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Review on Heavy Metal Pollution in the Southern Caspian Sea Basin and Phytoremediation as a Treatment Method

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Abstract: *This review mainly focuses on heavy metal pollution of the Caspian Sea in the southern drainage basin located in Iran, and it aims at proposing a remediation method for such a situation. About 150 papers were identified and reviewed for gathering information on this matter. Seven main rivers of the basin were focused on and the related field studies were reviewed for heavy metals concentration and hazardous risks. Reportedly, Nickel and Lead were the most high-risk metals. Although there was not a common agreement on the type of the plant for this method, the overall phytoremediation was reported to be an effective method for the removal of contamination. There was a lack of attention to the separation timing of plants after remediation as well as real situation experiments. In addition to these two matters, removal techniques of contaminated plants from the sites can also be studied in future research.*

Key Words: *Heavy metal pollution, Caspian Sea basin, Iran Caspian Sea basin, Water remediation, Phytoremediation.*

1. INTRODUCTION:

The water crisis is one of the most substantial issues all around the world which is not only about the minimum amount of freshwater available, as world water vision reports that there is a water crisis today, but also a crisis of managing water so severely that billions of people and the environment suffer seriously. Poor management skills and strategies in every field of water uses (domestic, agricultural, and industrial) have resulted in a clean water shortage as well as polluting significant water bodies. As the population and industries grow, the equivalence between water demand and water supplies grows farther and the crisis becomes more and more intense.

In recent years the use of plants as raw materials for keeping industries has led to deforestation. According to the UN report on deforestation, the net amount of forests in the global rate in 1995 was 4128 million hectares which this amount has dropped to 3999 million hectares within the year 2015 (TehranTimes, 2018). These industries also use water from different sources of the ocean, river, pond, etc. and bare lands to advance the production and in return the pollution and wastes -whether solid or water- come back to the environment and pollute the surrounding without any further plan to retreat and retrieve the natural sources.

These contaminants inside water bodies can cause several diseases and threaten the aquatic life when they are available inside the water as suspended solid, and enter the tissues of aquatic creatures rather by food chain or skin contacts. Heavy metals existing in the waters will end up in human bodies through the food chain and will cause health problems such as cancer, kidney problems, skin problems, and many others. The amount of contaminants inside waters is closely related to harms that are done to the marine animals, the amount of chemical absorption, and their effects on different organisms. In other words, this amount of contaminants is related to the term bioaccumulation, biomagnification, and bioavailability of contaminants inside the water.

Figure 1 Geographical position of the Caspian Sea basin

As for the Caspian Sea, the biggest landlocked basin (lake) in the whole wide world beneficial for five border countries surrounding it such as Iran, Russia, Turkmenistan, Azerbaijan, and Kazakhstan. The crisis is tangible for us as one of the coastal residents in the southern Caspian Sea region. The main focus of the paper is on the heavy metal sources of pollution inside the drainage basins of the southern Caspian Sea.

The Caspian Sea is one of the most well-known and the largest lakes around the world. It is a landlocked basin with no outflows located between Asia and Europe. The Caspian Sea is bordered by Russia in north and east, Iran from the south, Azerbaijan from the west, Turkmenistan from the southeast, and Kazakhstan from the northeast. It is mostly famous for its various fish, caviar, and oil production and it also provides a habitat for so many people living in its coastal cities (Qobeyshavi, 1382).

The southern region of the Caspian Sea ends in three Northern Provinces of Iran, Golestan, Mazandaran, and Gilan. Because of this area's geographical conditions and the climate situation, its population density is rather high and respectively various industries and industrial parks are located around the sea borderline. These industries use and produce chemical materials in different forms and eventually considerable fraction of these chemicals enter the seawater through the untreated wastewater, effluents of industries, and also municipal and urban sources. Unfortunately, the treatment and filtration methods and plans are inefficient for the industries and disposal systems within the area.

The Caspian Sea has been affected by various sources of pollution for years and since it is a closed basin with no external duct to the other seas or oceans its ability to absorb, annihilate and dilute the pollution is less than an open water source, and pollutions mostly become stabilized and localized and turn into a significant threat to aquatic life. One of the major threats to the sea is pollution associated with oil extraction processes (Jafari, 2010). But since coastal areas of the Caspian Sea are residential, people are also threatened by industrial and municipal wastes thrown into the sea either directly or through river flows along their way to flowing into the sea.

According to scientific estimation about 60,000 metric tons of petroleum byproducts, 24,000 tons of sulfites, and 400,000 tons of chlorine are cleared into the Caspian Sea (Aghai, 2003; Nadim et al 2006). These pollutants have endangered living organisms and marine species. There have been lots of plans, Implementation projects, and protocols to reduce and control pollution in the Caspian Sea over the years, but over the past 10 years, aquatic and marine species lives have been under the risk of extinction and reduction, and residents of the Caspian coastal cities have encountered environmental issues more than ever.

