A Critical Review of Removal of Zinc from Wastewater

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***Abstract*—Heavy metals are the most hazardous pollutants present in industrial and domestic waste water. In fact, they are rejected directly into the natural mainstream and if left untreated, they are in most of the time the major causes of nature degradation. Besides, industrial waste water contains metallic ions which represent a major loss of non-renewable resources and pose a huge problem in health and ecology since it is very well known that these metal-smearing of the environment are greatly affecting life on the fauna and the flora. Indeed there are many examples that can be given of human affected by this environmental pollution worldwide. For these reasons international agreements and directives issued by many countries around the world forbid and rigorously control the discharge of harmful heavy metals in the environment. This paper reviews and analysis the technological aspects of removal of zinc from industrial and domestic wastewaters.**

***Index Terms*—Heavy metals, wastewater, industrial, domestic, microorganisms.**

I. Introduction

THE term "heavy metal" is collectively applied to a group of metals (and metal-like elements) with density greater than 5 g/cm3 and atomic number above 20. These kinds of metals are directly related with environmental pollution and biological toxicity problems [12]. There are many techniques on how to remove these metals from wastewater. Primary treatment aims at removing large particles in the sewage by means of grids or sedimentation. Secondary treatment reduces the biochemical oxygen demand (BOD) in the wastewater by oxidizing organic compounds and ammonium. This process is most of the time carried out in aerated tanks with the activated sludge. It also involves both heterotrophic bacteria and protozoa. The bacteria degrade the organic material and the protozoa graze the bacteria, and in both cases organic material is converted to carbon dioxide and water. In addition to activated sludge, secondary treatment may also be performed with e.g. trickling filters or oxidation ponds.

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Tertiary wastewater treatment mainly aims at removing the plant nutrients nitrogen and phosphorus. Some of the techniques are for example chemical precipitation, distillation, or other ways of extraction. The disadvantage with these techniques is that as time goes on and raw material gets harder to find, they become more and more expensive. In addition, the rules and regulation of waste disposal is becoming so strict therefore making these techniques inefficient.

This brings us to making further researches on how to reduce these metals. One way to do so is by introducing the concept of microorganism interaction with dissolved metals. Many industries are employing this technique since this method reduces considerably, the amount of dissolved metals at lower costs.

Among all the heavy metals above mentioned, our focus will be on Zinc, therefore a brief introduction is preferable. Zinc is a lustrous bluish-white metal. It is found in group IIB of the periodic table. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen [9]. Its uses are quite variable from galvanization of steel to the manufacture of the negative plate in electrical batteries, passing through the preparation of some alloys. As a pigment, zinc is used in plastics, cosmetics, photocopier paper, wallpaper, printing inks etc, whereas in rubber production its role is to act as a catalyst during manufacture and as a heat disperser in the final product. Zinc metal is included in most single tablet, it is believed to possess anti-oxidant properties, which protect against premature aging of the skin and muscles of the body.

Zinc is the 23rd most abundant element in the Earth's crust and its concentrations are rising unnaturally, due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, coal and waste combustion and steel processing.

When it is present in less quantity in human's body, it affects considerably human's health. Although humans can handle large extent of zinc, too much of it can still cause eminent health problems [10].

Zinc is widely used in industries such as galvanization, paint, batteries, smelting, fertilizers and pesticides, fossil fuel combustion, pigment, polymer stabilizers, etc, and the wastewater from these industries is polluted with zinc, due to its presence in large quantities [7]. This wastewater is not purified satisfactory. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks.

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II. Materials and methods

To remove these dissolved metals and zinc in particular, numerous downstream physicochemical approaches [3]-[11], in addition to biological ones, can be applied to recover heavy metals from aqueous solutions or from aqueous solutions that saturate soils; but yet, all of them remediate rather than prevent. Although the revue will enumerate most of the possible methods, we will have a closer look as said earlier on the methods that use microalgae since microorganisms are considered intrinsically more efficient in the bioaccumulation of heavy metals when exposed to low concentrations in their surrounding aqueous environment.

