/ inorganic matter and parameter** BOD, COD, TDS, dissolved solids (DS) Chloride, sulphate, phosphate	Paper Industry	Devi et al., 2011
India, to unlined lagoon	**Organic/ inorganic matter and parameter** Sodium, chloride, calcium, COD, BOD	Cystine production industry	Srivivasa Gowd & Kotaiah et al., 2000
Croatia, to Sava River	**Metal** Fe, Zn, Cu, Ni, Pb, Cr	Pharmaceutical and food industries	Radić et al., 2009
India, to Uppanar river	**Metal** Fe, Mn, Pb, Zn, Cu, Ni, Cr, Cd , Co **Organic/inorganic matter and parameter** DO, COD	Chemicals, beverage manufacturing, tanneries, oil, soap, paint production, paper, and metal processing plants	Jonathan et al., 2008
India, to Bandi River	**Metal** Cu, Fe, Zn and Mn **Organic/inorganic matter and parameter** TDS, TSS, COD, BOD, chlorides, sulfates, carbonates and sodium, calcium and magnesium.	Dyeing and printing industries	Nepal Singh et al., 2000

Table 1. Contaminants discharge from different types of industry and location found from the studies conducted

Through the studies, we can deduce that most of the industrial discharge carries toxic substances. Due to the presence of high amount of toxic, carcinogen, and teratogen of metals, researchers are highly concerned with its effect on the environment and health of mankind. Rigorous investigations are currently being carried out to study the consequences of the contamination on the surface water, groundwater, and surface land due to industrial discharge. The result of these case studies will then be presented as a solid evident for the effects of metals ions, organic and inorganic matters to environment. The interactions and impacts which caused by these chemical contaminants towards the environment will be further explained.

3. The effects of industrial discharge to the freshwater

The industrial discharge carries various types of contaminants to the river, lake and groundwater. The quality of freshwater is very important as it is highly consumed by human for drinking, bathing, irrigation and etc. The presence of contaminants from industrial contaminant within the water may reduce the yield of crops and the growth of plant and it will harmful to the aquatic living organism too.

3.1 River

River is a system which includes the main course and its tributaries. It is responsible in carrying the load of dissolved and particulate phases from both natural and anthropogenic sources along with other contents. This substance moves downstream and will be experiencing chemical and biological changes. Thus, the water chemistry of a river is affected by the lithology of the reservoir, atmospheric, and anthropogenic inputs. Furthermore, the transport of natural and anthropogenic sources to the oceans and their state during land–sea interaction can be determined by the water quality from rivers and estuaries. Estuaries could be categorized as a geochemical reactor and its heterogeneous reaction could bring the understanding on the fate of metals, organic and inorganic matters along the river to the ocean. Through the studies conducted by Jonathan et al. (2008) noted that there is relationship between the water-particle interactions and solution chemistry, such as flocculation, organic and inorganic complexation, adsorption, and sediment resuspension.

3.1.1 Metals

The contamination of metals is a major environmental problem and especially in the aquatic environment. Some metals are potentially toxic or carcinogenic even at very low concentration and are thus, hazardous to human if they enter the food chain. Metals are usually dissolved into the aquatic system through natural or anthropogenic sources. Metal ions are distributed thoroughly during their transport in different compartments of the aquatic ecosystems, in biotic or abiotic compartment such as fishes, water, sediment, plant. Metals remain in contaminated sediments may accumulate in microorganisms which in return entering into the food chain and eventually affect human well being (Shakeri & Moore, 2010).

In 2010, Shakeri & Moore conducted a study to evaluate the distribution and average concentrations of Cu, Zn, Ni, Mo, Pb, V, As and Co in Chenar Rahdar river sediment. The result concluded that there is a strong association of elements such as Zn, Co, Ni, Sc, Cu, Al,

and Fe in the sediment at the study site. The authors indicated that Al and Fe hydroxides and clay content play a significant role in the distribution and sorption of metals in sediments. This study noted that metal inputs have brought negative impact to the freshly deposited sediments and the accumulation of the metal on the sediment surface.

Metal in sediment is affected by mineralogical and chemical composition of suspended material, anthropogenic influences by deposition, sorption, and enrichment in living organism or aquatic plant (Jain et al., 2005). Naturally, suspended and bed sediment are an important compartment to buffer metal concentration in an aquatic system especially by adsorption or precipitation (Jain & Ali, 2000; Jain, 2001; Jain & Sharma, 2002; Jain et al., 2004). However, the metal discharges from industry may change the role of sediment as it may not be able to act as a sink and buffer to higher concentration of metal. Metals contributed by man-made sources are possible to associate with organic matter in the thin fraction of the sediments, or adsorbed on metal hydrous oxides, or precipitated as hydroxide, sulfides and carbonates (Singh et al., 2005; Shakeri & Moore, 2010).

In India, the discharge from fertilizer industry has not undergone any treatments, is one of the major sources of pollution to water reservoirs such as lakes, ponds, rivers and ocean. The discharge contains certain toxic components such as metals, nitrates and ammonia which might be responsible for causing metabolic impairment in the aquatic organisms. At times, the toxic components could even cause fatality in aquatic living organism (Bobmanuel et al., 2006; Yadav et al., 2007; Ekweozor et al., 2010). A study has been conducted by Yadav et al. (2007) on freshwater fish, *Channa striatus* which are exposed to fertilizer industry discharge. It is found that the toxicity of the fertilizer discharge on the fish tissues could be due to metals and ammonia. Heavy metals such as Zn, Cr, Cu and Pb in the fertilizer industry discharge can bind with certain proteins in fish and disrupting membrane integrity, cellular metabolism and ion-transports that will bring harm to the maintenance of homeostasis. The result showed that the average protein concentration in various tissues of the control fish is, in descending order: gills>liver>brain>muscle>kidney>heart. However, the protein level reduced in all fish tissues at a higher sublethal concentration of industrial discharge at 7% higher than control fishes, the values of tissue reduced in descending order: liver, brain, muscle, gills, kidney, and heart at 76.23%, 55.95%, 52.16%, 50.06%, 49.28%, and 42.86%, respectively.

When metals associate with other chemicals compound in the fertilizer discharge may cause distortion in the cell organelles and inhibit the activity of various enzymes (Valarmathi & Azariah, 2003; Yadav et al., 2007), which may greatly disturb the physiological state of the exposed living organism. The heavy metals present in the fertilizer industry discharge are usually in dissolved state which could easily be uptaken by fish and enter human food chain. There have been studies showed that metals will cause damage to the human kidney and liver even at low concentration. The early studies suggested that higher concentration in metals can be carcinogenic and teratogenic (O'Brien et al., 2003; Yadav et al., 2007). Generally, carbohydrate metabolism is a major source of energy production and the activity of Lactate dehydrogenase (LDH). It has been a target for the action of various xenobiotics. The activity of LDH in different part of body tissues of *C. striatus* after exposing to the fertilizer industry discharge has been examined. In this study, the result showed that the exposure of *C. striatus* to fertilizer industry discharge resulted in a drastic reduction in the enzyme activity.

Rai & Tripathi (2009a) added that most metals in aquatic environment associated with particulate matter, then settled and accumulated in the bed sediments. The accumulation of contaminant in the bed sediments and the remobilization of contaminant are the most important mechanisms of contaminant in an aquatic ecosystem regulation. Furthermore, under certain circumstances such as deficit in dissolved oxygen or decreased in pH, the bed sediments can be another source of secondary water pollution when the heavy metals from bed sediments are released.

