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Treatment of Galvanized Waste Water by Membrane Distillation with Natural Adsorbent: A Review

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ABSTRACT
Wastewater containing high concentrations of metal ions can be harmful to aquatic life and degrade the water quality. The metal ions are removed by Adsorption and Membrane distillation process. However, these methods are less effective and relatively expensive. Therefore, there is a need for alternative technologies to improve the efficiency of metal ions removal from wastewater. This study deals with the process of removal of metal ions from galvanized waste water through a combination of adsorption in the membrane contactor and biological treatment. The parameters pH, COD, BOD, Adsorbent dosage and contact time is tested in the galvanized waste water. Oryza sativa, Arachis hypogea, Prunus dulcis, Citrullus lanatus, Citrus limon are used as a natural absorbent to treat the water before Membrane distillation. In this experiment, the wastewater from the galvanized industry was firstly collected and treated to remove the heavy metal ions present in the waste water. The treated water is finally utilized for irrigation purpose.
Keywords- *Galvanized waste water, Natural adsorbent (Citrullus Lanatus, Oryza Sativa, Arachis Hypogea, Citrus Limon) Membrane distillation, Adsorption.*

1. INTRODUCTION

Galvanizing is always carried out in an industrial works which contains all stages of the process. The galvanizing industry has set targets for energy efficiency and encouraged improved energy management and new technology to achieve these targets. As a step of effective utilization of water resources reuse of industrial waste is an important one in many places, industrial waste water has been directed into open ground. This waste water is hazardous to all life [1]. The ions present in galvanizing industrial waste are iron, lead, zinc, copper, HCL, ammonium and chloride.

Ammonia is characterized as a colorless, pungent, and a Corrosive gas in nature and is one of the abundantly found Nitrogen containing compounds in the atmosphere after Nitrogen and nitrous oxide [2,3]. There are several conventional methods to remove ammonia from wastewater such as aeration in pack tower, biological treatment[4] and adsorption as ammonium ion into the surface of zeolite [5]. However, these methods almost always depend on relatively high energy consumption[6]. One technology that can be used for ammonia removal from wastewater is a membrane technology. Membrane contactor is a contactor device for mass transfer in liquid-liquid systems and gas-liquid without mixing of these phases [7].

Chloride in concentration above 600mg/l tends to give water a salty taste. The concentration of chloride content above 200mg/l is considered objectionable. Presence of high quantity of chloride content in water resources indicates pollution due to human and industrial wastes and also from the earthen rocks in the subsurface [8].

Iron is normally found in spent pickle and etch baths from plating shops, steel mills, foundries, chemical milling, and wire drawing operations. It is also found in ground water. Iron in water is normally found in the ferrous state or iron 2. The ferric state or iron 3 is very insoluble at neutral pH's. Both the iron 2, ferrous, and iron 3, ferric, can be precipitated to low concentrations by pH adjustment, carbonate, phosphate and sulfide precipitation. Iron 2 can easily be converted to iron 3 by aerating the water allowing the precipitation to take place at a neutral pH.

One of the heavy metals that can cause many problems toward a human being and surrounding is Pb (II). The use of Pb in service pipes can cause the problem of Pb (II) pollution. The battery industry, auto exhaust, paints, ammunition and the ceramic glass industries are other sources of Pb (II) pollution [9]. The permissible level of lead (II) in drinking water and wastewater is 0.05 mg/L- 1 as given by the Environmental Protection Agency (EPA). Meanwhile, the level of lead (II) permitted by Bureau of Indian Standards (BIS) is 0.1 mg/L [10].

Copper is a transition metal that is stable in its metallic state. The effect of toxic copper entering the body may lead to gastrointestinal bleeding, food poisoning (headache, nausea, and diarrhea) [11].

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of theabsorbent. Adsorption offers significant advantages like low cost, availability, profitability easy of operation and efficiency, in comparison with conventional methods (such as membrane filtration or ion exchange) especially from economic and environmental points of view [12,13]. The main advantage of this method is there is no sludge formation.

