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A REVIEW ON REMOVAL OF HEAVY METALS BY USING LOW COST ADSORBENTS WITH REFERENCE TO ELECTROPLATING INDUSTRY

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ABSTRACT
The industrial wastewater from silver processing at Hupari is not provided with any treatment system for removal of heavy metals. Same wastewater is discharged to the sewage system and any sewage system has not any provision of removal of heavy metal. The issue of heavy metal pollution is very much concerned because of their toxicity for plant, animal and human beings and their lack of biodegradability. Excess concentrations of heavy metals have adverse effects on plant metabolic activities hence affect the food production, quantitatively and qualitatively. Heavy metal when reaches human tissues through various absorption pathways such as direct ingestion, dermal contact, diet through the soil–food chain, inhalation and oral intake may seriously affect their health. .The greatest damage to the environment is made by metal compounds that are washed out in wastewater from the electroplating industry.

INTRODUCTION
Water pollution caused due to addition of heavy metals resulting from the industrial activities is increasing tremendously and is a matter of global concern. [1] Mining, mineral processing and metallurgical operations are generating effluents containing heavy metals. The heavy metals present in the wastewater is persistent and non-degradable in nature. The heavy metals, if absorbed above the permissible labels, could lead to serious health disorders. In light of the facts, treatment of heavy metals containing industrial effluent becomes quite necessary before being discharged into the environment The conventional methods for heavy metal removal from wastewater includes chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electro dialysis etc. These methods are not very effective, are costly and require high energy input. Adsorption to be easiest, safest and most cost-effective methods for the treatment of waste effluents containing heavy metals.

1.1 Adsorption
Adsorption has emerged out as effective, economical and ecofriendly treatment technique. Adsorption is basically a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions [5]. It is a partition process in which few components of the liquid phase are relocated to the surface of the solid adsorbents. All adsorption methods are reliant on solid-liquid equilibrium and on mass transfer rates. The adsorption procedure can be batch, semi-batch and continuous. At molecular level, adsorption is mainly due to attractive interfaces between a surface and the group being absorbed.

1.2 Physical adsorption
It is a general incident and occurs in any solid/liquid or solid/gas system. Physical adsorption is a process in which binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction. The electronic structure of the atom or molecule is hardly disturbedupon physical adsorption. Van der Waals forces originate from the interactions between induced, permanent or transient electric dipoles. Physical adsorption can only be observed in the environment of low temperature and under appropriate conditions, gas phase molecules can form multilayer adsorption. Commercial adsorbents utilize physical adsorption for its surface binding.

1.3 Chemical adsorption

It is a kind of adsorption which involves a chemical reaction between the adsorbent and the adsorbate. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds (Covalent, Ionic). Chemical adsorption is also referred as activated adsorption. The adsorbate can form a monolayer. It is utilized in catalytic operations. In general, the main steps involved in adsorption of pollutants on solid adsorbent are: Transport of the pollutant from bulk solution to external surface of the adsorbent. Internal mass transfer by pore diffusion from outer surface of adsorbent to the inner surface of porous structure. Adsorption of adsorbate on the active sites of the pores of adsorbent. The overall rate of adsorption is decided by either film formation or intra particle diffusion or both as the last step of adsorption are rapid as compared to the remaining two steps.

1.4 Low cost adsorbents

The removal of heavy metals by using low cost adsorbent is found to be more encouraging in extended terms as there are several materials existing locally and profusely such as natural materials, agricultural wastes or industrial by-products which can be utilized as low-cost adsorbents [6]. To be commercially viable, an adsorbent should have high selectivity to facilitate quick separations, favorable transport and kinetic characteristics, thermal and chemical stability, mechanical strength, resistance to fouling, regeneration capacity and low solubility in the liquid in contact. Adsorption process has several advantages over the conventional methods of heavy metal removal. Some of the gains of adsorption process are: (I) Economical, (II) metal selectivity, (III) Regenerative, (IV) Absence of toxic sludge generation (V) metal recovery and most importantly (VI) effective. Various low cost adsorbent derived from various natural as well as anthropogenic sources have been implemented for treatment of waste water contaminated with heavy metals. The adsorbents mostly used are agricultural waste, industrial byproducts, natural materials or modified biopolymers

