Removal of Heavy Metals from Refinery Effluents using Water Hyacinth

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INTRODUCTION

It is already an established public knowledge and concern that soils and waters in many parts of the world are polluted by toxic heavy metals like cadmium, lead, chromium, mercury and others. In most developing countries, even collection facilities for domestic sewage do not exist, let alone adequate treatment facilities. Both the domestic and industrial wastewater effluents are often disposed directly into the surface waters as described by Gopal [1]. These heavy metals are of concern not only due to their existence and important role, but also due to their accretion in the human food chain which can have an adverse effect on living things as outlined by Dumont *et al*.[2] and Bailey *et al* [3]. It is accepted that there is an urgent need to develop technologies to remove or detoxify these materials. The use of plants can offer an effective, cheap and sustainable method to achieve this objective.

Phytoremediation or 'green clean' as defined by Rai and Pal [4] and Vassilev *et al* [5] is a general strategy of using plants to remove, to contain, to inactivate or to degrade toxic contaminants from the environment. The approach may be classified under three different methods. The first method is phytoextraction which makes use of the ability of certain plants to take up contaminants and accumulate them in their tissues. The plants could then be harvested and removed from the site. The second method is phytovolatisation which makes use of the ability of the plant to convert the contaminants into volatile forms which then escape into the atmosphere. The last method is called phytodetoxification which makes use of the ability of the plant to change the chemical species to a less or non- toxic form. Although there is growing public interest and commercial attraction and success in phytoremediation as a cost-effective and technically viable method of removal of metal ions from waste-water and contaminated soils, more basic research is still needed to better understand the complex interactions between the metal ions, plant roots and micro-organisms in the rhizosphere. Success in the use of genetic modification and selective breeding and other methods to enhance phytoremediation has been demonstrated, and a method to treat selenium was described by Terry and LeDuc [6] and Macek *et al* [7]. Similarly the method was also successfully applied by Eapen and D'Souza [8], Kramer [9], Lang *et al* [10], LeDuc and Terry [11], Meagher and Heaton [12], and Suresh and Ravishankar [13] for the removal and treatment of other metals.

Marshes have been proposed as sites for phytoremediation of metals. Most of the marsh plant species have generally similar metal uptake characteristics. Some species may alter the speciation of metals and some may also suffer toxic effects as a result of over-accumulation as described by Weis and Weis [14]. The metal accumulation in wetland plants differed among species, populations and tissues and the metals accumulated were distributed mainly in root tissues as mentioned by Deng *et al* [15]. Genetic modification of wetland grasses have also been successfully demonstrated by Czako *et al* in an attempt to reduce the possibility of over-accumulation [16]. Other factors affecting metal uptake are soil and climatic conditions such as pH, temperature and plant species as indicated by Anton and Mathe-Gaspar [17]. Suitability of weeds species as candidates for potential agents for phytoremediation have also been studied. Three weed species were identified by Wei *et al* [18] from among forty-five species studied as showing some promise for phytoremediation.

As mentioned earlier the wastewater effluents from petroleum refining and petrochemical plants contain a diverse range of pollutants including heavy metals. They also contain oil and grease, phenols, sulfides, dissolved solids, suspended solids and BOD-bearing materials. Generally, the maximum permissible concentration for metal ions is about 1 ppm each. The total limit should not be more than 5 ppm as indicated by Beychock [19]. Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic products in the receiving water bodies with potentially serious consequences on the ecosystem. It is understood that phytoremediation of effluents from the refineries in Port Dickson has for many years been successfully carried out through the action of naturally growing marsh species found around the refinery off-sites. The purposeful cultivation of water hyacinth to complement this method was adopted some years ago. It is understood that this method has brought about promising and encouraging results at the beginning, but it has been found that of late there appears to be no significant improvement achieved through the presence of the water hyacinth. This may perhaps be due to toxic accumulation.

HEAVY METALS

Heavy Metals in Refinery Effluents

Heavy metals in refinery effluents mainly originate from the feedstock. Others are from corrosion products of the equipment and pipes, from process chemical additives and from materials like catalysts and others used in processes downstream of the primary distillation. Some of the more common of these are nickel, vanadium, copper, cadmium, lead, chromium, zinc and selenium. Of late mercury has also started to appear as an impurity in our natural gas and crude streams.

