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Activated Sludge for Heavy Metal Removal-A Review

Sonali Dhokpande[1], Dr. Jayant Kaware[2], Sunil Kulkarni[3]

[1,3] *Datta Meghe College of Engineering, Airoli, Navi Mumbai,Maharashtra, India*

[2]*Bhonsala College of Engineering and Research, Akola, Maharashtra, India*

***Abstract*— The removal of heavy metals from the effluent is vastly studied topic among investigators. Activated sludge has been used for the heavy metal treatment efficiently by many researchers. It acts as good biosorbent for various metals. Present review presents the research carried out on various aspects of the sorption of heavy metals. The effects of various parameters like contact time, pH, initial concentration are reported. The effects of biological activities of sludge on metal uptake have been studied by the investigators. The use of activated sludge under optimized conditions is promising alternative for heavy metal removal.**

***Keywords*— Activated sludge, removal, isotherms, kinetics, heavy metal, concentration.**

I.INTRODUCTION

Industrial wastewater containing heavy metal should be treated before discharge to the water stream but its treatment is very costly. There are several techniques to remove heavy metals from wastewater such as filtration, electro coagulation etc. but there is some limitation such as long treatment time. Studies have been carried out using various waste materials for heavy metal removal by many researchers with reasonable success.

Heavy metals are considered to be the following elements: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese, and Aluminum. In the present review, the research on use of activated sludge for removal of heavy metal is summarized. Many investigators have carried out research on various aspects such as effects of time, initial concentration, pH, biological activity of the sludge and effect of aeration and feeding on the removal efficiency.

II.USE OF ACTIVATED SLUDGE FOR HEAVY METAL REMOVAL

Rosin et.al. carried out research on the influence of process parameters on removal of heavy metals(1). They studied the behavior of six heavy metals cadmium, copper, nickel, chromium, zinc and nickel at normal to elevated concentrations. The maximum removal was observed for the sludge age of 12 days. The shock loads does not have very significant effect on the removal efficiency. The soluble metals, i.e. nickel, cadmium and copper exhibited less removal efficiency than other three metals. Overall activated sludge found to be satisfactory biosorbent for removal of majority of heavy metals of concern.

Kumar et.al. investigated various parameters in the biosorption of heavy metals on activated Sludge(2). To understand the action of bio metals uptake, the essential role played by extra cellular polymeric substance (EPS) needs to be understood. They studied factors influencing the biosorption of the heavy metals are cleaning of the sludge, pH, initial metal ion concentration, weight of the adsorbent, mixing index, time and temperature. Also the isotherm study was carried out. It was observed that the removal efficiency increases as the sludge mass increases. As the sludge mass increases the number of binding sites for the ions also

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increases. Removal efficiency increases for Cadmium from 37.61 to 61.11%, for Copper 23.36 to 50.28%, for Nickel 12.04 to 27.54% and Zinc is 9.2 to 36.28% as the mass increases from 0.5g to 3g. As contact time was increased from 15 to 240 minutes the removal efficiency increased three to four fold. The maximum removal was obtained for 45 minutes contact time. With initial metal ion concentration the removal efficiency decreased. The reason may be agglomeration and aggregation of adsorbent particles at higher concentration, leading to decrease in surface area available. Mixing speed was found to increase the removal efficiency. With temperature the loading capacity of adsorbent decreases. The data obtained fitted well for both, Langmuir and Freundlich isotherms.

Adsorption of heavy metals by extracellular polymeric substances (EPS) of activated sludge was tried by Liu et.al(3). They extracted by high-speed centrifugation at 20,000 G for 30 min from an activated sludge treating municipal wastewater. From each gram of activated sludge as-is a total of 7.3 mg EPS was extracted, of which 6.5 mg was EPS and only 0.8 mg was EPS. The same sludge after extraction at 80°C yielded over 8 fold of total EPS (57.9 mg). As compared to the as-is sludge, extraction at 80°C yielded 18 fold of EPS(13.0 mg) and 7 fold of EPS(44.9 mg), lowering the EPSp/EPSc ratio from 8.6 to 3.5. This indicated that the carbohydrate fraction of EPS was more sensitive to the thermal extraction. It was observed that more metals were removed by the EPS than by the activated sludge process, despite the metal concentrations tested in this study (10–100 mg/l) being considerably higher than those in wastewater treated by the activated sludge process. The adsorption capacity of an adsorbent is normally dependent on the concentration of the adsorbed species at equilibrium. An adsorption isotherm is commonly used to correlate these two parameters. The two most common adsorption isotherms are:

