

Adsorption of Metal Ions from Galvanised Wastewater: A Review

Latha.A¹, Thoshibhaah.R² & Panimalar.T³

Department of Civil Engineering, Panimalar Engineering College, Chennai-600 123

Abstract: Galvanized water was considered as a source of contamination like Chloride, copper, lead and zinc. While reuse of wastewater after treatment is as a new source of water supply for the agriculture is the world now. Wastewater effluent from galvanizing process, can be used as irrigation water after treatment. The metal ions are removed by adsorption process by using natural adsorbents like *Oryza Sativa*, *Arachis Hypogea*, *Prunus Dulcis*, *Citrullus Lanatus*, *Citrus Limon*. This paper deals with the reuse of the galvanized wastewater for the purpose of agriculture. BOD, COD, DO, TSS, TDS, PH, phosphate, nitrate and turbidity will be measured and investigated if it could be used for irrigation purposes. The measured data is used to compare with the environmental standards and environmental regulations to evaluate the possibility of using for irrigation. Investigation of galvanized water compared with after treatment. In the context of continuous droughts, the search for alternative water sources and increasing environmental restrictions on discharge of treated wastewater into natural water bodies, treated wastewater recycling offers a potential solution. In this paper the methods needed to assess the waste water in to agriculture water.

Keywords: Galvanised waste water, Natural adsorbent (*Oryza Sativa*, *Arachis Hypogea*, *Prunus Dulcis*, *Citrullus Lanatus*, *Citrus Limon*), Adsorption.

1. Introduction: High zinc can cause eminent health problems, such as stomach cramps, vomiting, skin irritations, anemia, and nausea [6]. Various methods are available to remove and isolate these heavy metals from water and wastewater such as ion-exchange, chemical precipitation, membrane filtration, adsorption, and electrochemical treatment technologies [7]. Adsorption is one of the safest, easiest, and most cost-effective methods because it is widely used in effluent treatment processes [8].

Galvanization is a method of applying a protective zinc coating to steel or iron for industrial use, in order to prevent rusting. There are two common galvanization methods i.e. Hot dip method and

Electrolytic methods. Pollution of environment by industrial effluent has been a major concern in recent years. The raw materials, variety of chemicals and metals and the technologies used are the primary factors determining the quality of released effluent of an industry.

The components of the effluent contributed to the characteristics of the effluent and capable of altering the physical, chemical and biological characteristics of receiving ecosystem. The study of the industry effluent helps to understand quality of effluent and its impact on ecosystem [1]. The ions in galvanized waste water are iron, lead, zinc, copper, HCL, ammonium and chloride.

Ammonium ions are the primary form of widespread nitrogen pollution in the hydrosphere and cause a remarkable increase of oxygen demand and biological eutrophication in local by aquatic sources [2] and results proved that increase in concentration of this beyond a permissible cause damage to aquatic life [3,4]. Hence, the removal of ammonium from municipal and industrial waste water prior to discharge is now obligatory. Many methods are being used to remove ammonium ions.

Chlorides are generally present in water in the form of NaCl. Chloride in concentration above 600mg/l tends to give water a salty taste. WHO specifies Highest desirable concentration of chloride in portable water must be 200ppm. Chloride attack is one of the most important aspects for consideration when we deal with the durability of concrete. In industries there are various methods adopted to produce potable water, of which, the adsorption process is a widely used phenomenon. Here for the removal of chlorine we are using *E. crassipes* (A natural adsorbent) and Amberlite (a synthetic adsorbent). The adsorption capacity is found out by Batch studies which include Effect of dosage, Effect of pH, Effect of initial concentration and Effect of contact time. And adsorption capacity is found out theoretically [5].

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One of the heavy metals that can cause many problems towards a human being and surrounding is Pb. The presence of Pb above the permissible level in industrial waste water can cause many effects to human being and environment. One of the methods commonly used to remove heavy metal like Pb from aqueous solution is adsorption [9].

Copper, an element which has been used by man for many years can be regarded as a longstanding environmental contaminant. Use of water that exceeds the permissible level over many years could cause liver or kidney failure [10]

“*Adsorption*” may be defined as the process of accumulation of any substance giving higher concentration of molecular species on the surface of another substance as compared to that in the bulk. When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate at the surface. The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption. “*Adsorption*” is a well-established and powerful technique for treating domestic and industrial effluents. In water treatment, the most widely method is “*Adsorption*” onto the surface of activated carbon. The substance that concentrates at the surface is called adsorbate. The material upon whose surface the adsorption takes place is called an adsorbent.

2. Adsorption:

2.1. Mechanism:

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as liquid-liquid, gas-liquid, gas-solid or liquid-solid interface. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. If the interaction between the solid surface and the adsorbed molecules has a physical nature, the process is called physisorption.