A. *Physicochemical methods*

There is a wide range of treatment methods such as membrane filtration, adsorption, ion exchange, reverse osmosis, chemical precipitation, or solvent extraction, which have classically been employed for stripping toxic metals from wastewaters [2]-[21].

However, these methods have disadvantages, like incomplete metal removal, high reagent or energy requirements, and generation of toxic sludge or other heavy metal-containing waste products that may sometimes be more toxic than their parent ones.

For this reason, additional disposal methods are required. In addition, they are often expensive, especially when the heavy metal concentrations are very low (e.g., 10–100 mg/L) and ineffective, since a too large amount reduction of effluents is anticipated, so a narrow use in large-scale in situ operations will typically result [16].

B. *Biological methods*

Number of advantages for these methods can be enumerated such as reduced requirement for chemicals, low operating costs, eco-friendliness (as no toxic sludge results), and high efficiency at low levels of contamination. They also offer possibilities for metal recovery and biosorbent regeneration afterward [19].

A huge interest has recently arisen toward using various kinds of readily available and inexpensive biomass of several microorganisms and microalgae, in particular for removal of heavy metals. Microorganisms are in fact considered intrinsically more efficient in the bioaccumulation of heavy metals when exposed to low concentrations in their surrounding aqueous environment.

Microalgae are used in bioremediation of metal-contaminated sites due to:

- their ability to tolerate those metals,
- their high yields of recovery per unit mass,
- Their high specific outer area coupled with a cell wall loaded with ionisable groups [15].

They furnish an extensive collection of helpful mechanisms which, in natural environments, contribute to the global cycling of inorganic matter, and in particular lead to the formation of deposits of various minerals and ores such as gypsum, limonite, etc, within geological periods of time [1]. Thompson [20] hypothesized that such "bio mineralization" processes proceed according to the following sequence:

1. Formation of microbial biofilm
2. Biosorption [8] of soluble metals to microbial cells and exopolymers
3. Formation of metal hydroxides, oxides, carbonates (examples), and their maturation to amorphous mineral precursors
4. Stabilization of the precipitates forming a demineralization nucleation crystal template for further mineralization in the microenvironment generated by the metabolic activity of microorganisms. Let us not forget to mention that the pH and the cell's wall play by themselves one of the most important functions in the adsorption of heavy metals by micro-algal cells. The micro algal cell wall has indeed the capacity to bind with these ions via its negatively charged moieties [5].

III. Literature Review

Monteiro et al, 2011, found that Scenedesmus obliquus has a better performance in removing dissolved heavy metals than other species. They also found out that microalgae are quite different according to the fact that they are isolated from polluted environments are obtained from culture collections. They ended up with the conclusion that those isolated from polluted environment perform Biosorption better the ones from culture collection and also highlighted the pH interval in which the Biosorption was occurring at higher rates.

Rajamani et al, 2007, gave a noteworthy outlook of all the heavy metals, their properties and their effect to the environment. They continued by explaining the role of algal cell wall in heavy metal binding and showed the degree of tolerance the cell walls have. In fact it was proved that cell walls have high heavy metal binding capacity and these cells can be grouped in different categories according to their acidic/basic properties.

Pumpel et al, 2011, have described the various full-scale, pilot-scale, and expanded-laboratory-scale processes to show that new and stimulating projections exist for the treatment of wastewater with dissolved heavy metals and using living micro organisms. They highlighted the fact that already existing treatment methods were now and then inefficient due to the low concentration of the dissolved metals and to the actual cost of those methods. They ended by insisting in the revalorization of the actual work being accomplished in the matter of wastewater treatment and environmental protection to increase the interest of many individuals in this path.

