Removal of Heavy Metals From Paper And Pulp Industry Effluent: A Review

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Abstract- *Effluent from paper and pulp industry is known for containing different types of heavy metals like Zn, Pb, Cr, Cd, Ba, Cu, Ni etc. The presence of heavy metals that collects and eventually exceeds certain threshold concentrations will cause environmental pollution, thusly it is important to conduct wastewater treatment to eliminate or at least reduce the heavy metal concentration in industrial wastewater. The conventional method of treatment of heavy metal contamination includes reverse osmosis, chemical precipitation, membrane separation, chemical oxidation, ion exchange, electro dialysis etc. These methods are very expensive, energy intensive and regularly connected with generation of poisonous by-products. The development of efficient and eco-friendly technologies for treating wastewater is one among the appealing research area. Thus, the adsorption has been considered as a cost effective and efficient method for the removal of heavy metals from wastewater. In the current investigation different treatment techniques has been reviewed for the removal of heavy metal contamination from paper and pulp industry wastewater.*

Keywords- Paper and Pulp Industry, Effluent, Heavy Metals, Biosorption

I. INTRODUCTION

With the advancement in human civilization, different advanced industrial activities take place. Fast advancement in industrial activities release toxic solid wastes and discharge effluents which make potential risk to environment. Industrial processes consume enormous quantity of water and release heavy metal-contaminated effluents to the connecting sites. Pulp and paper industry is the third biggest industrial polluter to water, air and land. India positions the twentieth rank among the paper-producing nations of the world [9]. The Indian pulp and paper industry is exceptionally water intensive, consuming 100–250 m^3 of freshwater for each tonne of paper, and furthermore produces the relating wastewater, for example 75–225 m^3 per tonne of paper [9]. Paper mill effluent has high concentrations of phosphorous, biological oxygen demand (BOD) and chemical oxygen demand (COD) with increasing conductivity, colour and temperature. Paper and Pulp Industry contain heavy metals like Zn, Cd, Cu, Cr, Pb. These heavy metals are non-biodegradable and their discharge into aquatic environment is likely to pose risk to fauna, flora and human beings [1, 5].

Industries producing different sort of products for the satisfaction of human needs are quickly expanding in number. The expanding number of industries causing the quantity of waste additionally increased. Waste produced by the industry will have adverse impacts on the natural resources and environment; waste also can exacerbate the quality of the environment by turning out to be poison for air, water, and soil if no earlier processing of the waste is carried out. Endeavours to stop and affect pollution aren’t only directed by the government alone, yet in addition the duty of the industries that generate the waste. The conveyance of fluid waste produced by the paper and pulp industry encompasses the whole surrounding ecosystem. In laboratory experiments, the wastewater from the paper and pulp industry results in regenerative inconsistencies in invertebrates and zooplankton that are the source of food for aquatic creatures also as harm their genetics and immune system [11]. Hence, it takes a successful programme to limit the impacts of waste for the enforcement of hazardous waste management guidelines, in order that it’ll improve the quality of the environment and build up great connection with the society.

In the paper and pulp industry, the heavy metals are for most part contained in black liquor. Black Liquor may be a liquid containing 70%-72% solid added to the digester within the paper-production process. Black Liquor colour is black due to the chemical reactions that happen between wood chips and therefore the chemicals in liquor utilized for cooking. The chemicals contained in black liquor are $Na_2S_2O_3$, Na_2S, Na_2CO_3, NaOH, Na_2SO_4, and non-volatile sulphur [11]. Black liquor also includes hazardous metals like iron, barium, manganese, nickel, zinc, lead, cadmium, chromium, cobalt, copper and arsenic [11]. The existence of those metals will surpass and collect the quality standards will in the long run pollute the environment. Black liquor plays a crucial role within the paper and pulp industry, it tends to be reused into green liquor by adding sodium sulphate (Na_2SO_4) in boiler for recovery, to satisfy the inadequacy of SO_4^{2-}, the green liquor which has experienced the causticization procedure and turns into the white liquor is added to the digester [11].