In this case the attraction interaction are vanderwaal forces and, as they are weak the process results are reversible. Further more, it occurs lower or close to the critical temperature of the adsorbed substance. On the otherhand, if the attraction forces between adsorbed molecules and the solid surface

are due to chemical bonding, the adsorption process is called chemisorption. Contrary to physisorption, chemisorption occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake. Under favorable condition, both processes can occur simultaneously or alternatively. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic.

In a solid-liquid system adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm.

3. Methods of treatment:

3.1. Removal of ammonium

The watermelon rinds were washed thoroughly with tap water and rinsed with distilled water to remove any impurities. Next the adsorbent material is cut into pieces and dried in an oven at 40°C for 48 hours to a constant weight. The stock solution is prepared by soaking in 1L NaOH solution, 1L KOH solution and 1L H₂SO₄ solution for 24 hours. The rinds were then further dried in an oven at 40°C for 48 hours. The synthetic ammonium solutions were used throughout the adsorption tests. First ammonium chloride salt with calculated weight and distilled water were used for the preparation of stock NH₃-N solution of 50mg/L. Then, the experimental solutions at the desired ammonium concentrations were prepared by diluting the stock solution with distilled water. The initial pH was adjusted to 7.0 using dilute solutions of NaOH throughout the experiment. All the samples were adjusted to the optimum pH prior to the addition of the adsorbent. The effect of pH, Contact time, initial concentration of metal ions and adsorbent dosage were noted.

3.2. Removal of copper

Rice husk and Groundnut shell were crushed separately and sieved to particle size of 0.6mm. The sieved adsorbents were washed with distilled water to remove dust and kept in an oven at 65°C for 24 hours to reduce the moisture content. Then these adsorbents were used for batch experiments. Stock solutions were prepared by dissolving 1g of copper turnings in 20ml Nitric

acid and then make up in to 1000ml. Different initial concentrations of metals ions were prepared by diluting the stock solutions. The pH was maintained using 0.1N HCl and 0.1N NaOH solutions. The experiments were carried out under constant shaking of 100ml of synthetic solutions in conical flasks using heavy rotatory shaking apparatus. Samples were withdrawn after a definite time interval and filtered through filter paper. The effect of pH, Contact time, initial concentration of metal ions and adsorbent dosage were noted.

3.3. Removal of zinc

Rice husk has good chemical stability, is insoluble in water, possesses a granular structure, and has high mechanical strength, which shows it is a good adsorbent material for removal of heavy metals from wastewater. Many heavy metal ions studied include Zn, Pb, Cd, Cu, Co, Au, and Ni. Rice husk in the form of either untreated or modified by different modification methods has been widely used to treat heavy metals. Sodium carbonate and hydrochloric acid, epichlorohydrin and sodium hydroxide, and tartaric acid are common chemical treatment methods of rice husk.

Rice husks pretreatment can remove hemicellulose and lignin, reduce cellulose crystallinity, and increase the surface area or porosity. In general, unmodified rice husk showed lower adsorption capacities on heavy metal ions than on treated or chemically modified rice husk. interference with adsorption property might happen due to using the base treatment NaOH to remove base soluble materials on the rice husk surface.

It has been studied rice husk ash with pretreatment for Zn²⁺ removals. It was found that 96.8% of Zn²⁺ removals were obtained at a pH value of 5. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both of the models were fitted well. The adsorption capacity was obtained at 14.30 mg/g at optimum pH 5.0.

Rice bran adsorbent is able to successfully adsorb the metal ions from aqueous solutions. Maximum efficiency of 72% for Zn²⁺ removal was observed in chloride medium and NaCl 0.1 mol/L has been used throughout the work. The effect of pH, Contact time, initial concentration of metal ions and adsorbent dosage were noted.

3.4. Removal of lead

The tea waste used were collected from the local restaurant and the peanut shells were obtained from local small peanut industry. Both the materials were washed in boiling water to remove any soluble and colored components and then washed with distilled water and were dried in oven for 12 hours at 100°C. The dried tea waste was sieved to 600µm particle size. Meanwhile, peanut shells were crushed and sieved to get 600µm particle size. Both materials were kept in sealed container prior to use. Infrared spectra were recorded using Bruker, Fourier Transform Infrared (FTIR) model Tensor 27 with OPUS 6.0 software. Samples were tested using Attenuated Total Reflectance (ATR) in powder form. Stock solution was prepared by dissolving in deionized water. Before mixing with adsorbent material, the pH was adjusted to 6.0 for adsorption of Pb ions by adding 0.1M NaOH or 0.1M HNO₃. The desired Pb ion concentration was prepared from the stock solution by making fresh for the adsorption experiments. 0.5g of adsorbent is weighed and was added to the Pb solution in a 100ml flask. The mixture was stirred at 160rpm for 60minutes. After 60minutes the solution is filtered with filter paper. The amount of Pb ions in the solution was estimated by atomic absorption spectrophotometry (AAS). The experiment is then repeated with 0.1g and 1.5g adsorbent. The effect of pH, Contact time, initial concentration of metal ions and adsorbent dosage were noted.