Relevance:

The composition of wastewater generated from the electroplating industry typically includes washing waters (diluted effluents) and concentrated solutions (pickling, washing, degreasing, chrom- and cyano-containing electrolytes).The greatest damage to the environment is made by metal compounds that are washed out in wastewater from the electroplating industry. For example, cyano-containing effluents contain free sodium cyanide (potassium), complex cyanide salt of zinc, cadmium, copper and other metals, as well as salts of alkali and alkaline earth metals. Wastewater from electroplating facilities using chromium contain hexavalent and trivalent chromium, ions of metal, copper, nickel, zinc and sulfuric acid. Cadmium compounds, even in relatively small quantities, have a dramatic negative impact on fish and other inhabitants of fresh and saltwater resources. Other negative effects of heavy metals are also well-studied. They can enter the human body through food and water and can cause the pathogenesis of liver disease, heart disease, brain cancers.

The production of silver ornaments at Hupari, many chemical processes are involved. Liquid waste of these chemical processes is directly released in the gutters. Therefore, an attention be given to the release of wastewater and a study is needed as it results into water pollution which affect the environment.

The issue of heavy metal pollution is very much concerned because of their toxicity for plant, animal and human beings and their lack of biodegradability. Excess concentrations of heavy metals have adverse effects on plant metabolic activities hence affect the food production, quantitatively and qualitatively. Heavy metal when reaches human tissues through various absorption pathways such as direct ingestion, dermal contact, diet through the soil–food chain, inhalation and oral intake may seriously affect their health. Therefore, several management practices are being applied to minimize metal toxicity by attenuating the availability of metal to the plants. Some of the traditional methods are either extremely costly or they are simply applied to isolate contaminated site. Thus, the present review deals with different management approaches to reduce level of metal contamination in soil and finally to the food chain.

The common physicochemical treatment processes for metal remediation in water include: Precipitation, ion exchange and reverse osmosis. These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy consumption, and generation of toxic sludge or other waste products that require disposal or treatment

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Biosorption is a process that utilizes low-cost biosorbent to sequester toxic heavy metals. Biosorption has distinct advantages over the conventional methods, which include reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time and no chemical sludge. In the recent years many bio sorbent materials of agricultural based have been utilized for heavy metal biosorption. These include: coconut husk and shell, sea weeds, bagasse ash, hazelnut shell, peanut hull, tree fern, black gram husk, maize leaf, maize, sun flower waste, coffee beans, Ficusreligiosa leaves, wheat bran, almond shell, tea waste.

2 LITERATURE REVIEW:

1. AshutoshTripathi (2015) studied worldwide trend to achieve higher environmental standards favors the usage of low cost systems for treatment of effluents. In the meantime various low cost adsorbent derived from agricultural waste or natural products have been extensively investigated for heavy metal removal from contaminated wastewater. It has been found that after chemical or thermal modifications, agricultural waste exhibited tremendous heavy metal removal capability. Concentration of adsorbate, extent of surface modification and adsorbent characteristics are the factors responsible for metal adsorption capability. Cost effectiveness and technical applicability are the two important key factors for selecting effective low cost adsorbent for heavy metal removal.

2. A.K. DWIVEDI (2013) studied methods currently employed to remove and recover the metals from our environment and many physic-chemical methods have been proposed for their removal from wastewater. Adsorption is one of the alternatives for such cases and is an effective purification and separation technique used in industry especially in water and wastewater treatments. Cost is an important parameter for comparing the adsorbent materials. Therefore, there is increasing research interest in using alternative low-cost adsorbents. The use of tea waste as the low-cost adsorbents was investigated as a replacement for current costly methods of removing heavy metal ions from aqueous solutions. The experiment results showed that maximum removal of copper and cadmium ion by tea waste is 89% and 87% respectively at optimum condition.

3 Dr. Monika Singh (2016) This author studied characteristics of the waste stream from electroplating industries are so toxic and corrosive due to the presence of these heavy metals. The paper focuses on various easily available methods as chemical precipitation, low cost novel adsorption through coconut shell, mango seed and shell, bagasse, waste tea leaves, wood barks and user soil, membrane processes, which are capable of 90% -100% removal of these metals, bioremoval methods, removal by minerals and removal by newer technique as semiconductor photo catalysis technology.