OSHA Requirements

The Environmental Quality Act 1974 and its Regulations on Industrial Waste and

Table 1: Schedule B Limits

Metals	Concentration	(mg/litre)
	Standard A	*Standard B*
Mercury	0.005	0.05
Cadmium	0.01	0.02
Vanadium	0.01	0.03
Hexavalent Chromium	0.05	0.05
Arsenic	0.05	0.10
Lead	0.10	0.5
Trivalent Chromium	0.20	1.0
Copper	0.20	1.0
Manganese	0.20	1.0
Nickel	0.20	1.0
Tin	0.20	1.0
Selenium	0.01	0.02
Zinc	1.0	1.0
Boron	1.0	4.0
Iron	1.0	5.0

Effluents 1979 stipulate that the limits for Standard A and Standard B for some of the stated heavy metals and some other metals are as given in Table 1. Schedule A limits are for effluent disposal points discharging into environmentally sensitive catchment areas and water courses, for example, where there is an intake station for water supply domestic use downstream of these outfall points.

Health Effects

Some species of nickel can cause skin rashes from contact and it may also cause asthma and sinus problems as well as pose as a risk to respiratory track cancer if inhaled. Although nickel is an essential micronutrient for plants it can, however, become toxic at high concentrations. Vanadium may cause dehydration, weight loss and depressed growth. It may also cause breathing difficulties, and irregular cardiac and renal functions. Copper is another essential micronutrient for both plants and animals. However, at high concentrations in animals it can cause digestive system problems and can cause damage to the red blood cells and can affect the kidney, liver and pancreatic functions. The presence of cadmium in the environment is widespread. It is highly poisonous through the damage done to the membranes of all kinds of cells. The cells which are then exposed become susceptible to attacks by other poisonous materials. Lead poisoning has been known for many years. It is more frequent among children than among adults. Millions of children have suffered the ill-effects of lead. It can cause reduced IQ, learning disabilities, behaviourial problems, stunted growth, impaired hearing abilities, and kidney damage. At high intake it can make children mentally retarded, set into a coma and can even cause death. In adults it can cause high blood pressure, infertility and nervous disorders. Chromium (VI) can cause nasal problems and ulcers as well as kidney and liver damage and Chromium (V) is a known carcinogen. Zinc is an essential nutrient but too much of it can cause vomiting, fever, coughing and diarrhea. It also damages the red blood cells. In the gas processing plants and petroleum refineries, mercury can poison catalysts and damage equipment Mercury can cause reproductive failure, intestine, stomach and kidney damage, and DNA alteration in humans. It also attacks the central nervous system. The threat of selenium is mainly on livestock like sheep and cattle, but it also affects horses, goats and pigs. Selenium is an essential nutrient, but high intake, could cause blind staggers which is characterised by impaired vision, depressed appetite and wandering in circles. Further dosage may cause paralysis and even death from respiratory failure. At lower dosage and prolonged duration of intake it can cause alkali disease which is characterised by emanciation, loss of hair, skin dispigmentation, loss of vitality and deformation and shedding of hooves.

Disposal

Most of the heavy metals are separated from the main streams of product cuts during the various refining processes and eventually captured as sludge in the waste treatment process. The sludge can either be disposed off through sludge farming in the open fields where the heavy metals may undergo a phytoremediation process; or the sludge can undergo further treatment by Kualiti Alam as scheduled waste. The dissolved form may still be present in the effluent stream and this could go through a further process of chemical precipitation and filtration before disposal. There are various technologies for separating heavy metals from effluents generated by different industries. The physico-chemical treatment which is the conventional technology employed to treat heavy metals waste includes chemical precipitation, ion exchange, evaporation and membrane technology as described by Volesky [20]. Chemical precipitation is most commonly employed for most metals. Common precipitants include hydroxides, carbonates- and sulphides-. Metals are precipitated as the hydroxide through the addition of lime or caustic to a pH of minimum solubility. However, several of these compounds are amphoteric and exhibit a point of minimum solubility. Metals can also be precipitated as the sulfide or in some cases as the carbonate as indicated by Eckenfelder [21].

Metals can be removed by adsorption on activated carbon, aluminum oxides, silica, clays, and synthetic material such as zeolites and resins. In the case of adsorption, higher pH favours the adsorption of cations while a lower pH favours the adsorption of anions. Complexing agents will interfere with cationic species. There will be competition from major background ions such as calcium or sodium. For chromium waste treatment, hexavalent chromium must first be reduce to the trivalent state and then precipitated with lime. This is referred to as the process of reduction and precipitation

The heavy metal ions may also go through a process of phytoremediation with or without precipitation and filtration associated with the treatment process.

THEORY

Phytoremediation

A variety of plant species is found growing freely in natural marshes and in man-made wetlands. Some of these species are capable of uptaking heavy metals through the root system from both water as well as the soil. As mentioned earlier several research studies have demonstrated that the use of natural marsh species has been successfully practised widely for several years without facing any major operational problems. Some weed species are also known to be able to take up heavy metals from both water and the soil. The cultivation of these selected weed species could be done in association with sludge farming.