Monteiro et al, 2011, again insisted in the actual methods used in the removal of heavy metals from wastewater, they proposed new methods which are not exploited widely and which involve the used of microalgae since they clearly showed in their paper their interest in using a environment friendly and costless method. They indeed went deep on the subject by giving more information about the removal capacity of microalgae, the toxicity and tolerance mechanisms as well as the interactions between the heavy metal and the cell. More important they gave some factors affecting sorption capacity of microalgae. These factors are the temperature, pH, supernatant metal concentration, metal speciation, the presence of other metals, and the biomass concentration. Divers reviews compared the heavy metals uptake capacities of different macrophytes and the data were collected in the table below

Table I . Heavy metal uptake capacities [13]-[18]-[22]

Absorbents	Lead	Zinc	Copper
	mg/g		
M. spicatum	46.69	15.59	10.37
M. spicatum	55.6	13.5	12.9
P. lucens	141	32.4	40.8
S. herzegoi	----	18.1	19.7
E.crassipes	----	19.2	23.1

It has to be noted that zinc uptake capacity of different cells appears most of the time on the second position after lead uptake.

IV. Results and Discussions

Different investigations are being conducted aiming to reduce considerably the amount of dissolved heavy metals. Most of these methods, which were applied on a lab scale, can still be used to reduce the amount of Zn in wastewater streams. A brief presentation of the results of these experiments is hereby given.

Using a schematic designed algal and duckweed based stabilization pond system, during cold weather, it was seen that the BOD was lowered considerably, in fact the first pond of the system in place in which the micro algae were consuming nutrient from the wastewater for their growth. In order to reach this goal, the COD of the system was partially modified to allow the oxidation of organic nutrients to happen. Analysis of the water leaving the second pond revealed a huge potential for this treatment since for example the pH of the wastewater was increased as well as the DO. Certainly as per all experiments, a certain number of parameters have to be clearly set in order to give a good efficiency of the pollutant removal. Some of those parameters are for example the retention time, the water depth, the initial nutrient concentration, the micro flora and harvesting regimes [17]. It was also seen that the cultivable bacterial cell count in terms of colony forming units per milliliter of wastewater was also considerably lowered in wastewater after treatment than before treatment.

Also, the growth of microalgae was hindered seriously as the concentration of Zn went increasing. Although the growth was inhibited seriously, a huge increase in the metal removal was reported when the cells were in highly concentrated environments rather than in less concentrated ones. These living cells first showed an immediate high adsorption of Zn ions at the very beginning of the experiment and the slowly the adsorption went on decreasing as the Zn concentration decreased. Furthermore, it was seen that the same micro algal specie can act differently according to the fact that it is isolated from contaminated environments or grown artificially. Indeed the micro alga specie which was collected from contaminated environments showed an important removal capacity than the one artificially grown.

When performing the same experiment with inactivated cells, the same observation of sudden removal increase and an equilibrium reached after some time of the experiment was made. This lead to the statement that the fast removal of Zn ions was done by the ionic adsorption by the micro algal cell; reason why the equilibrium was remarked at a certain time since no cells were growing.

In case of pH, it was reported that cation's Biosorption and pH were directly proportional. Indeed the smallest Biosorption capacity was recorded at lower pH values, when the highest was reached at higher pH values approaching neutrality (between 6 and 7).

To give an end to the results, it was reported that high algal diversity results in efficient nutrient removal from primary settled wastewater [14]. Cold climate is normally not favorable for bioremediation of wastewater in pond system due to poor light availability and low temperature; however Gronlund in 2004 successfully demonstrated the feasibility of using certain micro algae with particular attributes to treat wastewater [6].

Algae are known for their capacity to accumulate heavy metals from wastewater since heavy metals such as Zn, Cu, Fe, Mn, Co and Mo are required as essential nutrients [4].

V. Conclusion

Throughout this paper the importance of removing heavy metals in general and zinc in particular from industrial or domestic wastewater was highlighted. Different methods with different aims are already available on the market. The article had a particular approach on the method using microorganism to recycle wastewater due to the fact that the treatment using algae is more efficient and faster since bacteriological treatment is a process of decay whereas algae treatment is one of conversion of organic matter to live, healthy plant life. Indeed algae can metabolize sewage far more rapidly than bacterial treatment.

However, we are confronted to the development of cheaper methods since in most countries wastewater treatment has to be a low-cost plan for its majority approval. More work by scientists and technologists is required in order to accomplish this objective.

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