Another study conducted in a kaolin refinery industry produces hazardous by-product such as Al, Fe, and Zn. In kaolin processing, sulphuric acid is used to improve the whitening (Jordao et al., 2002) is discharged to the river waters. This will influence the well being of aquatic organisms that adapted well at close to neutral pH. Also, in order not to affect the colour and whiteness of paper, impurities such as iron oxides is needed to be removed. This can be made through the reduction of Fe(III) to Fe(II) with metallic Zn. Therefore, Zn, Fe, Al are usually present in the discharge. The study examined the pH, conductivity and hardness values and various metals such as Al, Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, and Zn. Excessive concentration of these parameters in discharges that flows into rivers may also cause adverse effects to human health (Jordao et al., 2002). The discharges from the industry without proper treatment will decreased the pH of the river water. This is due to the usage of sulphuric acid in the kaolin processing. The pH values will bring effects in flora and fauna nearby, change the taste of water and lead to heavy corrosion in pipe lines. High conductivity naturally indicates the presence of ionic substances dissolved in the river water. However, the result showed that 90% of the study site exceeded the data reported for non-contaminated rivers due to excessive metal ions within the water. At the site nearer to kaolin industry the conductivity is 852 times higher than the non-polluted study site. The industrial discharge also changed the hardness in river water. However, the result showed that the study site is not exceeded the maximum limit (500 mg $CaCO_3$ L^{-1}) of hardness for drinking water as recommended by the Brazilian government (Jordao et al., 2002).

3.1.2 Organic/inorganic matter

The study conducted by Hiller et al. (2011) to investigate the concentrations, distributions, and hazards of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). PCBs are used mainly as coolant and electronic industries (capacitors, transformers), paints, sealants for wood, cutting and lubricating fluids, plasticizers, and as dielectric fluids. Therefore, at the former site of PCB manufacturing area in Slovakia, high concentrations of PCBs are detected in soils, sediments, humans, and wildlife (Kocan et al., 2001; Petrik et al., 2001; Hiller et al., 2011).

Due to their low aqueous solubilities, the PCBs and PAHs lay on the surface of soils and waters. PCBs and PAHs adsorb strongly to the organic fraction of soils (Girvin & Scott, 1997; Hiller et al., 2011). Soils contaminated with PCBs and PAHs are transported directly or indirectly by rivers to the water reservoir and are subsequently converted into the bed sediments. Therefore, soils could be considered as the primary sinks for these organic contaminants. PCBs and PAHs are persistent in the environment, resistant to degradation process, and accumulate in food chain. This will eventually bring health hazard to living organisms, including mutagenicity and carcinogenicity (Hiller et al., 2011).

Yadav et al. (2007) studied on fertilizer industrial discharge showed that some components in the discharge may interact with each other and produce toxic to aquatic organisms. For instance, the interaction between dissolved oxygen and ammonia changed the respiratory physiology in fresh water fish. In addition, results showed that the toxicity of the effluent in fish depends on concentration and duration of exposure. Several study showed that the excess concentration of ammonia, whether is ionized or unionized, is one of the major contaminants in fertilizer discharge and it is toxic to aquatic living organism. It could cause impairment to the cerebral energy in fish, such as *O. niloticus* and a hybrid catfish (Yadav et al., 2007; Ekweozor et al., 2010).

Surprisingly the toxicity level of fertilizer industry discharge may influence by the environmental factors such as conductivity, temperature, pH, cardon dioxide (CO_2), oxygen and elements. Through studies, these factors will influence the behavior and certain biochemical indices of the fish, such as *C. striatus*, by acting either in synergistic, antagonistic or simple additive manner (Yadav et al., 2005; Bobmanuel et al., 2006; Yadav et al., 2007). A high conductivity value indicates high concentration of dissolved ion within the industrial discharge. However, the conductivity value which recorded in this study was slightly below the required limit. Moreover, in this study the increased in fish mortality may due to the increased in water temperature, the increased uptake of industrial discharge components and low dissolved oxygen in the water (Yadav et al., 2007).

Carmago et al. (1992) found that the rivers nearer industrial discharge point have adverse impact to the environment as well as to macrobenthic communities. Toxic contaminants from surface runoff, sewage discharges and industrial discharge have caused negative impacts towards the freshwater macrobenthic communities. The presence of substance chemical such as ammonia, chlorine, cyanide, metals, PCBs, pesticides and phenols would caused a decline pattern on the number of species and changes in the species composition. Furthermore, when industrial discharge and river regulation interact, benthic macroinvertebrates will be highly exposed to the toxic contaminants. The living organism which will be deeply affected are shredders, which feed on coarse sedimentary detritus, and collector-gatherers, which feed on fine sedimentary detritus, were the macroinvertebrate functional feeding groups are most adversely affected. Furthermore, during the industrial process, high amount of hydrofluoric acid (HF) are used to separate different sandy materials which are subsequently used for manufacturing glass at industrial plants. Therefore, high concentration of fluoride ion and suspended inorganic matter discharged by the industrial into the study site. Carmago et al. (1992) noted that short-term flow fluctuations, low concentration of dissolved oxygen and also the siltation of suspended inorganic matter caused by industrial discharge contribute greatly to the changes in sediment and directly affect the structure of macroinvertebrate community. The high siltation of suspended inorganic matter caused significant reductions in taxa richness and abundance of zoobenthic communities as it changes the natural structure of the substratum. Other than that, the fluoride pollution which generated by the industrial discharge was also contributed to adverse effects on the macrobenthic community.

3.2 Groundwater

Groundwater is regarded as the largest reservoir of drinkable water for mankind. To many countries, groundwater is one of the major sources of water supply for domestic, industrial

and agricultural sectors. In India, groundwater supplies more than 50% for irrigation, and 80% for drinking water (Singh et al., 2009). It is estimated that approximately one-third of the world's population are using groundwater for drinking purposes. Pollution of ground water due to industrial effluents is a major issue (Vasanthavigar et al., 2011). Poor groundwater quality brings negative impact to human health and plant growth. In developing countries like India, it is estimated that around 80% of all diseases are directly related to poor drinking water quality and unhygienic conditions (Olajire & Imeokparia, 2001; Vasanthavigar et al., 2011). Human activities like industrialization are responsible to the groundwater quality and the groundwater contamination and spread of contaminant are amongst the major factor lead to human hazards.

3.2.1 Metals

Khe´rici et al. (2009) reported that there is high concentration of Cr(VI) during low precipitation and upper aquifer in the groundwater at the town of Annaba, which is also an important location for heavy industries

During high precipitation, infiltration of sulphates and chromates occurred, and subsequently when low precipitation, the aquifer without recharge becomes a confined environment favourable to a reduction of sulphates to sulphide (H_2S and HS^-) by a complex biochemical process (a phenomenon called sulphatoreducing), due to the bacterial activity. Subsequently, this reduction results from the sulphur rejected (Khe´rici et al., 2009) by a sulphato-reducing bacteria (Desulfovibrio desulfricans), which can transform of Cr(VI) to Cr(III) which is a stable substance. Cr(III) is stable at pH 7 with the presence of oxygen. While, chromate in the thermodynamic form is stable under these conditions, however, it is toxic to many organisms at very low concentrations. Chromate is further subjected to microbiological reduction.

In upper aquifer, the chromate concentrations increase during high precipitation. Long precipitation resulted in higher concentration of Cr(VI) in the upper aquifer. In contrast, during low precipitations, chromate concentrations in the upper aquifer are lesser. Similarly, during high precipitation, the infiltration of chromates, sulphate and dissolved oxygen is higher in the upper aquifer (Khe´rici et al., 2009).