3.5. Removal of HCL

Often, synthetic sorbents (chloride guards) are used in the chemical industry to reduce HCl vapor levels to extremely low levels. These sorbents are usually sodium compounds (typically sodium carbonate) impregnated on a high surface area support such as alumina (~200 m²/g). The major drawback of these materials is that they are expensive (typically \$1 to \$2 per kg, resulting primarily from the high cost of the alumina support). This cost factor tends to preclude the use of commercial chloride guards in syngas applications.

As an alternative to the high cost of catalyst supports, several low cost and moderate surface area materials were considered as support media for the active ingredient, sodium carbonate. Such materials include (1) pyrolyzed rice hulls, (2) diatomaceous earth, and (3) sepiolite minerals. A bench-scale system is being used at SRI to determine the achievable residual HCl vapor level, the rate of chloride uptake as a function of time, and the maximum achievable chloride capacity of the adsorbents.

3.6. Removal of iron

Natural or synthetic zeolite can be used as a filtration material for removal of iron from water. Birm, Greensand, Pyrolox, and MTM are the most frequently used materials in filtration. Birm is a granulated filter medium (imported from the USA) used for iron and manganese removal from water. It is a specially developed material containing MnO_2 film on the surface (catalyst). It is recommended to use Birm for lower iron concentrations (to Fe^{2+} concentration of $6.0\text{ mg}\cdot\text{l}^{-1}$ and Mn^{2+} about $3.0\text{ mg}\cdot\text{l}^{-1}$) and for household water treatment. It can also be used in gravity or pressure filters. Contact with filter material results in oxidation of dissolved iron. Subsequently, precipitated Fe (pH of 8 to 9 is required for Mn removal) were easily removed by filtration. Filter medium is cleaned by backwashing. There is no need of chemical regeneration. In cleaning process the time of backwashing and wash water velocity are important factors. Long service life is also one of the advantages of this medium. Based on water analyses carried out during these tests, the iron concentration in raw water after aeration and sedimentation values are noted. Raw water passed through the filtration columns in downward direction and the average filtration rate was noted. The quality of raw water (Fe content) and treated water at outlets from separate filtration columns was monitored during the experiments. At the same time, the amount of water at inlets to filtration columns and water discharge at outlets from the columns were measured by water meter.

3.7. Removal of chlorides

Parthenium is considered to be one of the ten worst weeds in the world, using this weed the removal of chloride was done. Collection of sample was done on the basis of the health of the plant through visual observations. Young plants having a fresh green shoot and sizable stem thickness were selected. On collection, the specimens were washed with tap water and then distilled water. Further, for biomass collection, the specimens were subjected to drying in an oven at 500°C for two days. Drying was followed by careful crushing of the specimen, and then sieving the mixture through a 500-micron sieve. The obtained biomass was used for the study. The biomass was added to the test solutions in the ratio of 0.10 g: 100 ml test solution. The pH of the sample was maintained at 7, and the chloride concentration at 100% of the initial wastewater solution. The mixture was then incubated in a rotary shaker incubator at 150 rpm and 300°C for 60 minutes. On the termination of contact time, the solution was filtered using an ordinary filter paper.

The sample was titrated for chloride content using the argentometric titration. The tests were repeated by carrying out variations in pH, by using different chloride concentration levels, and with variable contact time.

4. Factors on which adsorption depends

4.1. Temperature:

Adsorption increases at low temperature conditions. Adsorption process is exothermic in nature. According to Le Chatelier principle, low temperature conditions would favour the forward direction.

4.2. Pressure:

As depicted by adsorption isotherm, with the increase in pressure, adsorption increases upto a certain extent till saturation level is achieved. After saturation level is achieved no more adsorption takes place no matter how high the pressure is applied.

4.3. Surface area:

Adsorption is a surface phenomenon, therefore it increases with increase in surface area.

5. Advantages of adsorption method:

- Low energy demand.
- Low land required.
- Low sludge production.
- Less expensive than other anaerobic processes.
- High organic removal efficiency.
- Can be recycled, regenerated and reused.
- Easy operating conditions.
- High metal-binding capacities.
- Wide pH range.

6. Conclusion:

There were many methods carried out to remove metal ions from industrial waste water out of which adsorption process is the best and economical method and has more advantages over other methods. In adsorption method, the use of inactivated biomass as adsorbents offers an attractive potential alternative to their conventional methods. Natural bioadsorbents can offer an economical solution for metal removal. Among various waste water treatment technologies, the adsorption process is considered better because of lower cost, simple design and easy operation.

Although many techniques can be employed for the treatment of wastewater loaded with heavy metals, it is important to note that the selection of the most suitable treatment for metal-contaminated wastewater depends on some basic parameters such as pH, initial metal concentration, the overall treatment performance compared to other technologies, environmental impact as well as economics parameter such as the capital investment and operational cost. Finally, technical applicability, plant simplicity and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment system for inorganic effluent.

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