Freundlich isotherm

$$Qe= k\, Ce^{1/n} \quad (1)$$

Langmuir isotherm

$$Qe= Q_m bC_e/(1+bC_e) \quad (2)$$

where Qe is the adsorption capacity (expressed in mg/g-adsorbent) and Ce is equilibrium concentration of the adsorbed species. The Langmuir parameter represents the maximum adsorption capacity of the adsorbent. It was found that the Freundlich isotherm correlated satisfactorily with the adsorption data of Ni^{2+}, Cu^{2+}, Cd^{2+}, and CrO_4^{2-} (R_2rang-ing 0.89–0.97), whereas the Langmuir isotherm correlated satisfactorily with those of Zn^{2+}, $Cr^{3+}$and Ni^{2+}(R_2ranging 0.93–0.96). Both correlated poorly for those of Co^{2+}.

Hasani et.al. carried out investigation on fixed activated sludge system for removing heavy metals (Cr, Ni and Ph) from industrial waste water(4). In their research, they studied the operation of fixed activated sludge system for treatment of wastewater containing heavy metal compounds (chromium, lead and nickel), by using of fixed activated sludge (FAS) system . It was observed that while chromium, lead and nickel removal efficiency in the fixed activated sludge at concentration of 1 mg/lit. is 84%, 75% and 80%, respectively, by increasing concentration of them to 5 mg/lit, the removal percentage increased to 90%,84% and 87%, respectively.

Niec et.al. carried out research on Influence of anoxic selectors on heavy metal removal by activated Sludge(5). They carried out experiments to compare the metal binding characteristics of an an-oxic selector activated sludge system and a conventional activated sludge system. Metal biosorption by biomass harvested from experimental systems was determined by a series of batch experiments. The metals under consideration were zinc, cadmium, and nickel. It was observed that, from sorption isotherm that the selector sludge had significantly higher sorption capacity than did the control sludge. Freundlich isotherm model for equilibrium concentrations was followed by solute uptake. The higher metal sorption capacity of selector sludge may be due to the selection of the ECP-producing bacteria (i.e., Zoogloea sp.) by the selector system.

Oviedo et al. studied The toxic effects of the metals cadmium, zinc and copper on microbial activity in the activated sludge process (6). The presence of the metal led to a decrease in the rate of organic material elimination throughout the duration of the experiment. Zinc produces the least negative effects, with the elimination rate decreasing from 90 % to 77 % over the 8days of the test, and with stabilization, virtually complete from the fourth day onwards. They concluded that that cadmium is the most highly toxic metal for the microbial communities present in the activated sludge process, followed by copper, and lastly zinc.

The research on immobilization of heavy metals on activated sludge was carried out by Suo et.al (7). They used

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Calcium alginate beads to immobilize the sludge. The sorption of copper, zinc and chromium was carried out. The adsorption rate of pretreated activated sludge was much greater than immobilized sludge. The effects of pH and temperature were also studied. It took around 20 hours for the equilibrium. The metal removal process followed Langmuir isotherm. The entrapped, sterilized pretreated activated sludge is better option for heavy metal removal.

Jalilzadeh and Parvaresh investigated the removal of heavy metals ions from wastewater with conventional activated sludge process(8). In this comparison, some metal concentration of effluent was higher according to standard limits of Iran. Results of research illustrated that, conventional activated sludge process alone cannot remove heavy metal sufficiently.