In the study performed by Purushotham et al. (2011) showed that about 28% of total hardness in the study site exceeded the desirable limits at 600 mg L^{-1}. Naturally, the water hardness is due to the presence of alkaline earths such as calcium (Ca) and magnesium (Mg). Excess of magnesium affects the soil quality, which results in poor crops yield. The high concentration of magnesium and calcium can cause decrease in water quality and may cause encrustation in the water supply structure. High concentrations of sodium can deteriorate soil quality and damage the sensitive vegetation due to its phytotoxcity. Water containing high concentrations of carbonate and bicarbonate ions tends to precipitate Ca and Mg as their carbonates. As a consequence the relative proportion of sodium increases and settled in the soil, and decreased soil permeability.

3.2.2 Organic matter/inorganic matter

The salts present in the groundwater influence the soil structure, permeability and aeration, which indirectly affect the plant growth. Study conducted by Purushotham et al. (2011)

showed high sodium conductivity (>1500 µs cm^{-1}) around 17.5% of the groundwater samples and this probably due to high salinity in groundwater. Sodium concentration in irrigation water replaces calcium by the process of Base Exchange, therefore reduces soil permeability. Furthermore, excess salinity in groundwater used for irrigation decreased plants osmotic activity and interfere water absorption and nutrients from the soil.

Nearly 5% of groundwater from the study site exceeds the desirable limit (1000 mg L^{-1}) of chloride. The natural source of chloride is due to the weathering of phosphate mineral apatite present in granites. However, apart from natural sources, industrial discharge is one of the sources that contribute chloride in groundwater. Excessive chloride concentration leads to salinity, which deteriorate the soil (Purushotham et al., 2011).

4. The effects of industrial discharge to the seawater

Contaminants from the industry discharge flows through river. Some are accumulate, interact and settle with the living organism, plant and sediment and finally reach the coastal and ocean. Plants and living organism in the ocean are important food sources for human intake. Contaminants may then enter human food chain and accumulate in fishes, molluscs (octopus, shellfish, and cockle), crustaceans (shrimp, crab, and lobster), seaweed, sea cucumber and etc. Therefore, it is essential to understand the effect to aquatic environment.

4.1 Metals

Metals which have altered biogeochemically along the flows from river to estuaries and coastal area are transported to the ocean and the original composition of seawater and sediments is altered (Jonathan et al., 2008).

Abbas et al. (2008) studied on the blood cockles (*Anadara granosa)* found in two rivers in Penang state, Malaysia, namely, Juru River and Jejawi River nearby Prai industrial zone. The result showed that the average content of arsenic and metals found in cockles are arranged in the order: As >Hg >Cd > Zn >Cu >Cr > Pb and As >Hg > Zn >Cd >Cu >Cr > Pb for Juru and Jejawi River, respectively. The mean concentration of As was higher than the permissible limit (1 mg kg^{-1} wet weight) established by the Malaysian Food Act 1983 and Food Regulations 1985 Fourteen Schedule. The result for this study is important as there is an extensive culture of cockles is being carried out in the coastal areas. The excessive contamination of this bivalve sea food is not safe for human intake.

In the study conducted by Yap et al. (2002) at coastal areas adjacent to industrial areas, the authors noted that sediment plays an important role for the contaminant transport and metal repository. Impact to human health may possible to identify via sediment analyses as it is also a long term integrator of geochemical processes. There are four types of sediments that could results in different adsorption of metals in sediment, namely, 'easily, freely leachable and exchangeable' (EFLE), 'acid-reducible', 'oxidisable-organic' and 'resistant' types. Characteristic of sediment is important to determine in order to understand the chemical reaction of sediment and metal or organic matter. The study indicated that the affinity is lower for metals in the 'acid-reducible' fraction of the sediment for both offshore and intertidal sediment. The reducing conditions are mainly caused by decomposition of organic matter by microorganism activity (Yap et al., 2002). The 'acid-reducible' fraction involves metals associated with manganese and iron oxides and hydroxides and carbonates.

Apart from that, the 'oxidisable-organic' sediment proved to organically bind with metal and increase the adsorption of metals in the sediment. For instance, the adsorption of Cu and Pb in 'oxidisable organic' fraction is high and it is due to the organic matter and its physico-chemical properties of the sediments, respectively. The study also concluded that the 'bioavailabilities' of the metals on EFLE fraction and 'resistant' fraction are poor. On the other hand, the 'nonresistant' (non-lithogenous) fractions, tend to adsorb Cu and Pb into the 'oxidisable organic' fraction. Higher adsorption capability may due to higher affinities exist between metals and humic substances, which are the fractions of organic matters. They are chemically very active in complexing elements such as heavy metals. Furthermore, the metals may be associated with living organisms, and detritus or coating on mineral particles.

The organic phase of sediment could also play a dominant role in the transport of metals in natural water systems. The organic substances in sediments may break up to free the soluble metals in waters under oxidized conditions. The fate of metals in aquatic systems is significantly influenced by dissolved organic matter as dissolved organic matter is capable to alter the distribution between the oxidized and reduced forms of metals (Yap et al., 2002).

At Pakistan, Saifullah et al. (2002) studied on the mangrove which is the habitat for some marine organism and shrimp fishery. However, the mangroves are deteriorating rapidly due to several anthropogenic stresses and industrialization is one of the important reasons. In the Karachi area (the largest industrial city of Pakistan), there are more than 6000 different industrial units such as chemical industries, metal industries, oil refineries, petrochemicals, tanneries, pharmaceuticals, textiles etc. Due to the marine pollution cause by industrialization, the mangroves health is at risk. Metal contamination is the most significant source of pollution to the marine environment. Furthermore, high industrialization activity is partly contributed to around 2000 tons of untreated BOD that discharge to the seaside daily. This directly affects the marine organism and the shrimp fishery.

4.2 Organic matter/ Inorganic matter

Jonathan et al. (2008) conducted a study in Uppanar River. In their study, the loadings of industrial effluents were found to change the dissolve oxygen (DO) in water. Such changes have affected the environmental quality in the river and its coastal zone. In the coastal zone, the dissolved metals behave in a reversible manner with physicochemical parameters, indicating that fresh water input has changed the coastal water (Kuppusamy & Giridhar, 2006; Jonathan et al., 2008). The river water showed that low content of DO situated very close to the river bank. This is due to contamination of industrial discharge with high COD. The low DO is due to the discharge of industrial effluents and the toxicity of the combined effect from chemicals and heavy metals (Jonathan et al., 2008).

The study performed by Din & Ahamad (1995) on cockles' growth at coastal receiving industrial discharge from the nearby Prai Industrial Estate. Cockles are facing mortalities nearer to the discharge point. The surrounding industrial activity in year 1995 includes textile and chemical manufacturing, and electroplating work. The study conducted at different located given 2, 4, 6 and 8 weeks of exposure to the pollution by those industrial discharges. The result showed that the effects of on the cockles' growth seem significantly as

early at week two. Several parameters were taking into account, namely, temperature, TSS, BOD, oil and grease. The parameters were found relatively high at the discharge point. However, parameters such as temperature, salinity, pH, DO and BOD directly affect the well being of all livings organism. They affect living organisms through the intake and activities of toxic materials.

5. The effects of industrial discharge to the land

Generally, the land is contaminated due to the uncontrolled and unplanned disposal of industrial waste onto the soil surface. The contaminant will infiltrate to the groundwater. The contamination on the soil surface may interrupt human daily activity and bring adverse effect to the growth of plant as well as human health.