Furthermore, another problem related to the geographical condition and climate situation is the high amount of tourists and travelers who usually reside near the sea area or surroundings of the river thus, consequently another significant pollution source of the Caspian Sea is pollutions related to municipal and urban wastes (Nouri, Karbassi, & Mirkia., 2007). According to the present research in the field, the main threat posed by industrial wastes, partly municipal wastes, to water bodies around them, is the inflowing of heavy metals inside them.

There were reports of waste minimization programs and strategies practiced in several industries to minimize the effects but the results as the reports indicate were only focused on reducing the amount of COD by decreasing the use of chemicals with toxic effects on the surroundings by disposing of their wastes. The chemicals which were excreted employing wastewater were accumulated on the surface of the water and reduced the amount of required oxygen and reflected on the odor ascending the water body. Another plan was focused on collecting the black liquor containing high amounts of COD distributed from filtrate tank leakage into the wastewater from the wood and fiber industry of CHUKA in Gilan. Another significant plan mentioned, was focusing on recycling the wastewater for other purposes. Wastewaters of industries were reported to be high COD containers even if the chemical treatment was applied to them, thus, they were not a good option for using as basic water but reusing them in other processes was an efficient method. all the plans and reports above focused on reducing the amount of COD, color, and odor of wastewaters but yet, there is no significant practical program for reducing the number of heavy metals inside the wastewaters that leave factories and enter the environment (Jafari, 2010).

Heavy metal is one of the greatest dangers caused by waste disposal to seawater, consequently, aquatic life and respectively food chain is regular ingoing of significant amounts of heavy metal compounds in different chemical types. These heavy metals such as Pb, Cd, Cu, Cr, Mn, Zn, Ni, and Fe have high densities as well as having atomic numbers higher than 20. These chemicals can be toxic and cause health problems and are viewed as worldwide issues since they exist in many sources such as industrial wastes, municipal wastewater, landfill leaches, and electronic disposals (Jafari, 2010).

2. Treatment Methods Considered - Proposed and Practiced in the Literature:

There are different categories of treatments and remediation plans and each one is suitable for a different site with different characteristics. As for the first step, type, level, amount, and form of the contaminants should be determined. One of the best methods widely used in recent years to characterize the metals inside the contaminated site is called sequential chemical extraction.

This method (SCE) is a selective process of removing the metals (usually from the sludge) using different reagents to determine the mobility and distribution of heavy metals as well as defining the most efficient remediation method. This technique includes five steps during which different forms of chemical extractant are used by the sequence of reagents, and each step removes heavy metals in a specific form. These steps are briefly known as the commutable phase, carbonate phase, reducible phase, oxidizable phase, and residual phase (Ukiwe I, & Nwoko, 2010).

Most of the remediation techniques are available in two categories called in situ and ex-situ. In situ is referred to as a method that is applied inside the contaminated soil or water while the ex-situ method is applied after the excavation of the contaminated site by pumping them out. Remediation techniques can be categorized into three major methods: physical, chemical, and biological.

3. Proposed Treatment Methods – Phytoremediation:

Phytoremediation as an alternative plan to retreat the industrial wastewaters containing heavy metals. This method is more frequently thought of recently since it is a green technology and has the lowest cost amongst other methods. Another advantage of this method is that phytoremediation is a selective way of removing heavy metals. Although there are some limits and disadvantages to this technique such as the low efficient age of plants, being a time-consuming method, and as it will be explained below low biomass production for some plants. The Northern Province of Iran was chosen for further investigation. This area is known for its massive and diverse vegetation and fertility, the most efficient and applicable method proposed as the remediation technique is decided to be phytoremediation (Tangahu, et al., 2011).

This method uses plants to absorb, extract, and excrete the contaminants from the soil or water bodies. This process generates by the use of different parts of a plant: roots, shoots, and leaves. Each part participates in transferring, accumulating, and degrading of contaminants. Generally, through the process of phytoremediation, contaminants get absorbed by the plant’s roots and tissues and the toxicity level of metals decreases in soil or water. Since heavy metals cannot be degraded, plants can accumulate and immobilize them by taking them through their roots and tissues. Under better circumstances– for specific types of plants-, plants can even convert and detox the contaminants into lower toxicity levels (Beans & Writer, 2017).

Generally, there are two categories of plants used for phytoremediation processes. The first category consists of plants such as Thlaspi. These plants have a high capacity of keeping metal concentration inside their biomass although the annual biomass provided by these types of plants is not very high. The second category consists of plants such as Brassica Juncea, Indian mustard, which have a lower potential for metal concentration but higher biomass production. According to this information, higher amounts of heavy metals are removed using the second classification of the plants (Robinson, et al., 1998).