The removal of heavy metals from industrial effluent is one of the growing concerns. The heavy metals present within the wastewater is non degradable and constant in nature. In addition, they are dissolvable in aquatic condition and hence can be easily absorbed by living cells. Along these lines, by entering the food chain, they can be biomagnified and bio accumulated in higher trophic levels also [4]. The heavy metals, if absorbed above the permissible limits, could lead to dangerous health issues. Considering the realities, treatment of heavy metals containing industrial wastewater becomes essential before being released into the environment. The environmental engineers and researchers are accordingly facing a troublesome assignment of low cost and effective treatment for the removal of heavy metals from industrial effluent. The present work focuses toward contributing in the search for cost effective and efficient treatment technologies for the removal of heavy metals from industrial wastewater. The below table illustrates Maximum Contamination Level (MCL) standards for few heavy metals established by USEPA:

Table 1 the MCL standards for the most hazardous heavy metals [4]

Heavy Metal	Toxicity	MCL (mg/L)
Lead (Pb)	Damage the fetal brain, diseases of kidney, circulatory system and nervous system	0.006
Chromium (Cr)	Headache, diarrhoea, nausea, vomiting, carcinogenic	0.05
Arsenic (As)	Skin manifestations, visceral cancers, vascular disease	0.050
Zinc(Zn)	Depression, lethargy, neurological signs and increased thirst	0.80
Copper (Cu)	Liver damage, Wilson disease, Insomnia	0.25
Mercury (Hg)	Rheumatoid arthritis and disease of kidneys, circulatory and nervous system	0.00003
Nickel(Ni)	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Cadmium (Cd)	Kidney damage, renal disorder, human carcinogen	0.01

II. LITERATURE REVIEW

Al-Shannag, M., Al-Qodah, Z., Bani-Melhem, K., Qtaishat, M. R., & Alkasrawi, M, Heavy metal ions removal from metal plating wastewater using electrocoagulation: Kinetic study and process performance (2015) had studied that the removal of heavy metals, namely Cu^{2+}, Cr^{3+}, Ni^{2+} and Zn^{2+}, from metal plating wastewater using electrocoagulation method. An electro-reactor was used with six carbon steel electrodes of monopolar designs. Three of the electrodes were designated as cathodes meanwhile the other three as anodes. The results indicated that the removal efficiency of heavy metals increases with increasing both electrocoagulation (EC) residence time and direct current (DC) density. Over 97% of heavy metals were removed efficiently by conducting the EC treatment at current density (CD) of 4 mA/cm^2, pH of 9.56 and EC time of 45 min. These working conditions led to specific energy consumption and specific amount of dissolved electrodes of around 6.25 kWh/m^3 and 1.31 kg/m^3, respectively.

Arivoli, A., Mohanraj, R. & Seenivasan, R. Application of vertical flow constructed wetland in treatment of heavy metals from pulp and paper industry wastewater had studied that the feasibility of constructed wetlands to treat the heavy metals from paper and pulp industry effluent by using vertical flow constructed wetlands planted with normally available macrophytes like Typha angustifolia, Erianthus arundinaceus, and Phragmites australis. Results demonstrate that the extraction efficiencies of the planted constructed wetlands are iron (74%), copper (80%), manganese (60%), zinc (70%), nickel (71%), and cadmium (70%).Then again, the extraction efficiency of the unplanted system was significantly lower ranging between 31 and 55 %. Among the macrophytes, T. angustifolia and E. arundinaceus showed similarly higher bioconcentration factor (102 to 103) than P. australis.