4 Hala Ahmed Hegazi(2013)had discussed in adsorption process, Activated carbon is extensively used as an adsorbent to remove heavy metals from water or wastewater stream. However, it is used in large amount for treatment of waste water, it is more expensive. In recent years, Searching for low cost alternative is necessitated to treat the waste water. Our objective is to study the utilization feasibility of less expensive materials like industrial by-product and agricultural waste as an adsorbent to exclude the heavy metals from waste water effluent. For that, waste water had been collected from EL – AHLIA Company for electroplating industries. Then after, it was treated by using rice husk and fly ash and heavy metal removal efficiency would be checked. It reviews, Risk husk can be fruitfully used to eliminate Fe, Pb, Ni and Fly ash can be effectively used to remove Cd and Cu. It was also concluded that the percentage removal of heavy metals was dependent on the dose of low cost adsorbent and concentration of adsorbate. For heavy metal adsorption, the optimum pH range was 6-7.[3]

5 I Nhapi (2013) studied that adsorbents Carbonized Rice Husk (CRH) and Activated Rice Husk (ARH) made out of rice husks, available as agriculture waste, are investigated as viable materials for treatment of Pb, Cd, Cu, and Zn containing industrial wastewater at controlled pH. The results obtained from the batch experiments revealed a relative ability of the rice husk in removing some heavy metals at pH 7. One hand one, the CRH adsorption capacity decreases in the order of Cu >Pb> Zn > Cd in batch adsorption whereas during Rapid Small Scale Column Tests the adsorption capacity decrease as follow Cu> Zn>Pb> Cd. On the other hand, ARH adsorption capacity performance is similar to CRH. However, during Rapid Small Scale Column Tests the adsorption capacity decreases in the order Zn>Cu>Pb>Cd. The kinetic removal in batch experiment shows that the net uptake of Pb, Cd, Cu, Zn was 54.3%, 8.24%, 51.4% and 56.7%, respectively whereas using CRH, while it varied as 74.04%, 43.4%, 70.08% and 77.2% for the same dosages of ARH. Therefore, it is concluded that as regards to CRH, ARH demonstrated higher potential to remove relatively all selected heavy metals.

6 Jou-Hsuan Ho1 (2013) studied the adsorption capacity of eggshells with membrane (ESWM), eggshell membrane (ESM), and eggshells (ES) for the removal of nickel and silver ions in synthetic wastewater. Reaction time (1 to 72 h), metal ion concentration (25 to 200 mg/L), adsorbent dosage (0.1 to 0.8 g/20 mL), temperature (15℃ to 45℃), and pH (1 to 9) were evaluated. Post-treatment nickel and silver concentrations were later analyzed using a spectrophotometer. Our results indicated increased removal of nickel and silver ions with increased adsorbent (all three ESWM, ESM, and ES) dosage, whereas the removal of nickel and silver ion decreased with increasing initial metal concentration. Among ESWM, ESM, and ES, ESM has the highest removal capacity and was the best adsorbent. The 0.8 g of ESM could remove 90.91% of nickel ions (100 mg/L) at 25℃, pH 5.76 and 24 h. On the other hand, approximately 100% of silver ions (25 mg/L) could be removed by 0.2 g of ESM at 25℃, pH 5.2, and 24 h. There was no difference in the adsorbability of ES and ESWM on nickel and silver ions. In summary, all three adsorbents, ESWM, ES, and ESM, can remove heavy metal ions from aqueous solution, with ESM having the highest efficiency. Hence, eggshell and its derivatives can be promising 'green' adsorbent materials for treating wastewater containing nickel and silver ions.