Ong et.al. investigated the activated sludge and powered activated carbon for heavy metal removal(9). Powdered activated carbon (PAC), activated sludge, and dried sludge were investigated under laboratory conditions to assess its ability to remove heavy metals.T he adsorption of Cu, Cd, Ni, Zn, and Cr from synthetic solutions on these adsorbents were studied. It was observed that the adsorption efficiency increased rapidly within the first 30 min and then slowed, approaching a steady state after 5 h. Dried sludge, which is non-living biomass, is generally used for adsorption studies because it eliminates the problem of heavy metal toxicity. The results obtained show that the activated sludge and dried sludge could be used as bio-adsorbents in removing heavy metals from wastewater. Since powered activated carbon is costlier, activated sludge is proposed as a cheaper alternative. In fact, biological wastewater systems are mainly designed to remove organic matter and the side-benefits can be observed in the treatment of heavy-metal-bearing streams. In a biological treatment process, the activated sludge from the final clarifier must be returned to the aeration tank depending on the desired mixed liquor, suspended solids, or sludge age. The investigation also indicated that the adsorption of Cu, Cd, Zn, Ni, and Cr followed the Langmuir isotherm and it did not fit well to the Freundlich model. It was found that the addition of heavy metals inhibited the activities of microorganisms in biodegradation processes. It was also observed that the Cu is the most adsorbed and toxic to activated sludge microorganisms. Cadmium was less adsorbed but more toxic than Ni. Uptake of nickel increased with sludge age. Sequence of heavy metal was observed in the order Cu > Ni > Cd > Cr > Zn and Cu > Ni >Cd > Zn > Cr, respectively for activated sludge and dried sludge. Activated sludge showed better adsorption capacity of Cr and Cd than powered activated carbon Waste sludge was used for heavy metal treatment by Atkinson et.al.(10). They collected waste activated sludge samples on a weekly basis from the drying beds of a water-treatment facility dealing exclusively with domestic waste. Sludge samples were dried at 105 °C. Heavy metals analyzed included Cd^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Ni^{2+} and Zn^{2+}. Metal-loading capacity of sludge was calculated as follows:

$$q = (Ci - Cf).V/m \qquad (3)$$

where:q=metal-loading capacity of biosorbent (mg·g/1),Ci=initial metal concentration (mg·/1),C_f =final metal concentration (mg·/1),V =batch effluent volume(l),

m =dry mass of biomass (g). They observed that the sludge has greater affinity for zinc. Variances in sludge bioadsorption capacity throughout experimentation were attributed to differences in the concentration of bacterial extracellular polymers at different sludge sampling times. They concluded that bioadsorption of heavy metals by activated sludge in mixed-metal streams occurs in a non-specific fashion, with preference shown towards those metals which are present in the greatest concentrations.

The research on optimization and/or acclimatization of activated sludge process under heavy metals stress was carried out by Bestawy(11). Their study was to overcome the toxicity of the heavy metals load, discharged with the industrial effluents into Alexandria sewerage network, on the activated sludge treatment system through effective acclimation for organic matter and heavy metals removal. They performed acclimatization through abrupt and stepwise addition of tested metals using sequencing batch reactors treatment approach. The parameters evaluated were microbial oxygen uptake rate (OUR), dehydrogenase activity (DHA), organic matter (COD) and heavy metals removal. Abrupt addition of metals adversely affected sludge bioactivity leading to decline in the removal efficiency of the targeted contaminants. Controlled stepwise application of the tested metals exhibited high sensitivity of DHA and OUR activities only at the highest metal concentrations.

Saniedanesh et. al carried out studies to explore the potential for recovery of heavy metals from the wastewater and sewage sludge(12). They reviewed various heavy metals recovery technologies(HMRT). Their work provides a criteria

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and selection guideline in selecting the best HMRT for an industrial or domestic wastewater. They used copper as the sample metal for their research considering its cost effectiveness. They presenting screening criteria for HMRT based on the selective adsorption, percentage recovery and cost effectiveness. They observed that, the bisulphate technology was most effective with high percentage recovery, 99.5 percent and three years payback period. Methods like Biosulphide Process, Biogenic sulphide reagent, Electrodialysis (ED), Kyanite adsorbent Column operation , Electrochemical reactor, Taguchi method, An ultrasonically enhanced two-stage acid leaching process were analysed. Each method is efficient for certain metal or group of metals. Depending on the type of effluent, its content, one can choose the effective HMRT.

Ong et.al. investigated the effect of heavy metals on the activated sludge activity(13). They evaluated the inhibitory effect of heavy metals on the activity based on dissolved oxygen and specific oxygen uptake rate(SOUR).The specific oxygen uptake rate is given by,

$$SOUR= 60.G/X(mgO_2/(g\ MLSS.h) \qquad (4)$$

where G is the slope of linear portion of DO decline curve in mg/l and X the mixed liquor suspended solid(MLSS) concentration in gram/l. The addition of heavy metals decreased the SOUR. There was decrease in the activity of microorganisms because of heavy metals. Copper was found to be more toxic than cadmium. The microorganisms consumed maximum oxygen during fill period, while during react period they consumed minimum oxygen.