Qdais, H. A., & Moussa, H, Removal of heavy metals from wastewater by membrane processes: a comparative study (2004) had studied that the reverse osmosis (RO) and nanofiltration (NF) both technologies are used for the treatment of wastewater containing Cu and Cd to reduce fresh water consumption and environmental degradation was investigated. Synthetic wastewater samples containing Cu^{2+} and Cd^{2+} at different concentrations were prepared and subjected to treatment by RO and NF in the laboratory. The results demonstrated that high removal efficiency of the heavy metals could be accomplished by RO process (98% for Cu and 99% for Cd). NF, however, was capable of removing more than 90% of the copper ions existing in the feed water. The viability of RO and NF membranes in treating wastewater containing more than one heavy metal was also investigated. The results demonstrated that the RO membrane was capable of treating wastewater with an initial concentration of 500 ppm and reducing the heavy metal concentration to about 3 ppm (99.4% removal), while the average removal efficiency of NF was 97%.

Surindra Suthar, Poonam Sajwan, Kapil Kumar, Vermiremediation of heavy metals in wastewater sludge from paper and pulp industry using earthworm Eisenia fetida (2014) had studied that removal of heavy metals from paper mill wastewater (PMS) sludge spiked with cow dung (CD) utilizing Eisenia fetida. A sum of seven set-ups were prepared: CD (100 percent), PMS: CD (1:1), PMS: CD (1:2), PMS: CD (1:3), PMS (100 percent), PMS: CD (2:1) and PMS: CD (3:1) and changes in chemical parameters were observed for 60 days. Vermistabilization caused the noteworthy diminishing in the level of Pb (95.3–97.5%), Cu (68.8–88.4%), Cd (32–37%) and Cr (47.3–80.9%) and significant increment in total-N, available P and K and Electrical Conductivity at the end. Toward the end, the tissues of inoculated worms demonstrated the high load (mg/kg, dry biomass) of Pb (8.81–9.69), Cd (2.31–2.71), Cr (20.7–35.9) and Cu (9.94–11.6), respectively which showed bioaccumulation of heavy metals by worms. The PMS: CD (2:1 or/and 3:1) appeared to be appropriate waste mixture as far as high metal removal and earthworm development rates. Bioaccumulation, as evaluated using bio-concentration factor (BCF), was in the order: Cd>Cr>Pb>Cu. As per results authors recommended that vermiremediation as suitable technology for bioremediation of heavy metals from PMS.

Thippeswamy B, Shivakumar CK, Krishnappa M, Bioaccumulation potential of Aspergillus niger and Aspergillus flavus for removal of heavy metals from paper mill effluent (2012) had studied that Aspergillus niger and Aspergillus flavus separated from paper and pulp industry effluent demonstrated tolerance and accumulation of toxic heavy metals Zn, Pb, Cu, Cd, Ni and Cr from synthetic medium and paper and pulp industry effluent. Physico-chemical and heavy metals characterization of industrially treated paper and pulp industry effluent indicated miserable reduction in TDS, BOD, hardness and heavy metals as compared to permissible limits of WHO and BIS. Aspergillus niger and Aspergillus flavus were treated with synthetic medium containing 100-1000 mg/L of six heavy metals. A. niger was able to tolerate and grow in 1000 mg/L Pb, 500 mg/L Cu, 250 mg/L Zn and 100 mg/L Cr, Ni respectively. No growth of A. niger was seen in 100 mg/L of Cd. A. flavus was capable to tolerate and grow in 1000 mg/L Pb, Zn and Ni, 100 mg/L Cu. A. flavus growth was totally restrained in 100 mg/L of Cd and Cr. The Zn, Pb, Cd and Cu reduction were discovered significant ($p < 0.05$) in the paper and pulp indstry effluent inoculated with A. niger and A. flavus biomass compared to industrial treated effluent. A. niger and A. flavus accumulated maximum of Pb (75.82%), Zn (49.40%), Cu (45.34%), Ni (25.20%), while only 41% Cr was accumulated by A. nigerfrom 100 mg/L of Cr solution.