2. METHODS OF TREATMENT

2.1. REMOVAL OF AMMONIUM BY USING CITRULLUS LANATUS

The removal of ammonium process will start from adsorption method by using natural adsorbent. Watermelon rinds for the removal of ammonium from waste water were collected from market area. The rinds were washed with tap water and rinsed with distilled water to remove impurities [21]. Next, the samples were cut into small pieces (around 1 to 2 mm) and dried in an oven at 40°C for 48 hours to a constant weight. For chemically modified adsorbent, the material was soaked in 1 L NaOH solution (20mmol/L), 1 L KOH solution (20mmol/L) and 1 L H_2SO_4solution (20mmol/L) respectively for 24 hours. The watermelon rind was then dried further in an oven at 40°C for 48 hours. Synthetic ammonium solutions were used throughout the adsorption tests. First, ammonium chloride salt (NH_4Cl) mixed with distilled water were used for the preparation of a stock NH3-N solution of 50 mg/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 (0.1 N) throughout the experiments. Prior to the addition of adsorbents all the samples were adjusted to optimum pH value. In order to determine the residual concentration by using UV-Spectrophotometer at maximum wavel-ength of 425nm, the solution was taken at certain intervals. Hence, the amount of ammonia nitrogen is adsorbed at equilibrium [22].

2.1.1. MEMBRANE DISTILLATION

Then the stock solution is subjected to filtration method. Polyvinyledenefluorid (PVDF) hollow fiber membrane were prepared by spinning polymer dopes consisting of K-760 PVDF polymer and lithium chloride (LiCl) as additives. waste water containing ammonia were diluted by the distilled water and the waste water is added with sodium hydroxide in order to maintain the pH of the solution. Before starting the process, ammonia concentration in the solution was measured using Ammonia Meter. The ammonia solution pumped to the membrane at the concentration of 800ppm and valve is used to control the flow of water. Then water was flow over the hollow fiber membrane. On the other hand, vacuum gas and strip gas is applied to the inside of membrane. Because of the membrane is hydrophobic it acts as an inert support which allows direct contact between a gas and liquid phase without dispersion. zeolite powder addition was performed to enhance attached microbial growth as well as to get higher ammonia removal. The solution was continuously recycled at a high pressure at the same time the ammonia which is separated from the solution was collected through the outside of membrane. Finally, the concentration of ammonia after filtration measured by the ammonia meter [14].

2.2. REMOVAL OF CHLORIDE

The adsorbent, for this experiment, is prepared in the form of activated carbon. As the raw material for the preparation of activated carbon is an aquatic weed, the production of this carbon is economically feasible. The water hyacinth plants are collected from a nearby pond. It is then sundried for about one week. The plants are then washed several times with clean water to remove the dirt, mud, mosses, etc. Subsequent washing with distilled and double distilled water are also done to remove the tedious material. It is then dried. Acid Activation: About 25 grams of this material is treated with 20ml of concentrated sulphuric acid and the charred material was kept overnight. The charred material is heated in an oven at 100˚C for about 4-6 hours. This is cooled and washed with distilled water to remove any trace of acid, so that the pH ranges between 6 and 8, which is suitable for the determination of chloride by argentometric method. The main purpose of acid activation is to ensure a highly protonated surface on the adsorbent material. Higher adsorption rate of chloride in the acidic range can be explained by the surface charge of the adsorbent. By acid treatment the surface of the adsorbent is highly protonated and hence more chloride can be attracted to the surface of the adsorbent. High chloride sorption rate in the acidic medium is contributed due to strong columbic forces between positively charged surface and negatively charged chloride ions. Hence acid activation ensures higher efficiency in the removal of chloride ions. Thermal activation is done in order to prepare activated carbon with a definite pore structure possessing efficient adsorption capacity. The activation provides a material of high surface area and strong sorption capacity towards various adsorbates. A large surface area increases the adsorption rate, which is ensured only due to thermal activation.

2.3. REMOVAL OF COPPER BY USING ORYZA SATIVA

Rice husk were collected from Rice Mill. The rice husk was burned at controlled temperature using a microwave incinerator at 500°C and 800°C to produce microwave incinerated rice husk ash. Then it was soaked in 10% hydrochloric acid (HCl) for 24 hours and then washed with distilled water thoroughly to remove excessive acid until the water from the residue reached pH 4. Therefore, adsorption would be dominant process when pH is less than 6. It also can be noted that at low initial pH, the removal of Cu(II) is less and vice versa. This happened due to the competition between the H_3O^+ ion and Cu^{2+} ion to fill the surface of the adsorbent.