Sorption of co^{2+} , zn^{2+} , cd^{2+} and cs^{+} ions by activated sludge of sewage treatment plant was studied by Maresova(14). They reported cobalt, zinc, cadmium and cesium sorption by suspension of non-treated activated sewage sludge (14 g/dm^3, dry wt.) from waste water spiked with $CoCl_2$, $ZnCl_2$, $CdCl_2$ or CsCl were determined in laboratory experiments at 20°C. They observed that the efficiency of sorption increased in the order $Cs < Co < Zn < Cd$. The process of metal uptake was not inhibited because of pretreatment with formaldehyde or deactivation at $60^{o}C$. It means the sorption was not dependent on the metabolic activity of the sludge. That metal cation biosorption is diminished below pH 4. It was also observed that sorption efficiency of activated sludge increases above pH 8. Cadmium showed the highest affinity to the sludge and the lowest extract ability with mineral acids and salt solutions. They were able to desorb high percentage of Co, Zn, Cd and Cs from the sludge by one step washing with $CoCl_2$, $ZnCl_2$, $CdCl_2$ and CsCl solutions respectively, as well as with EDTA and HCl solutions.

Removal of lead by using waste activated sludge was carried out by Rahmani et.al (15). The lead removal efficiency increased up to first 45 minutes and remained constant thereafter for initial concentration of 5 g/l. For treatment of lead solution with 10 mg/l concentration this equilibrium time was reduced to 30 minutes and for 50 mg/l, lead it was about 15 minutes. The continuous aeration was marked by increase in removal efficiency, but considerable increase in the contact time. It indicated that the activated sludge was not able to adsorb the metal without required nutrients and as expected the microorganism had reached to endogenous phase. Continuous aeration and feeding led to maximum efficiency of lead removal which was 94.2 % and was obtained in treatment of 5 mg/L lead solution . The contact time required was 48 hours. It can be concluded that the performance of activated sludge can be increased by using continuous aeration and feeding for metal removal.

Danesh et.al. used microwaves for generation of exceptional quality biosolids for phosphorus and heavy metal extraction from wastewater treatment plant sludges(16). The aim of the study was to evaluate how much phosphorus and metals in sludge can be released into solution by microwave irradiation when applied to sludge prior to anaerobic digestion, and to determine the effectiveness of subsequent lime precipitation. It was observed that phosphorus release from thickened Pretreated sludge(PS)/Waste Activated Sludge(WAS) or unthickened WAS was proportional to both the temperature and duration of heating. The phosphorus released consists of a significant fraction of phosphorus that is not orthophosphate. Microwave heating exhibited more phosphorous removal than conventional heating. Microwave heating and use of heat recovery system is good alternative for generation class A biosolids. It may not be as economically competitive as alternative systems for phosphorus removal, due to the considerable capital and operational and maintenance costs associated with the microwave units and solids separation as a standalone method.

Benaissa and Elouchdi investigated the usefulness of dried activated sludge for the removal of copper ions from aqueous solutions(17).The objective of their work was to obtain the

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basic information to the design of sorption equipment, i.e. kinetic data and equilibrium in batch system. In this work, biosorption of copper from aqueous solutions, by dried activated sludge in single metal solutions was investigated in a well-stirred batch reactor. The equilibrium isotherm was determined by contacting a constant mass (0.2 g) of activated sludge with a range of different concentrations of copper solutions. The necessary time to reach this equilibrium was observed to be about 3 hours . Also, at equilibrium, about 60% of initial copper solution was removed by dried activated sludge. The pseudo second order reaction rate model adequately described the kinetics of copper sorption with high correlation coefficient ($R_2 > 0.986$). The capacity of copper removal at the equilibrium increases with the initial copper concentration. It was also observed that, with pH, the metal removal increases. As the pH is increased, there is a decrease of positive surface charge which results in a lower columbic repulsion of the sorbing metal ions. Also it can be explained by competition between the proton and metal cation for surface sites at low pH.

III.CONCLUSION

Activated sludge process has been used effectively for removal of heavy metals with maximum removal efficiency of 95 percent. Various parameters like contact time, pH, initial concentration have significant effect on the heavy metal removal. The uptake of metal followed pseudo first order and/or peudo second order kinetics on various studies. The metal removal, in many instances followed Langmuir and Freundlich isotherms. It can be concluded that activated sludge can be used effectively for heavy metal removal. The efficiency of removal can be increased by techniques such as immobilization and use of anoxic selectors.

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