5.1 Metals

Last few decades, the drainage basin of the Gangetic plain has been used for the disposal of domestic and industrial wastes which bring negative impact to the water quality, sediments and soil surrounding (Ansari et al., 1999). Unplanned disposal of industrial waste directly on the land is one of the factors that caused the pollution to surface water and groundwater. A study conducted by Singh et al. (2009) showed high concentration of Cr(VI) in ground water from various industrial cities in India. The Cr in the groundwater resulted from on-land burial of Cr sludge (5-10% Cr_2O_3 by wt) by various industries engaged in the manufacture of Basic Chrome Sulphate (BCS) ($Cr(OH)_2SO_4$), an important input for local tanneries. The sludge resulting from the initial stage of BCS manufacture is a product of incineration of chromite ore ($FeCr_2O_4$) and has remnant of Cr(VI) which is water soluble. The leachate of Cr (VI) in the sludge ultimately reached the groundwater.

Kisku et al. (2000) noted that for soil contaminated by industrial discharge, the plant could accumulate the toxic metal such as iron (Fe), zinc (Zn), copper (Cu), and manganese (Mn) are essential trace elements to plant life while lead (Pb), chromium (Cr), nickel (Ni), and cadmium (Cd). They are toxic even at a very low concentration. They indicated that the concentration of metal in the soils and plants of the polluted field were significantly higher than non-polluted field. Soil-plant bioaccumulation relationships are varies by element and plant. The highest accumulation of Fe, Mn, Zn, Cu, Pb, Ni, Cr, and Cd were found in *Spinacea oleracea*, *Raphanus sativus*, *Amaranths viridis* and *Lycopersicon esculentum*, *Coriandrum sativum*, *Solanum melongena*, *Spinacea oleracea*, *Lycopersicon esculentum*, and *Coriandrum sativum*, respectively. Furthermore, results reflected that *Spinacea oleracea* having more affinity to Fe and Ni, *Lycopersicon esculentum* showed higher affinity to Zn and Cr and *Coriandrum sativum* showed high affinity to Cu and Cd. The toxicity symptom is different by plant species, however, the most common and nonspecific symptoms are chlorosis, intervenial chlorosis, necrosis, stunted growth, shorter root length, and narrow leaves. For example, fertilization and fruiting phenomena of brinjal plant was significantly affected, tomatoes grew smaller and lesser, cabbage showed abnormal growth. Usually, plants do not always show visible morphology symptoms, they may have hidden injury due to contaminant or a change in metabolic pathways. Eventhough Fe, Mn, Zn concentration in plant tissues are well below the critical concentration, while Cu, Pb, Ni, Cr and Cd are within the prescribed plant critical concentration range, these toxic metals are obviously

affecting the plant life and reduce the yield capacity about 10%. Generally, metals could cause a decrease in total chlorophyll content and therefore changing the metabolic pathways of the plant. However, weeds in exception where it grows luxuriously with heavy metal contamination. It can be suggest an ideal agent for metal remediation.

Govil et al. (2008) conducted a study at an industrial zone which has 300 various types of industry nearby such as manufacturing chemicals, pharmaceutical, batteries, metal alloys, metal plating and plastic products, dyeing, edible oil production, battery manufacturing, metal plating, chemicals, etc. There are three sources of contamination exist within the industrial area, dumpsites of solid waste, untreated industrial discharge, and emission from smokestacks. And most of these industries directly release their discharge into nearby ditches and streams and the solid waste is randomly dumped on open land, and along roads and lakes. The soil contamination is suggested to be the main causes from the random dumping of solid waste from the industry and it could be spread by rainwater and wind. The result showed that the land around the industrial area is heavily contaminated by As and then Pb, Zn. Furthermore, there is an analysis conducted at the pre- and postmonsoon over two hydrological cycles in 2002 and 2003 indicated that As, Cd and Pb contaminants are more mobile. Subsequently, these heavy metals can cause groundwater pollution through the infiltration by soil.

6. The impact to human health

The impact to human health is the utmost important criteria to look into apart from the effect to surface water and groundwater on the living organism and sediments. Metals, as described in the above case studies showed the potential for health risk. However, the organic matter also will bring adverse health impact to human. The health hazard to human is further described in the following.

6.1 Metals

6.1.1 Aluminium

High concentrations of Al can cause hazard to brain function such as memory damage and convulsions. In addition, there are studies suggested that Al is linked to the Alzheimer disease (Jordao et al., 2002).

6.1.2 Cadmium

Cd is harmful to both human health and aquatic ecosystems. Cd is carcinogenic, embryotoxic, teratogenic, and mutagenic and may cause hyperglycemia, reduced immunopotency, and anemia, as it interferences with iron metabolism (Rehman & Sohail Anjum, 2010). Furthermore, Cd in the body has been shown to result in kidney and liver damages and deformation of bone structures (Abbas et al., 2008).

6.1.3 Chromium

Cr(III) is essential nutrient for animal and essential to ensure human and animal lipids' effective metabolism but Cr(VI) is carcinogenic. Cr(VI) is the most toxic form of chromium and having equivalent toxicity to cyanides. It can cause skin ulcer, convulsions, kidney and

liver damage. Moreover, it can generate all types of genetic effects in the intact cells and in the mammals in vivo (Khe´rici-Bousnoubra et al., 2009). It has also been reported that intensive exposure to Cr compounds may lead to lung cancer in man (Jordao et al., 2002).

6.1.4 Iron

Iron is an essential element in several biochemical and enzymatic processes. It involved the transport of oxygen to cells. However, at high concentration, it can increase the free radicals production, which is responsible for degenerative diseases and ageing (Jordao et al., 2002).

6.1.5 Lead

Lead could accumulate in kidney, liver, bone, and brain. Chronic intoxication can lead to encephalopathy mainly in children (Jordao et al., 2002).

6.1.6 Mercury

Mercury can cause brain damage, heart, and kidney and lung disease in human. At very low concentration, Hg can permanently damage to the human central nervous system (Rai & Tripathi, 2009a). Inorganic and mercury through biological processes, can converted into MeHg. MeHg is organic, toxic, and persistent (Wang et al., 2004; Rai & Tripathi, 2007). Furthermore, MeHg can cross the placental barriers and lead to foetal brain damage (Rai & Tripathi, 2009a).

6.1.7 Nickel

Nickel is an essential element to both plant and human, but high exposure to this metal can lead to cancer in organs of the breathing system, cardiovascular and kidney diseases (Jordao et al., 2002).

6.1.8 Zinc

Zinc is an essential element to human and plant (Jordao et al., 2002). Recent studies indicated that Zn is also involved in bone formation. However, elevated intake of Zn can cause muscular pain and intestinal haemorrhage (Honda et al., 1997; Jordao et al., 2002).

6.2 Organic/inorganic matters

6.2.1 Fluoride

High concentration of fluoride can cause dental and skeletal fluorosis such as mottling of teeth, deformation of ligaments and bending of spinal cord (Janardhana Raju et al., 2009).

6.2.2 Nitrate

High concentrations of nitrate cause methemoglobinemia in infants and could cause cancer. In the blood, nitrate convert hemoglobin to methemoglobin, where it does not carry oxygen to the body cells, which may lead to death from asphyxiation (Purushotham et al., 2011).

6.2.3 Potassium

High potassium concentration may cause nervous and digestive disorders (Purushotham et al., 2011), kidney heart disease, coronary artery disease, hypertension, diabetes, adrenal insufficiency, pre-existing hyperkalaemia. Infants may also experience renal reserve and immature kidney function (WHO, 2009).

6.2.4 Sulphate

Excessive sulphate concentration may lead to laxative effect (Purushotham et al., 2011) and it affects the alimentary canal (WHO, 2004).