Natural Water Hyacinth

Water hyacinth (Eichhornia crassipes) is an aquatic plant which can flourish and reproduce floating freely on the surface of water or it can also be anchored in mud. It can proliferate extremely quickly causing infestation over very large areas of water. It can reduce the amount of light and oxygen in the water, it can change the water chemistry of the ecosystem, it can affect the biodiversity of the surrounding by suffocating other species from flourishing, and it can also increase water loss due to excessive evapotranspiration. It can cause transportation problems and create difficulties and damage to equipment for fishing activities. It can cause problems of clogging at water intake stations for irrigation, water supply and industrial cooling. It can further cause flooding problems by blocking or restricting river and canal flows. It can also pose as a health hazard through the harbouring a variety of disease vectors. All in all it has been considered as a menace to the ecosystem and millions of dollars have been spent to exterminate or control its prolific growth and spreading. There are three main mechanisms of control; the first being the use of chemical herbicides like 2,4-D amine and glyphosate which are systemic, and paraquat which is not systemic and only destroys the tissues above ground and leaves the root system fairly intact. This chemical method may be associated with long-term negative effects due to the chemicals as well as their breakdown products. The second method is the use of physical control which is, however, labour intensive and expensive; and the last method is the use of biological control by engaging host specific natural enemies which is found to be the most suitable approach for the purpose of control.

Use of water hyacinth for water purification has been employed successfully. Several researchers have reported success in its use as an agent to uptake metal ions. They have shown early promise but the method has its shortcomings. Population control is important because of the stated fact that it can easily flourish and spread very fast into lush green vegetation and can become troublesome to maintain and to prevent it from suffocating the ecosystem through the reduction of light and dissolved oxygen. Biological, physical as well as chemical control may have to be employed to maintain an optimum population. Just like in other cases of phytoremediation, water hyacinth is also susceptible to toxic accumulation. Once a population has become ineffective due to toxic accumulation it has to be harvested and disposed off and a new batch planted to replace it. This process can be very tedious and expensive. It can also be hazardous due the possible presence of poisonous water reptiles like snakes and even crocodiles and alligators.

Removal Process

Most common heavy metals in water are in the form of positive ions. One possible basis of a way to remove these ions is to place a negatively charged material into the water which would attract the positively charged ions as shown in Fig 1. The roots of many plants, including water hyacinth, have a negative charge. This negative charge acts as a magnet to the positively charged ions. Even the dried and dead roots still have the negative charge, and this would be strong enough to attract the positive ions of heavy metals. This is the reason why the water hyacinth can and do absorb significant amount of nutrients [22].

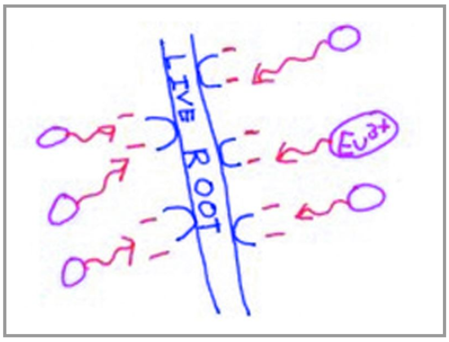

Figure 1: Positively charged metal ions and negatively charged root system

DISCUSSION AND RECOMMENDATION

Selected Marsh Species

Selected species from natural marshes as well as artificially developed wetlands could be genetically engineered to be capable of uptaking more types of heavy metal ions and up to levels several times their natural capabilities before toxic accumulation sets in.

Water Hyacinth

There is a general need for further research into the utilisation of water hyacinth as a means of removing heavy metal ions from water and soil. For example, there is a need to determine the optimum population of the species per surface area of the body of water in order to strike the right balance between the possible amount of uptake of heavy metal ions and the tendency to suffocate the ecosystem through the depletion and reduction of light and dissolved oxygen. Similarly there is a need for better understanding the process of enhancement of the capability to uptake heavy metal ions before the on-set of toxic accumulation. This could be done through genetic engineering and selective breeding which means therefore that further research should also be encouraged and supported financially. Other related areas of interest are studies on the utilisation and commercialisation of the enormous amount of biomass produced by converting it into products like pulp, fibre-boards, fertilisers, animal feed and others.

CONCLUSION

Several researchers have demonstrated success in the use of natural water hyacinth in the phytoremediation process and limited success has also been indicated locally. More genetic engineering research work needs to be done on this plant species to make it as a cheap and effective means of removing and detoxifying heavy metals from refinery and other effluents. Research on the utilisation of the biomass would also be useful. ■

REFERENCES

[1] Gopal, B. 'Water Hyacinth, Aquatic Plant Studies Series', ELSEVIER, 1987.