7 Jabbar H. Al-Baidhanistudied aims to evaluate the performance efficiency of the proposed adsorbent (rice husk). The adsorptive capacity and removal efficiency of the rice husk were evaluated for the removal of heavy metals of (Cd, Pb and Cr) from aqueous solutions. The results showed the following removal efficiencies: (97.96% for Cd, 90% for Pb, and 84% for Cr). Adsorbent loading capacities for cadmium determined by batch studies were verified through continuous column experiments (fluidized bed). It was found that the maximum adsorption capacity of the candidate adsorbent (5.54) mg/g in Cd batch system. A set of equilibrium isothermal experiments were conducted and fitted with two models; Langmuir and Freundlich. The equilibrium isotherms of rice husk were found to be of a favorable type and Freundlich isotherm model gave the best fit to represent the experimental data of this system with correlation coefficient equals to 0.9934. Eleven continuous experiments were carried out in fluidized bed column to study the effect of initial concentrations, bed depth and flow rate on the performance of adsorption process. Also it was made a comparison between the efficiency of the rice husk adsorbent in removing of Cd(II) with the well-known adsorbent of activated carbon in continuous fluidized bed process. The results proved that the rice husk to be an efficient and economic adsorbent for the removal of different heavy metals from wastewater.

8 Jitendra Singh Raghuwanshi1, Prof. NavneetaLal2(2018) investigated adsorption efficiency of tea waste towards the removal of copper. Batch experiment was performs for the removal of copper by using tea waste as adsorbent. Various process parameters studied like effect of bio-sorbent dose, contact time, pH, and effect of various initial copper concentrations. Adsorption methods show the maximum removal of copper was found to be 84% at pH 5 with initial copper concentration, 20 mg/l and 0.5g/100 ml tea waste amount use. The equilibrium uptake was attained within 180 min at 300c temperature. According to experiment result indicate that tea waste could be successful employed as effective low-cost adsorbents for removal of copper from aqueous solution

9 Khalid M. El–Moselhystudied rice husk was used as a low cost adsorbent to remove copper and cadmium ions from wastewater by batch method. The effects of pH, initial adsorbent concentration, contact time, initial metal ion concentration and temperature were studied. The experimental data were agreement with the pseudo-second-order kinetic model; and analyzed by Langmuir and Freundlich isotherm models to investigate the adsorption of copper and cadmium ions on rice husk. The adsorption

mechanisms of metal ions onto the rice husk were examined using: Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FT-IR). As a conclusion, rice husk could be one of the low cost and effective adsorbent to be used in large amount operation of water treatment.

10 LokendraSingh (2015) studied that Tea waste is a cheap and effective adsorbent for the removal of Cu, Zn and Ni ions from wastewater without requiring any pretreatment. Experiment results showed that maximum removal of Nickel ion by tea waste at optimum condition (5 pH, 120 min. contact time, 0.5g/100ml adsorbent dose and 20ppm concentration) is 94% and for Copper & Zinc ion are 89% & 91% respectively at optimum condition (5 pH, 120 min. contact time and 0.5g/100ml adsorbent dose, 10ppm concentration). These experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.

11 Maitri M. Raval1(2017)studied adsorption method has been proved to be one of the best alternatives for collection of heavy metals from industrial effluent and is as efficient as conventional methods. In this article, an attempt has been made to use two alternatives as an adsorbent- activated carbon and pumpkin to treat the metal contaminated industrial waste water. The efficiency of heavy metal removal was checked by monitoring effluent quality parameters like BOD, COD, pH and intensity of heavy metal. It was very difficult to arrange the industrial waste water containing heavy metals, so he prepared the synthetic waste. It was found from the experimental work that pumpkin power is as efficient as activated carbon in heavy metal removal and hence can be used as more economical option for removing heavy metal from industrial effluent. Low cost as compared to activated carbon and it is easily available in nature, the pumpkin should be introduced in the industries as a better alternative of activated carbon to eliminate lead from effluent. The recent running rate of activated carbon is 900-1000 Rs. /kg and pumpkin cost is 70 Rs. /kg, excluding the cost of man power or machinery used. As per the industrial effluent, the most optimum material should be used by the industries to keep our environment safe and healthy and the pumpkin is fitted into that category.

12 M.A. Barakat *(2010)this author studied the recent developments and technical applicability of various treatments for the removal of heavy metals from industrial wastewater. A particular focus is given to innovative physico-chemical removal processes such as; adsorption on new adsorbents, membrane filtration, electro dialysis, and photo catalysis It is evident from survey that new adsorbents and membrane filtration are the most frequently studied and widely applied for the treatment of metal-contaminated wastewater. Although many techniques can be employed for the treatment of wastewater laden 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 costs.