7. Corrective action

There are several ways to solve the environmental problem caused by industrial discharge. Some of the methods are bioremediation, biosorption, phytoremediation, application of green chemistry and green monitoring. Many studies have been conducted on bioremediation using bacteria, fungi and yeast. Bioremediation is the use of microbial in remediating the contaminant while phytoremediation uses plant. The examples of bioremediation are land farming, composting, bioreactors, bioventing, biofilters, bioaugmentation, biostimulation, intrinsic bioremediation, pump and treat of groundwater (Boopathy, 2000). Brown algae and yeast are examples of the application in biosorption. The examples for phytoremediation could be the use of plant in surface and submerged aquatic plant. Green chemistry and green monitoring are alternative option to prevent and to monitor the contamination of industrial discharge. Types of corrective actions are illustrated in the following with selective case studies.

7.1 Bioremediation

Many research have been performed on bioremediation for other types of contaminant such as pesticide like DDT (Purnomo et al., 2011), herbicide like Pendimethalin (Venkata Mohan et al., 2007) petroleum and diesel oil contamination (MacNaughton et al., 1999; Watanabe, 2001), a few to name.

Conventional methods to cleanup pollutants usually involve physical treatment such as sedimentation and filtration, and chemical treatments such as flocculation, neutralization, and electro-dialysis. Very often, the treatment efficiency does not meet the regulation limits. Hence, further treatments are to be applied as well. Of all the technologies that have been investigated, bioremediation has emerged to be the most desirable approach for cleaning up contaminant from industrial discharge (Shedbalkar & Jadhav, 2011). Bioremediation can be defined as a technology that utilizes the metabolic potential of microorganisms to clean up contaminated environments (Wanatabe, 2001). Indeed, numerous studies have been carried out to search for the appropriate and useful bioremediation agent, such as bacteria, yeast and filamentous fungi.

7.1.1 Bacteria

A study conducted by Taheri et al. (2008) on organic sulphur compounds in petroleum and other fossil fuels. Disulfide oil (DSO) may be channeled to water ecosystem and surface land

mainly by refinery activities from its reservoir tanks. For refineries site near in seaside, DSO can pollute sea water through penetration of sandy soil. This study worked on seven microbial strains which is isolated from DSO contaminated soil. However, only two strains, namely, *Paenibacillus* and *Rhodococcus* have high potential to remove DSO from contaminated soil. The result showed that *Rhodococcus* and *Paenibacillus* were found to be suitable for bioremediation of DSO contaminated soil. It removed DSO with 19.3% and 24.3% for *Rhodococcus* and *Paenibacillus*, respectively, at after 48 hr. The author suggested the best condition for bioremediation which is to provide ample amount of water 20 μL g^{-1} soil day at and d-glucosa at 4 g L^{-1} (added water) as nutrient. Adding more than 4 g L^{-1} glucose added water showed an adverse effect.

Faisal & Hasnain (2004) reported that there are two chromium-resistant bacterial strains, CrT-1 and CrT-13. CrT-1 successfully reduced 82%, 28% and 16% of Cr(VI) after 24 hr at 100, 500, and 1000 μg mL^{-1} respectively. While CrT-13 reduced 41%, 14% and 9%, at 100, 500, and 1000 μg mL^{-1} respectively, after 24 hr. Cr(VI) at 150 and 300 μg mL^{-1} reduced by 87% and 71%, respectively, with CrT-1 and by 68% and 47% with CrT-13. Uptake and reduction of toxic Cr(VI) into Cr(III) by the bacterial strains *O. intermedium* CrT-1 and *Brevibacterium* CrT-13 showed a very high-level resistance to chromate. In addition, the chromate resistance level of these strains is very high in minimal medium relative to strains reported by other researcher (Megharaj et al., 2003).

7.1.2 Yeast

Machado et al. (2010) demonstrated a study on bioremediation using sub-product of fermentative industries, such as wine or brewing industry. The biomass can be obtained in large quantity and cheap. This study has shown that brewing flocculant yeast cells set a new approach for heavy metals bioremediation. According to Wang and Chen (2006), yeast cells of *Saccharomyces cerevisiae* is among the different types of biomass suggested for metals bioremediation. Hence, *S. cerevisiae* were used in the bioremediation, in a batch mode, of a real electroplating wastewater containing metals like Cu, Ni, and Cr. In their approach, no pretreatment of Cr(VI) to Cr(III) was required. Using heat-inactivated cells of *S. cerevisiae*, the result showed that 98% of Cr(VI) is removed after the first batch at an initial pH 2.3.

7.1.3 Protozoa

A study has been conducted by Haq et al. (1998) on protozoa and algae tannery discharge. It showed that the presence of protozoa in these industrial discharge suggest their strategies to tolerate, resist or detoxicate organic substances and metals. Therefore, protozoa are suitable to be utilized as an agent in bioremediation. Furthermore, protozoa may cooperate with other microbial during remediation. Since, protozoan can tolerate and resist heavy metals and toxic compounds, it can therefore provide an insight into detoxication mechanisms in human cells as protozoa are true eukaryotes and the results can be easily and safely extrapolated to higher eukaryotic organisms, even to human being. The results showed that *Stylonychia mytilus*, and *Tetrahymena pyriformis* is found after inoculation. The number of cell almost doubled for *Stylonychia mytilus* while *Tetrahymena pyriformis* did not show any duplication and disappear in the medium containing chromium after 15 days. *Stylonychia mytilus* showed the ability to tolerate Cr(VI) at a concentration of 1 μg mL^{-1}. The disappearance of *Tetrahymena pyriformis* with the presence of Cr may be due to cannibalism among the spesies (Haq et al., 1998).

7.1.4 Fungus

Sani et al. (1998) studied on the degradation of dye wastewater using white-rod fungus, *P. chrysosporium.* The researchers added that biodegradation becomes popular as it is economical. The decolourization of industrial discharge from dyeing industry could be due to either adsorption on fungal biomass or to biodegradation (Sani et al., 1998). In addition, previous studies have shown the degradation of recalcitrant xenobiotic compounds, including azo dyes using *P. chrysosporium*. The result has shown that more than 80 % colour reduced in most of the dyes (Red HE-8B, Malachite Green and Navy Blue HE-2R) by *P. chrysosporium* in shake culture. Malachite Green was more readily decolourized than Crystal Violet and Magenta, eventhough they have similar dye structures.

The result showed that decolorization ability increased with inoculum concentration with 5, 10, 15 and 20 % inoculum, maximum decolorizations recorded as 24, 68, 95 and 98 %, respectively, in shake culture. 20, 56, 55 and 57 % colour were removed, respectively for static culture. It proved that the *P. chrysospotium* is an agent to decolourize dye wastewater (Sani et al., 1998).

Morales-Barrera & Cristiani-Urbina (2008) conducted a study on leather factory discharge. The remediation in using fungus, the strain identified as *Trichoderma inhamatum.* The experimental results showed that this fungus is capable to transform Cr(VI) to Cr(III) where Cr(III) having lower toxicity level. The fungus could reduce Cr(VI) up to 2.43 mM. The author suggested this strain of fungal to be potential apply in bioremediation of Cr(VI) containing wastewater. The other genera is *Aspergillus* (Gouda, 2000; Acevedo-Aguilar et al., 2006), *Penicillium* (Acevedo-Aguilar et al., 2006), and *Phanerochaete* (Pal, 1997). The authors suggested that this fungus could be a better agent for bioremediation as at the highest concentration of Cr(VI) reduced by *T. inhamatum* was much higher than concentrations commonly found to be reduced by bacteria, fungi, and yeast.