[2] Dumont, N., Favrereguillon, A. and Dunjic, B. 'Extraction of Cesium from an Alkaline Leaching Solution of Spent Catalyst using an Ion Exchange Column.' Separ. Sci. Technol., Vol.31, pp 1001-1010, 1996.

[3] Bailey, S.E., Olin, T.J, Bricka, R.M. and Adrian, D.D. 'A Review of Potentially Low Cost Sorbent for Heavy Metals.' Water research, Vol.33, No.11, pp 2469-2479, 1999.

[4] Rai, U.N. and Pal, A. 'Toxic metals and phytoremediation' EnviroNews, Int Soc of Environ Botanists, Vol.5(4), Oct 99.

[5] Vassilev, A., Schwitzguebel, J.P., Thewys, T., Van der Lelie, D. and Vangronsveld, J. 'The use of plants for remediation of metal-contaminated soils' Scientific World Journal, Vol 4, pp 9-34, Jan 04.

[6] Terry, N. and DeLuc, D. 'Phytoremediation of Selenium and other toxic trace elements' ICPEP-3 (2005) Souvenir, Int Soc of Environ Botanists.

[7] Macek, T., Francova, K., Kochankova, L., Lovecka, P., Ryslava, E., Rezek, J., Sura, M., Triska, J., Demnerova, K. and Mackova, M. 'Phytoremediation: biological cleaning of a polluted environment' Rev Environ Health, Vol 19(1), pp 63-82, Jan-Mar 04.

[8] Eapen, S. and D'Souza, S.F. 'Prospects of genetic engineering of plants for phytoremediation of toxic metals' Biotechnology Advances, Vol 23(2), pp 97-114, Mar 05.

[9] Kramer, U. 'Phytoremediation: novel approaches to cleaning up polluted soils' Current Opinion on Biotechnology, Vol 16(2), pp 133-141, Apr 05.

[10] Lang, M.L., Zhang, Y.X. and Chai, T.Y. 'Advances in the research of genetic engineering of heavy metal resistance and accumulation in plants' Sheng Wu Gong Cheng Xue Bao, Vol 20(2), pp 157-164, Mar 04.

[11] LeDuc, D.L. and Terry, N. 'Phytoremediation of toxic trace elements in soil and water' J Ind Microbio and Biotechnol, Vol 32(11-12), pp 514-520, Dec 05.

[12] Meagher, R.B. and Heaton, A.C. 'Strategies for the engineered phytoremediation of toxic element pollution: mercury and arsenic' J Ind Microbio and Biotechnol, Vol 32(11-12), pp 502-513, Dec 05.

[13] Suresh, B. and Ravishankar, G.A. 'Phytoremediation – a novel and promising approach for environmental clean up' Crit Rev Biotechnol, Vol 24(2-3), pp 97-124, 2004.

[14] Weis, J.S. and Weis, P. 'Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration' Environ Int, Vol 30(5), pp 685-700, Jul 04.

[15] Deng, H., Ye, Z.H. and Wong, M.H. 'Accumulation of lead, zinc, copper and cadmium by twelve wetland plant species thriving in metal-contaminated sites in China' Environ Pollution, Vol 132(1), pp 29-40, Nov 04.

[16] Czako, M., Feng, X., He, Y., Liang, D. and Marton, L. 'Genetic modification of wetland grasses for phytoremediation' Z Naturforsch, Vol 60(3-4), pp 285-291, Mar-Apr 05.

[17] Anton, A. and Mathe-Gaspar, G. 'Factors affecting heavy metal uptake in plant selection for phytoremediation' Z Naturforsch, Vol 60(3-4), pp 244-246, Mar-Apr 05.

[18] Wei, S.H., Zhou, O.X., Wang, X., Cao, W., Ren, L.P. and Song, Y.F. 'Potential of weed species applied to remediation of soils contaminated with heavy metals' J Environ Sci, Vol 16(5), pp 868-873, 2004.

[19] Beychok, M.R. 'Aqueous waste: From petroleum and petrochemical Plants' John Wiley & Sons Ltd, 1967.

[20] Volesky, B. 'Biosorbent for metal recovery.' Trends Biotechnol. Vol 5, pp 96, 1987.

[21] Eckenfelder Jr. W.W. 'Industrial water pollution control. 3rd Ed. McGraw Hill, 2000.

[22] Beddri, A.M. 'Removal of Heavy Metals in Refinery Effluents using Water Hyacinth.'Graduate Thesis, Civil Eng Dept, University of Malaya, 2006.