Verma, V. K., Gupta, R. K., & Rai, J. P. N., Biosorption of Pb and Zn from pulp and paper industry effluent by water hyacinth (*Eichhornia crassipes*) (2005) had studied that bioaccumulation of Zn and Pb by water hyacinth was discovered concentration and duration dependent. The plant had capacity to neutralize the effluent. It could effectively absorb Zn (0.26-1.30 mg/L, 16.6-73.4%) and Pb (0.28-1.39 mg/L, 17.6-80.3%) following 20 days of treatment. Heavy metal removal efficiency was seen as most extreme (73.4% for Zn, 80.3% for Pb) at 20% effluent concentration, hence highlighting that phytoremediation could be utilized alongside or/and in some cases as a substitute of costly heavy metal removal technologies in industrial wastewater treatment.

Wirojanagud, W., Tantemsapya, N., & Tantriratna, P, Precipitation of heavy metals by lime mud waste of pulp and paper mill (2004) had studied that precipitation of heavy metals in synthetic and actual wastewater with lime mud (solid waste generated from the paper and pulp production process) was experimented using Jar-tests. Separate synthetic wastewater samples were prepared for each of the following heavy metals: lead (1433.7 mgPb/L), chromium (506.7 mgCr/L), cadmium (1095 mgCd/L) and mercury (9.37 mgHg/L). The actual wastewater was tanning wastewater containing 74.49 mgCr/L and COD wastewater containing 683 mgHg/L. Adjustments of pH in the acidic range, pH 2-7, were made for each type of synthetic wastewater except for the Hg synthetic wastewater. The optimum conditions obtained from the tests of the synthetic wastewater were used for the actual wastewater samples. Precipitation of heavy metals with lime mud was effective as indicated by the removal efficiency as high as 90% up for Pb, Cd and Hg and 100% for Cr. However, the removal efficiency for the Hg-COD wastewater was only 67%.

III. TREATMENT TECHNOLOGIES

Ion-exchange: In this procedure, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin [6]. This technique is very expensive. The drawback of this technique is incomplete removal of certain ions.

Ultra-filtration: They are pressure driven membrane operations that utilize porous membranes for the heavy metals removal. The main drawback of this technique is it produce large amount of sludge.

Phytoremediation: Phytoremediation is the use of certain plants to clean up sediment, soil and water contaminated with metals [6]. It requires a long time for removal of heavy metals and the regeneration of the plant for further biosorption is difficult.

Reverse Osmosis: It is a procedure where heavy metals are isolated by a semi-permeable membrane at a pressure more prominent than osmotic pressure caused by the dissolved solids in wastewater. This technique is very costly.

Chemical Precipitation: Precipitation of metals is accomplished by the addition of coagulants like lime, alum, iron salts and other organic polymers. The enormous amount of sludge containing toxic compounds generated during the process is the main disadvantage.

Electro-dialysis: During this procedure, the heavy metals are isolated using semi-permeable ion-selective membranes. Utilization of an electrical potential between the two electrodes causes a movement of cations and anions towards particular electrodes. Due to the substitute separating of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The drawback is the structure of metal hydroxides, which clog the membrane.

Biosorption: Biosorption can be characterized as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [6]. Algae, bacteria, fungi and yeasts have proved to be potential metal biosorbents [6]. The main advantages of biosorption over conventional treatment methods are [6]:

- Regeneration of bisorbent
- High efficiency
- Minimization biological or/and chemical sludge
- Low cost
- No additional nutrient requires
- Possibility of metal recovery.

The biosorption procedure includes a liquid phase (solvent, normally water) and a solid phase (biosorbent; biological material) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher attraction of the sorbent for the sorbate species, the latter is attracted and bound there by various mechanisms. The procedure proceeds until equilibrium is built up between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent attraction for the sorbate decides its distribution between the liquid and solid phases.

IV. CONCLUDING REMARKS

The review from different research paper and processes showed that most of the conventional treatment has some disadvantages such as high cost, incomplete metal removal, and complex treatment process, generation of poisonous sludge, high reagent and energy requirements. Out of all these processes biosorption process is energy efficient, easy to operate and cost effective treatment of paper and pulp industry effluents. Biosorption has the high potential for removing heavy metals which can abatement the toxicity to the effluent. Since it was only a review further investigation should be carried out in future towards the advancement of a few new technologies to treat paper and pulp industry wastewater.

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