Phytoremediation divides into different mechanisms regarding the types of contaminants – organic or inorganic. Organic mechanisms involve Phytostabilization, Phizodegradation, Rhizofiltration, Phytodegradation, and phytovolatilization. Inorganics, mechanisms involved are Phytostabilization, Rhizofiltration, Phytoaccumulation, and Phytovolatilization (Voijant Tangahu, et al., 2011).

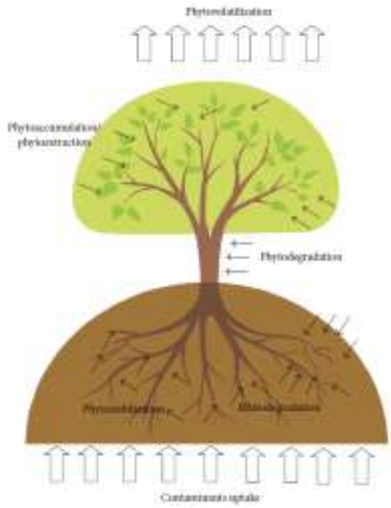

Figure 2General mechanism which is being used by plants after up taking heavy metals from soil or water in phytoremediation technique

4. Phytostabilization & Rhizofiltration:

The first step, phytostabilization, is a common step for organic and inorganic compounds. This method is used for the immobilization of contaminants in soil employing root plants. Roots of plants accumulate, absorb, and precipitate the contaminants from the soil, thus reducing their bioavailability. This mechanism applies to soil, sediments, and sludge (Voijant Tangahu, et al., 2011; Faraji, 2014).

Through the next level, which is Rhizofiltration, the contaminants and pollutants, specifically metals, excess nutrients, and radionuclide contaminants in groundwater, surface water, and wastewater medium, using some specific processes, are absorbed by the root of plants from the aqueous solution underneath the soil, thus the contaminants are excreted from the soil or water.

There are two other excess steps between the previous ones namely Rhizodegradation and Phytodegradation. Rhizogradation is used for organic compounds and contaminants including organic carbon binds. Through this step, to produce energy and food, organic substances existing in the soil breakdown by the microorganisms inside the soil body. The broken contaminants also get ingested by plants' tissue as a nutrient which is called Phytodegredation. These two steps are applicable for soil, sediment, sludge, groundwater, surface water, and wastewater (Voijant Tangahu, et al., 2011; Robinson, et al., 1998; Faraji, 2014).

5. Phytoextraction and Phytoaccumulation:

Contaminants and pollutants which are fragmented in the soil, get absorbed by the plants and accumulate inside their roots, and shoots tissues through phytoextraction and phytoaccumulation levels. Within these levels, some special plants with higher absorbing and accumulating capacity, called hyperaccumulator are used. These kinds of plants usually have a shoot to root metal concentration ratio of more than 1, while this ratio for other normal plants is less than 1. This fact stands correct for metals, metalloids, radionuclides, nonmetals, and organics contaminants in soils, sediments, and sludge medium (Voijant Tangahu, et al., 2011; Robinson, et al., 1998; Salido, Hasty, Lim, & Butcher, 2010).

6. Phytovolatization

The final step is directly connected to the ability of plants to volatile and transfer the contaminants into the atmosphere. This process is called Phytovolatization is for metal contaminants in groundwater, soils, sediments, and sludge medium. Within this step, contaminants move from Shoots to leaves by the water and are volatiled there (Voijant Tangahu, et al., 2011; Salido, Hasty, Lim, & Butcher, 2010).

7. Laboratory Experiments Pilot Scale Field Trials and Results:

According to experiments, the increasing amounts of lead concentration in the soil lead to an increase in the amount of absorbed heavy metals in their green tissue. The Lead inside the soil is naturally immobile and rather not bioavailable. Pb is mostly insoluble in soil, consequently, aqueous solutions containing chelating agents such as ethylene diamine tetra-acetate (EDTA) anion are commonly applied to soil to mobilize Pb and facilitate extraction. Therefore, the experiment was conducted to discover whether adding a chelator as a chemical enhancement will increase the Indian mustard's capacity of up taking the Pb or not. “The application of EDTA, DTPA, CDTA, EGTA, and citric acid to the soil solubilized Pb in the soil and increased Pb uptake and translocation to the shoots” so the experiment shows that, adding a chelator to the soil will increase lead's solubility as well as raising the amount of Pb concentration in plants' shoot. Although this process was effective for Cd, Cu, Zn, and Ni compounds but the elements Cu, Pb, and Zn were more accurately processed using this method (Blaylock, et al., 1997).