As bioremediation uses living systems, especially microorganisms, in the degradation of wastes without disruption of the environment, thus, fungal systems appear to be most appropriate for the treatment of colored effluents (Ezeronye & Okerentugba, 1999; Shedbalkar & Jadhav, 2011). Another study conducted on textile industry discharge by Shedbalkar & Jadhav (2011) to reduce the colour, COD and BOD using *Penicillium ochrochloron*. This study is mainly targeting Malachite green. Malachite green and in its reduced form, leucomalachite green, remain in food chain as it may persist in edible fish tissues for a long period of time (Mitrowska & Posyniak, 2004; Shedbalkar & Jadhav, 2011). Also, Zahn & Braunbeck (1995) reported that in vitro studies proved that malachite green target the nuclei and mitochondria are major cellular in fishes and mammals (Shedbalkar & Jadhav, 2011). Malachite green was detoxified into p-benzyl- N,N-dimethylaniline and N,N-dimethyl-aniline hydrochloride by Penicillium ochrochloron. It successfully reduces the colour to 93% in czapek dox broth after 14 h with an optimum condition of pH 7 at 30°C. In addition, high BOD, COD, TDS and TSS values pose major environmental problems. These values were found lower in all of the treated samples than the control.

7.2 Biosorption

Esteves et al. (2000) used a waste biomass *Sargassum* sp. (brown macroalga) from an alginate extraction industry from Rio de Janeiro, Brazil to cleanup metals in wastewater via

biosorption. Biosorption is sorption of metals onto biological materials. It could become an alternative way to remove toxic and recover precious metals from industrial discharge. In this work, the ability of *Sargassum* sp. to remove cadmium and zinc from a real effluent was investigated as well as its suitability to be reused in several consecutive metal adsorption-desorption cycles were investigated. The results showed that it could biosorbed 100% of Cd^{2+} and 99.4% of Zn^{2+} from a 3 and 98 mg L^{-1} industrial discharge at pH 4.5, respectively, using HCl, $CaCl_2$, and NaOH as adsorbent-desorbent. On the other hand, when $CaCl_2$ was used as desorbent, the metal removal efficiency after the first cycle can achieve recovery at about 40%. The potential for metal recovery suggests that *Sargassum* sp.-based adsorption can be used as an alternative treatment method.

The biosorption may chemically occur due to the function of sulphated polysaccharides, which are absent in land plants, it enabled marine aquatic vegetation like algae to selectively adsorb trace metal ions (Chu et al., 1997; Esteves et al., 2000).

For brown algae, the carboxyl groups of alginate and sulfonate groups of polysaccharides were identified as the two important groups for binding metal (Kratochvil et al., 1997; Esteves et al., 2000). The other factors which are believed to contribute to the metal sorption capacities are electro-chemical properties of the metal ions (Esteves et al., 2000; Valdman & Leite, 2000) and the characteristic of a real wastewater.

Sargassum sp. has demonstrated its potential to be reused in metal-adsorption or recovery and it is cost effective. It showed a strong indication that such a system could be carried out commercially for the wastewater treatment as this biosystem could be fully regenerated and showed good treatment ability (Esteves et al., 2000).

Another study conducted by Rehman & Sohail Anjum (2010) used a yeast, *Candida tropicalis* to uptake the Cd from industrial discharge. *C. tropicalis* could reduce Cd^{2+} at 57%, 69%, and 80% from the medium after 48, 96, and 144 hr, respectively, and, reduction of Cd^{2+} 56% and 73% from the wastewater after 6 and 12 days, respectively. Apart from Cd, the yeast showed tolerance towards Zn^{2+} (3100 mg L^{-1}), Ni^{2+} (3,000 mg L^{-1}), Hg^{2+} (2400 mg L^{-1}), Cu^{2+} (2300 mg L^{-1}), Cr^{6+} (2000 mg L^{-1}), and Pb^{2+} (1200 mg L^{-1}).

C. tropicalis was found to be resistant to Cd up to a concentration of 2,800 mg L^{-1}. Cd-resistant yeast was also found to be resistant to other metal ions, in descending order was Zn^{2+}>Ni^{2+}> Hg^{2+}>Cu^{2+}>Cr^{6+}>Pb^{2+}. Zafar et al. (2007) reported the metal tolerance and biosorption potential of filamentous fungi having tolerance of metal in descending order of Cu>Cr>Cd>Co>Ni. Many Candida *spp.* have the capacity to absorb or accumulate metals. For instance, *C. albicans* and *C. tropicalis* are highly resistant to water-soluble ions Hg^{2+}, Pb^{2+}, Cd^{2+}, arsenate (AsO_4^{3-}), and selenite (SeO_3^{2-}) (Rehman & Sohail Anjum, 2010).

7.3 Green chemistry

A good management is important for a sustainable environment. Gar´cıa-Serna et al. (2007) has mentioned on the concept of sustainability which link between industries with philosophies and disciplines i.e. The Natural Step, Biomimicry, Cradle to Cradle, Getting to Zero Waste, Resilience Engineering, Inherently Safer Design, Ecological Design, Green Chemistry and Self-Assembly. Green chemistry is one of the possible sustainable environmental managements. Green chemistry is defined as the design of chemical products

and processes that could reduce or eliminate the application and generation of hazardous substances (Kirchhoff, 2005; Tiwari et al., 2005, 2007, 2008; Seung-Mok & Tiwari, 2009; Rai, 2011).

There are three important areas in green chemistry:

i. Application of alternative synthetic pathways
ii. Application of alternative reaction conditions
iii. Design for safer chemicals compound that are less toxic or inherently safer with regards to accident potential (Gar´cıa-Serna et al., 2007; Rai, 2011).

For example, instead of using commercial-activated carbon, research based on inexpensive materials, such as chitosan, zeolites and other adsorbents, which have high adsorption capacity and economical have been conducted (Babel & Kurniawan, 2003). Yavuz et al. (2008) reported the adsorption of Cu^{2+} and Cr^{3+} onto pumice (Pmc) and polyacrylonitrile/Pmc composite (Rai, 2011). Similarly, Pehlivan & Arslan (2007) reported the adsorption of lignite (brown young coals) to remove copper, lead and nickel from aqueous solutions at the low concentrations. The implementation of green chemistry is essential in order to promote sustainability (Kirchhoff, 2005; Rai, 2011). Kirchhoff (2005) added that the collaboration between academia, industry and government are essential to expand and enhance the sustainability through the adoption of green chemistry (Rai, 2011).

7.4 Phytoremediation

A critical and complete review by Rai (2011) suggested another approaches to clean up the metals contaminant from industrial discharge. Green chemical processes could also reduce the impact to environment. However, they still pose threat in a long run. Therefore, the phytoremediation could be a better alternative where it could update the metals from contaminated areas a bio-cleanup technology.

Phytoremediation can be prepared from the naturally abundant plants which are very economical (Kratochvil & Volesky 1998; Rai, 2011). Wetland plants are important tools for heavy metals removal from aquatic ecosystems (Rai, 2011). Also, the wetland sediment provides metal reduction, chemically. According to Rai (2011), wetlands are proved to be effective in metal pollution abatement. *Typha, Phragmites, Eichhornia, Azolla, Lemna* and other aquatic macrophytes are important wetland plants for heavy metals contamination clean-up. The benefit of wetland plants is that it can absorb pollutants in their tissue and provide a surface and an environment for microorganisms to grow (Vymazal, 2002; Scholz, 2006; Vymazal et al., 2007; Rai, 2008; Rai, 2009b). In other words, wetland plants can stimulate aerobic decomposition of organic matter and the growth of nitrifying bacteria (Brix, 1997). However, in a wetland system, microorganism has a better capability in organic matters degradation compare to wetland plant. (Stottmeister et al., 2003; Rai, 2011). As the organic matter binds with metals directly, they provide a carbon and energy source for microbial metabolism. Microorganisms has the ability to grow in the presence of metals and metal uptake, hence, it can potentially bioremediate contaminant (Shakoori et al., 2004; Rehman & Sohail Anjum, 2010).