13 Prabha R.T.1 in this paper the batch experiments were conducted to know the influence of various parameters of adsorption on removal of lead metal ions by agricultural byproducts (Groundnut shell, Rice husk and combined adsorbents). It has been found that the percentage of adsorption increases with increase in pH (in acidic range) and decreases with the increase in metal ions concentration. Equilibrium time required for the adsorption of lead by agricultural byproducts was found to be 2 hrs. The obtained results showed that the adsorption of lead by rice husk and Groundnut shell are of second order reaction.

14 Sandeep Chauhan studied that Effluents of many industries like chemical manufacturing, paper, textile, refinery, petrochemicals, metal manufacturing, electroplating, printing, dye, paint, leather goods manufacturing, fertilizer and pesticides and many more are loaded with various heavy metals and their ions. Most extensively investigated and used such materials include low cost, eco-friendly and abundant waste biomaterials including chitin, chitosans and cellulosics various forms. Rice is most widely eaten food that fulfils the food needs of half the world’s population. Many research groups have evaluated unmodified rice husk for removal of toxic heavy metal ions. In order to enhance sorption abilities of rice husk for metal ions, many other groups have used various modifications of rice husk. This review will summarise some latest developments using rice husk and its derivatives for removal of heavy metal ions.

15 R.A. Williams(2007) studied on the studied to enable comparison with alternative commonly available absorbents. Batch experiments were conducted to determine the factors affecting adsorption and

kinetics of the process. Fixed bed column experiments were performed to study practical applicability and breakthrough curves were obtained. Tea waste is capable of binding appreciable amounts of Pb and Cu from aqueous solutions. The adsorption capacity was highest at solution pH range 5–6. The adsorbent to solution ratio and the metal ion concentration in the solution affect the degree of metal ion removal. The equilibrium data were satisfactorily fitted to Langmuir and Freundlich isotherms. Highest metal uptake of 48 and 65 mg/g were observed for Cu and Pb, respectively. Pb showed higher affinity and adsorption rate compared to Cu under all the experimental conditions. Kinetic studies revealed that Pb and Cu uptake was fast with 90% or more of the adsorption occurring within first 15–20 min of contact time. The kinetic data fits to pseudo second order model with correlation coefficients greater than 0.999. Increase in the total adsorption capacity was observed when both Cu and Pb ions are present in the solution. Higher adsorption rate and the capacity were observed for smaller adsorbent particles. Tea waste is a better adsorbent compared to number of alternative low cost adsorbents reported in literature

PROBLEM DEFINITION:

As seen in per the literature review study of research work has been carried out on the removal of heavy metals from the industrial wastewater. The industrial wastewater from silver processing at Hupari is not provided with any treatment system for removal of heavy metals. Same wastewater is discharged to the sewage system and any sewage system has not any provision of removal of heavy metal.

Objectives:

1. Analyzing the industry wastewater for selection of heavy metals for study purpose.
2. Experimental study is carried on adsorbents which are chemically modified by using acid like tea waste, rice husk for Industrial wastewater containing selected heavy metals.
3. Assement and finalization of adsorbent for optimum treatment of industrial Waste Water.
4. Application of optimize Dosage ofadsorbents on the industrial wastewater.

Methodology:

Work Plan:

1. Review of literature related to project.
2. To study the wastewater flow in the Hupari village and its start point and the end point of the raw wastewater.
3. To do the sampling of the wastewater from Hupari silver cluster drainages.
4. To analyses the parameters of the raw wastewater in the laboratory.
5. After analyzing the parameters the preparation of synetic wastewater containing heavy metals in laboratory.
6. Treating the synetic wastewater by various combination of natural adsorbents and finding out the best combination.
7. To give the proposal treatment option to the Hupari silver cluster association.
8. Preparation of the report

Activity chart:

Phase	Detail	Time
I	**Literature survey:** • Survey of existing literature in the heavy metal removal from the wastewater.	July – September, 2018
II	**To conduct the laboratory work to analyze the wastewater characteristics.**	October 2018 – Nov, 2018
III	**Experimental study of adsorbents and results**	Dec – Feb , 2019
IV	**Conclusion and report preparation**	March – May, 2019

Cost estimation:
approximate Rs.5000
For Glass and silver sampling

Resources required:
1. Heavy metal detection by using AAS (atomic absorption spectrometer
2. Internet facility
3. Library and digital library

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