There is a positive relationship between Pb uptakes in roots and PH. In other words, an increase in the Pb uptakes results in increases in the pH of roots. However, the increasing amount of Pb in shoots ends up in decreasing the pH. In the previous experiment on the same sequence, it was proved that the pH efficiency on As and Pb removal from the soil by phytoextraction is under the compromise. Although the relation between pH levels and plant's ability to transfer and extract the Arsenic and lead was not the same, as it was mentioned above lowering the pH increases the Pb removal and it works the other way round for arsenic, the mean effective amount of pH level for efficient removal of both As and Pb is 5. The experiment also verified that the addition of a chelator is necessary since, without enhancement, the root concentration of Pb will be much higher than shoots. Within all the chelator, EDTA was claimed to be the most effective procedure of all (Salido, Hasty, Lim, & Butcher, 2010).

As the above experiments and results were related to soils polluted with heavy metals, there is an experiment that indicates the same results feasible for metal polluted wastewaters. According to a study by Sampanpanish to investigate the effects of EDTA in removing the Pb from wastewater by the plant c. esculent, it was confirmed that the more amount of time and concentration of EDTA being applied to wastewaters, the more amounts of Pb uptakes. At EDTA of 0.02 mM/l, the amount of Pb inside the solution declined from 5 mg/l t 3.4 mg/k in 90 days. It was also suggested that other plants with higher potential of Pb uptakes such as Jatropha curcas, Meliosmapinnata, Leucaenaleucocephala, and eucalyptus camaldulensis, especially PennisetumpurpureumSchum cv, can be effective (Sampanpanish & n.d., 2007).

Amongst the articles and experiments studied in this field, one of the most suitable ones is research conducted by Ziarati and her colleagues on the Anzali lagoon situated on the southwest shore of the Caspian Sea. This research focuses on investigating the potential of the Nymphaeaceae, known as niloofar-e-abi, high-biomass plants to uptake the Ni and Cr inside water bodies. According to revisions, the main industries which are threatening the Anzali lagoon water are the Wood and Paper Company in Talesh, Wood Fiber Company in Hassan Rood, Iran Poplin textile, Gilan Carpet, Pars Khazar houseware, Zam-Zam soft drink, and several food industries in Rasht. The results show that Cr and Ni uptake ratios increase with an increment in the amount of metals' concentration. Nonetheless, it was precisely mentioned that "concentrations remained high in roots compared to shoots in Cr (III) and Cr (VI), treated groups, while metal content was higher in shoots than roots in Ni -treated groups." Phytoextraction seems to be the best mechanism for these plants regarding its captivation capacity of these metals (Ziarati, Asgarpanah, & Makki, 2015).

8. Conclusion and Recommendation:

Amongst the papers that were chosen for this review, phytoremediation was generally reported as an effective method for the removal of heavy metals. Although there were not any inferences on a significant type of plant as the best option, the results of each experiment show that each type of plant was suitable for absorbing a specific sort of metal regarding the situation and the condition of the contaminated sites. Overall, the results gathered, consider phytoremediation as an economic and an effective technique in total.

Since the most hazardous contaminants reported for the southern Caspian Sea were Ni and Pb, related articles were also reviewed for finding suitable plants discovered to replicate the research. To determine the most appropriate plant for phytoremediation procedures, regarding the different scale units, mg/kg dry weight was the most proper and precise unit to discuss the most effective plant for up taking metals. Amongst 10 plants and experiments that were studied, for this part of the project, the water hyacinth plant, E. crassipes which is a hyperaccumulator, and 'Elephant Ear' were reported to have the most uptake amount of Pb (Sampanpanish & n.d., 2007). Since the experiments of the second plant, elephant ear was a field study rather than a laboratory, it might be a better proposition for contaminated sites of the Caspian Sea. According to the field experiments of Japan's rivers using E. acicularis as a hyper accumulator for Pb, considering the very high number of BCF calculated for this element, it also reported being a good option. However, at the end of the experiment, the concentration of Pb stayed the same as the beginning amount.

The permanent amount of Pb showed that this plant is not a potentially effective plant for Pb up-take. Although according to these articles, it would be effective to add EDTA as a chelator to increase the Pb uptake, it is not the main focus of this paper. For up taking purposes, Ni, Typha domingensis was proposed by the author since the amount of nickel uptake by this plant is high.

There would still be several matters to be taken into consideration. The most important one is the fact that most of the experiments which were studied for this review were merely a laboratory study, thus the same experiments for real situation and fields are suggested to be conducted. In such situations, it should be taken into account that a substantial number of contaminants are likely to be adsorbed by surrounding and to route media of water flow for water contaminated sites. Another point is the removal and harvesting of the contaminated plants after treatments regarding the effective amount of time in which each type of plant can participate in the removal process. Although, timing and removal were two of the factors which were overlooked in most of the reviewed articles. The elimination of these factors decreases the research's reliability. I believe the eliminated factors have a crucial role in the remediation of wastewaters because, if plants are not harvested within the proper period, all the heavy metals inside their tissues will eventually return to the water as it was in the first place.

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