Water hyacinth (*Eichhornia crassipes*) is commonly used in constructed wetlands because of its rapid growth rate and its ability to uptake a lot of nutrients and contaminants (Rai 2008,

2009b). Due to its exotic invasive nature and multiplication, water hyacinth might also cause problems to constructed wetlands. Therefore, Rai (2011) recommended the use of artificial and high-rate algal ponds (HRAP) on industrial discharge before releasing the discharge to reservoir.

Hyperaccumulator, a term for plant species that could accumulate metals for 50- to 500-times concentration than normal plant, without any severe symptom of toxicity (Roosens et al., 2003; Kra¨mer, 2005; Dwivedi et al., 2008; Tiwari et al., 2008; Dwivedi et al., 2011). A hyperaccumulator has minimum threshold tissue concentration achieved for specific metal such as 0.001% for Hg whilst 0.1% for Cu, Pb, Ni, Al, or Se of the dry weight of plant (Pickering et al., 2003; Grata˜o et al., 2005; Dwivedi et al., 2011). However, slow growth and restricted distribution are the disadvantage of using hyperaccumulators. Dwivedi et al. (2011) conducted a study using *P. tuberosa* and *P. oleracea*, to accumulate metals such as Cu, Ni, Mo, Se, Hg, Pb, Al. The result showed that both of these two family member of Portulacaceae were able to hyperaccumulate Cu, Ni, Hg, and Pb. Selective hyperaccumulation of Se by *P. oleracea* and Al by *P. tuberosa* was were also reported in their study. Furthermore, these plants also showed higher accumulation of Mo than plants which could accumulate only in the range of 1–2 μg g^{-1} dw (Hale et al., 2001; Dwivedi et al., 2011) and they could accumulate significant amount of Ni (Rooney et al., 2007; Dwivedi et al., 2011). These plants have shown to adapt and to grow naturally by uptaking, accumulating and detoxifying high load of metals and metalloids (Mishra et al., 2006; Dwivedi et al., 2008, 2010). In the study, Dwivedi et al. (2011) has also identified the parts of the plant which is able to accumulate better. The result showed that roots and shoots have the highest accumulation of Ni and Pb, respectively, whilst, Ni and Mo showed higher accumulation of metal in leaves than in stem. Adversely, other metals showed higher accumulation in stem than in leaves. They concluded that *P. oleracea* as a better accumulator species for various metals than *P. tuberose*.

Another study performed by Kisku et al. (2000) at Kalipur, Bangladesh, receiving industrial discharge of steel plant, thermal power plant, chemical plant, coke oven, pharmaceutical industry, and others. Bioaccumulation from soil to plant varies by element and plant. The result showed that the highest accumulation of Fe, Mn, Zn, Cu, Pb, Ni, Cr, and Cd were found in *Spinacea oleracea, Raphanus sativus, Amaranths viridis and Lycopersicon esculentum, Coriandrum sativum, Solanum melongena, Spinacea oleracea, Lycopersicon esculentum*, and *Coriandrum sativum*, respectively. Also, the results showed that *Spinacea oleracea, Lycopersicon esculentum and Coriandrum sativum* having more affinity to Fe and Ni, Zn and Cr and Cu and Cd, respectively. Furthermore, the growth of weeds at study site was similar to the growth of weeds at uncontaminated site, namely, Madhabpur. Weed grows better with positive growth for vegetative, root length, and number of rootless, number and colour of leaves and other but not crops and vegetables. This indicates that plant species has different capability in contaminant absorption, accumulation, and tolerance.

Rai & Tripathi (2009) studied on aquatic plant for effective phytoremediation at G.B. Pant Sagar located in Singrauli Industrial Region, India. Phytoremediation of *A. pinnata*, a water fern and *V. spiralis*, a submerged macrophyte, are studied. Result showed that the percentage removal of Hg was higher for *A. pinnata* (80–94%) than *V. spiralis* (70–84%). This indicated that free floating plant has higher capability than submerged macrophyte to remove Hg from wastewater. However, the authors suggested the possibilities of *V. spiralis*

are higher to remove Hg remove from sediments. There is other research to study the removal of Hg from aquatic plants for phytoremediation purposes. Bennicelli et al. (2004) found that *Azolla caroliniana*, a small water fern could remove up to 93% of Hg contamination from water in 12 days. Kamal et al. (2004) also studied on aquatic plants parrot feather, creeping primrose and water mint and found to be able to remove 99.8% Hg from contaminated water after 21 days. However, a noticeable decrease showed in chlorophyll, protein, RNA, DNA and nutrients (NO^{3-} and PO_4^{3-}) in *A. pinnata* more than *V. spiralis* which is due to the Hg toxicity. The decreased in chlorophyll may be due to the increased of Hg concentration and it is also observed to be having same result for several aquatic plant. The decline is caused by metal induced inhibition of chlorophyll biosynthesis. Furthermore, mercury inhibited biosynthesis of chlorophyll through targeting –SH groups of d aminolaevulinic acid dehydratase (ALAD) in seedlings of mung bean and bajra. At higher Hg concentrations, it can degrade pigments and result in great reduction (Rai & Tripathi, 2009).

There are a few studies suggested to use transgenic plants such as *Arabidopsis thaliana* Thal [Brassicaceae], and tobacco, *Nicotiana tabacum* L. [Solanaceae] to remove Hg from contaminated sites (Bennicelli et al., 2004; Rai & Tripathi, 2009). These plants have a modified bacterial mercuric reductase gene, merA, hence, it may convert Hg(II) to Hg(0) which is less in toxicity, or the bacterial organomercurial lyase gene, merB that convert methylmercury to sulfhydrylbound Hg(II) when taken up by plant roots (Rai & Tripathi, 2009).

Lesage et al. (2008) used *Myriophyllum spicatum* L. (Eurasian water milfoil, Haloragaceae) as an agent for bioremediation. *M. spicatum* L. is a rooted, perennial plant which reproduces primarily by vegetative fragmentation. Usually, deep root plant can survive at highly polluted condition and accumulated better while shallow roots are easily injured. The plant is able to tolerant wide water quality both in fresh and brackish water. In this study, the author studied the potential of *M. spicatum* L. in Co, Ni, Cu and Zn removal from industrial discharge. As comparison, the removal of Co and Ni by *M. spicatum* L was slower than of Cu and Zn. Co and Ni removal at 0.2 mg L^{-1} need two weeks residence time, while Cu and Zn achieve 0.05 and 0.2 mg L^{-1} removal only at 48 hr. The removal of about one third of Co and Ni removal involved precipitation with CO_3^{2-} and OH^- with the presence of the plant. As a submerged plant, *M. spicatum* L is having the ability to cleanup metals directly from the water. Hence, *M. spicatum* L is suggested as useful species in reducing metal concentrations from wastewaters. Furthermore, the toxic wastewater was not influence the growth of *M. spicatum* L. The use of aquatic plants for the removal of heavy metals from wastewater has been investigated by many authors. Other aquatic plants have been investigated in metal removal with good results are *Eichhornia crassipes* (Zhu et al., 1999), *Pistia stratiotes* and *Salvinia herzogii* (Maine et al., 2001, 2004).