2.4. REMOVAL OF IRON

The mechanism underlining the physico-chemical iron removal has always been considered to be the oxidation of soluble Fe(II), leading to the formation of flocs of iron(III) hydroxide precipitates, which is subsequently removed by sand filters. This process is termed as “oxidation- floc formation”. The possibility of iron(II) being adsorbed onto surfaces of coated filter media, proceeded by quick oxidation of the Fe(II) to Fe(III) hydroxides in the system has also been identified, known as the “adsorptive filtration” mechanism. The two processes that predominate in filters, they may occur concurrently during the deferrisation process. The addition of oxidants to the raw water becomes necessary on rare occasions in Denmark, where ground water contains contaminants that are difficult to be oxidized by simple aeration. When this happens, then oxidants such as ozone or potassium permanganate may be employed under permission from the Danish environmental authorities.

Fill the container about half way or more with distilled water, add the acid, and then bring up to volume with more water. In the example above, fill a flask with about 150ml or more with distilled water, add 6.9ml of concentrated sulfuric acid, then continued to dilute with water to the 250ml mark.

2.5. REMOVAL OF LEAD BY USING ARACHIS HYPOGEA

Peanut shells were collected. The peanut shells washed with boiling water to remove any soluble and colored components. Both materials were then washed with distilled water and were dried in oven for 12 hours at 100 °C. The dried tea waste was sieved to obtain 600 µm particle sizes. Meanwhile, peanut shells were crushed and sieved to get 600 µm particle sizes too. Both types of adsorbents 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. The scans were carried out from 400 to 4000 cm^{-1}. FTIR spectra can showed appropriate transmittance of functional group. A stock solution of Pb (II) (1000 ppm) was prepared by dissolving $Pb(NO_3)_2$ in deionized water[18]. Before mixing with the adsorbent material, the pH of each solution was adjusted to 6.0 for the adsorption of Pb (II) ions, by adding 0.1M NaOH or 0.1M HNO_3. The desired Pb (II) ion concentration was prepared from the stock solution by making fresh for the adsorption experiments. Adsorbent dose 0.5 g of adsorbent is weighed and was added to the Pb (II) solution in a 100 ml Erlenmeyer flask. The mixture was stirred at 160 rpm for 60 minutes. After 60 minutes, the solution is filtered with filter paper [23]. The amount of Pb(II) ions in the solution was estimated by atomic absorption spectrophotometry (AAS) at a 283.3 nm wavelength. The experiment is then repeated with 1.0 g and 1.5 g adsorbent. The Pb (II) solution was put into a 100 ml Erlenmeyer. Then, 1.0 g of adsorbent was added into the solution. The mixture was stirred at 110 rpm at different duration which is 30, 60, 90 minutes. Then, the solution was analyzed by using AAS to measure the adsorption of Pb (II). The adsorption percentage (removal (%)) of pb. The percentage removal by the Arachis hypogia is 74.57% at the dosage of 1g peanut shell [19].

2.6. REMOVAL OF ZINC BY USING CITRUS LIMON

Lemon peel was collected and washed with distilled water and it is dried for some time. The prepared bio adsorbents is added to the waste water and thus the stock solution is prepared. The removal of zinc ion involves batch adsorption. The solution is stirred at 30˚C at medium rpm. Finally, the filtrate is collected and the parameters like pH , adsorbent dosage, temperature, contact time are determined.

3. BENEFITSOFMEMBRANE DISTILLATION

- This process is Flexible; can be used in the separation, concentration and purification of a huge variety of materials across a wide range industry
- No phase changes involved, both feed and product streams remain the liquid form.
- The process can function effectively at low temperature. Energy requirements are low.
- Process are relatively simple to scale up**.**
- Membranes can be manufactured in a uniform and highly precise manner.

4. BENEFITS OF ADSORPTION

- Easy to carry out.
- No reagents are required are required.
- Maximum activation steps involved.
- Comparatively cheap method of immobilization.
- Less disruptive to enzyme than chemical methods.
- Easily desorbed, simple and cheap, enzyme activity unaffected.

5. CONCLUSION

This paper concluded saying that galvanized waste water can be treated and reused by advanced method of Membrane distillation and Adsorption method by using natural bio adsorbents which helps to reduce the parameter level which will satisfy the required need of reuse of water.

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