However, there is a limitation in promting the use of *M. spicatum* L as full scale in a constructed wetland to cleanup industrial discharge. The reasons are explained by Kivaisi (2001) when countered the full-scale use of *E. crassipes* in developed countries, which also fit to the application of *M. spicatum* L:

i. The poor performance in temperate region like in northern-hemisphere winters
ii. Land acquisition
iii. The intensive harvesting schemes
iv. The construction and operation of systems for bioenergy recuperation.

7.5 Green monitoring

Phytotoxicity as part of green monitoring is a useful way for environmental risk assessment. For example, Seeds of *L. sativum* are very sensitive during seed germination and the early root growth period to change in environment (Ferrara et al., 2003; Montvydienė & Marčiulionienė, 2004; Montvydiene et al., 2008). Hence, it is suitable to use as screening tests and acute tests (seed germination and root growth). The other advantages using *L. sativum* is due to its simplicity, cheapness, and short duration. The turions of *S. polyrrhiza* at the first stage leafy stem development are very sensitive to change of surrounding, and the changes in meristematic tissue are reflected to the propagation of plant (Marčiulionienė et al., 2002; Montvydiene et al., 2008). *S. polyrrhiza* is suitable to apply as chronic tests (plant growth, various physiological parameters, and morphological alterations). *L. sativum* and *S. polyrrhiza* showed different sensitivity to tested samples of industrial discharge to water and sediments. However, it is hard to differentiate which is more sensitive as the duration of test, the time of plant contact with industrial discharge is different. Lastly, *Tradescantia* could determine genotoxicity of sample while other tests do not indicate the toxic effects. The investigations clearly indicated *L. sativum* and *Tradescantia* successfully used in the toxicity assessment of liquid or solid environmental component contaminated in different degree. *S. polyrrhiza* can be used in the examining various liquids (Montvydiene et al., 2008).

Shedbalkar et al. (2008) studied on phytotoxicity to determine the malachite green toxicity after treatment as part of green monitoring. The result showed that the treated wastewater was non-toxic to the plants of *Triticum aestivum* and *Ervum lens* Linn, and the amount of total chlorophyll was higher in plants with treated effluent when compared to control effluent. Phytotoxicity analysis showed high germination rate and significant growth in the shoots and roots for both plants grown after decolorization. Hence, phytotoxicity studies confirmed biodegradation of the dye by fungal culture, which resulted in detoxification. It is reported that the germination rate for *Triticum aestivum* and *Ervum lens* Linns was at 50% and 70%, respectively, using treated with effluent. Surprisingly, higher total chlorophyll contents of the leaves from *Triticum aestivum* and *Ervum lens* Linn plants were found in treated wastewater at pH 7. Furthermore, the result showed that there is low concentration of chlorophyll in leaves of plants grown in untreated wastewater as to compare with the control grown in water.

Radic´ et al. (2010) used Duckweed (*Lemna minor* L.) to monitor heavy metals and other aquatic pollutants over a 3-month period from the stream near the industrial estate of Savski Marof, Croatia. Duckweed is used due to its selective potential to accumulate certain chemicals. In previous study of Horvat et al. (2007) *L. minor* exposed to electroplating wastewater accumulated more Fe and Zn, and then followed by Pb and Ni. However, the authors also found that toxicity of metals in Lemna tissues damage in decreasing order: Zn>Ni>Fe>Cu>Cr>Pb (Radic´ et al., 2010). In this study, significant increase of duckweed growth which determined by Dry weight/ Fresh Weight (DW/FW) and also increased of inhibition of Relative Growth Rate (RGR) observed and suggested to be metals bioaccumulation. However, it has been shown that accumulation of heavy metals affect the plant water status which will results in osmotic stress and growth reduction (Perfus-Barbeoch et al., 2002; Radic´ et al., 2010). In the study, the increase of DW/FW after the

treatment with industrial wastewater could be explained by the change of the plant's water status and accumulation of compatible solutes. In addition, according to Matysik et al. (2002) plants are shown to accumulate organic solutes such as carbohydrates and quaternary ammonium compounds.

In plants, pigment content (chlorophyll and carotenoids) and enzyme activities (like peroxidase) are commonly used as biomarker for toxicity tests (Mohan & Hosetti 1999; Radic´ et al., 2010). The result showed decreased in chlorophyll and carotenoids compared to the control sample plant. The carotenoids content affected lesser to chlorophylls. The decline in total chlorophyll and carotenoids contents and growth inhibition may be associated with metal toxicity (Radic´ et al., 2010). The growth reduction reported the study may be due to the decrease of chlorophyll content produced by heavy metals present in the industrial discharge. And Ku¨pper et al. (1996) proposed that photosynthesis and growth reduction caused by Zn, Ni, Cu and Pb. Lastly, from the results, the authors suggested that phyto- and genotoxicity tests with *L. minor* should be applied to biomonitoring of municipal, agricultural and industrial discharge due to its simplicity, sensitivity and economical (Radic´ et al., 2010).

8. Conclusion

This chapter gives an overview of the source and types of industrial discharge, the effects of industrial discharge to the environment and human health and lastly the corrective action that could be taken to minimize the negative impact of the discharge. Many ways have been proposed to protect the environment from contamination including enforcement of stringent rules and regulations. However, the discharge from some industries is still exceeding the permissible limits. Before designing good corrective actions, the knowledge of effects to environment and human health, and, the interaction between the contaminants and biotic and abiotic compartment are crucial to explore. In short, corrective actions for industries contamination clean-up are important to implement. A number of remedial actions presented in the previous sections, there is still factors which hinder the development of large scale of cleanup technology.

i. Characteristic of organic, inorganic and synthetic chemical elements is well documented in literature. Research on the synthesis of new green chemical elements for industry application is important to replace the original materials in order to protect the sustainable environment.
ii. Although most of the bioremediation studies for surface water and soil contamination were proven to be effective in removing or reducing contaminant, such studies were done at lab scale. Thus, there is a need to investigate on large scale to better understand the suitable condition for optimization remediation process.
iii. The groundwater is a major important water resource for some countries for irrigation, drinking and bathing. However, waste dump brought adverse impact to the groundwater quality. Hence, an effective corrective action is necessary to improve the water quality, especially the metal contamination, which may lead to serious illness and death. Study on the in situ bioremediation by the indigenous bacteria could be carried in depth for cleanup process.

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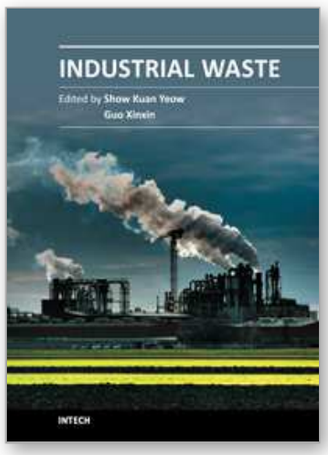
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This book is intended to fulfil the need for state-of-the-art development on the industrial wastes from different types of industries. Most of the chapters are based upon the ongoing research, how the different types of wastes are most efficiently treated and minimized, technologies of wastes control and abatement, and how they are released to the environment and their associated impact. A few chapters provide updated review summarizing the status and prospects of industrial waste problems from different perspectives. The book is comprehensive and not limited to a partial discussion of industrial waste, so the readers are acquainted with the latest information and development in the area, where different aspects are considered. The user can find both introductory material and more specific material based on interests and problems. For additional questions or comments, the users are encouraged to contact the authors.

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