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Removal of Heavy Metals Using Adsorbents at Low Cost

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Abstract – The heavy metals discharged in industrial waste water are having toxic properties and may become harmful for biotic environment, animals &humans. Due to a variety of industrial processes these heavy metals are released into the environment by industrial waste water. Some of the industries like battery, mining, electroplating, electronic equipments, etc. use Lead, Zinc, Nickel, Cadmium, Chromium and Copper heavy metals which are having the acute toxic nature. These heavy metals impart various detrimental health and environmental effects due to their presence in waste water. The removal of heavy metal ions from wastewater is critical for environmental and human health reasons. Heavy metal ions were removed from various wastewater sources using various documented procedures. Treatments based on adsorption, membranes, chemicals, electricity, and photo catalysis are among the options.

Keywords – Removal, Heavy Metals, Adsorbents, Low Cost and Adsorption etc.

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INTRODUCTION

As industry and human activity has grown, the amount of heavy metals in wastewater has increased, including plating and electroplating, batteries, pesticides, the rayon and metal rinse processes of the tanning industry and fluidized bed bioreactors in the textile industry as well as metal smelting and paper manufacturing. Wastewater that contains heavy metals has a detrimental effect on human health and the environment. Due to the non-biodegradability and carcinogenicity of heavy metals, water containing them might pose a serious health risk to living organisms if they are present in excessive concentrations [1].

A whole of the living organism's environments, including natural forces and other living entities, that offer circumstances for development and growth as well as danger and injury, are described as the environment. The environment might be the physical, chemical or biological environments. So there are two abiotic and biotic components in the environment. Air, water and land are part of the abiotic environment. Plants, animals and microorganisms are involved in the biotic environment. Environmental aspects are also separated into two categories: natural environment and environment created. The atmosphere, hydrosphere, lithosphere, and biosphere are components of our environment, and hydrosphere has a critical function to play. The quality and the contamination of groundwater in many regions of the world are highly significant [2].

Adsorption

Adsorption has evolved as a cost-effective, efficient, and environmentally friendly method of treatment. It's a technique capable of meeting industry demands for strict effluent standards and water reuse. Mass is transported from a liquid to the surface of a solid via a process called adsorption, which is essentially a mass transfer process. In this partitioning process, a small number of liquid phase constituents are transferred to the solid adsorbents' surfaces. As with any type of adsorption technique, solid-liquid equilibrium and mass transfer rates are crucial. Batch, semi-batch, and continuous adsorption methods are available. Molecular adsorption is primarily the result of attractive interactions between a surface and the group being absorbed on the molecular level. Adsorption can take one of the following forms, depending on the nature of the intermolecular attraction forces [1-2]:

- Chemical adsorption
- Physical adsorption

Adsorption method

Therefore a constant search goes on to find out more low cost and efficient methods. Adsorption has emerged as a simple, effective & economical method for metal removal. The adsorption process takes place at the boundary layer between the two phases. These phases may be in solid-liquid combination, gas-liquid combination or even liquid liquid combination. Since it is a surface phenomenon, the surface properties and number of pores of adsorbent becomes the major factors in the determination of adsorption equilibrium. The work on adsorption process is continuously going on and the new and better adsorbents are being discovered & developed. The main advantages of adsorption process are its simple design, selective removal of metals at low concentration, can operate over the broad pH ranges 2- 9,temperature ranges of 4-900C, requires low capital investment and low operating cost. Many waste biomasses are found having good adsorption properties. Biomass mainly consists of cellulose materials. The cellulose materials are having good adsorbing properties for heavy metals. Some of the biomass which have been reported having good adsorption properties are orange peel, mango peel,tea waste, neem leaves and saw dust [3].

Adsorption-based separation

Physical and chemical features of adsorbents, heavy metals, and operating circumstances all contribute to determining the adsorption mechanism (i.e., temperature, adsorbent amount, pH value, adsorption time, and initial concentration of metal ions). This technology has been shown to have cheap operating costs, high removal capacity, ease of implementation, and simple treatment through the regeneration of the adsorbed heavy metal ions.

- Carbon-based adsorbents
- Chitosan-based adsorbents
- Mineral adsorbents
- Magnetic adsorbents

Water Quality and Water Quality Parameters

Water quality means a technical word that is appropriate for human consumption and for domestic uses including personal hygiene on the grounds of water characteristics and guideline values. The microbiological, biological, chemical and physical components of water quality include. A key instrument for water quality assessment is the water quality parameters (WQPs).

The monitoring of water quality by means of representative sampling in various hydro geological units is an effort to acquire information on chemical quality. The Central Ground Water Board once a year monitors the chemical purity in the course of a routine monitoring programme, using a network of over 15000 monitoring wells around the country. In addition to these wells the quality is checked by different studies such as soil water management research, soil water investigation etc. The activity of groundwater monitoring aims to produce baseline data on a regional basis on various chemical components in groundwater [5].

Sources of Water Pollution

There are two kinds of water pollution sources. They are pointless or dispersed sources. Pollution sources develop when hazardous chemicals are directly released into a water body. Existing technology makes it easy to identify and regulate it. The effluents collected from these sources in an integrated treatment plant that are subsequently treated and re-used to a reasonable level are minimized by this form of pollution. eg. industrial wastewater, municipal wastewater, treatment facilities etc. The source of pollutants cannot readily be determined from non-point sources. It therefore provides the environment with toxins indirectly. In this case, contaminants spread across the landscape and can reach sources of water such as streams and lakes, producing water contamination. Thus [4-5], it is considerably more difficult to regulate non point or dispersed sources. Example: Surface rush, which in turn influence water life, from agriculture and forest soil and mining sites and building sites, etc.

CHEMISTRY AND TOXICITY OF HEAVY METALS

Heavy metal contamination is a major and widespread problem in water bodies that has a major impact on human and animal health. Human and industrial activities, in particular aquatic ecosystems, have affected the natural environment. The production and usage of heavy metals in urban as well as rural regions has led to widespread pollution.

The toxicity of several of these chemicals is being investigated and known to be stable in the aquatic environment. The USEPA has identified twelve trace elements as 'hazardous pollutants,' (Al, Sb, As, Be, Cd, Cr, Co, Pb, Mn, Hg, Ni, and Se). Living organizations tend to collect heavy metals, a highly pollutants category, recognized to have negative consequences. Heavy metals, at certain degrees of exposure, are non-degradable and dangerous to plants, aquatic creatures and human health. In addition to an aquatically system, heavy metals are transferred across various compartments of aquatic ecosystems such as waters, sediments and biota by natural and man-made sources. The entry into the environment of hazardous heavy metals is subject to geoaccumulation, bioaccumulation and bioamplification. A variety of animals, including human people via food chains, are potentially at danger from the accumulation of toxic heavy metals in the aquatic area.

WASTE WATER TREATMENT

Waste water treatment becomes very important in order to maintain a sustainable habitat for aquatic life. Water purification procedures are primarily conventional and industrial waste water solutions have been highly efficient in the past. Many water purification technologies have been created during recent years, notably in industrial water treatment and wastewater treatment. Water and wastewater treatment procedures are used as follows:

Sedimentation: Sedimentation is the fundamental method of initial treatment in most municipal and industrial recycling plants. A range of methods for improving the gravity settlement of suspended particles are available, including chemical flocculants, sedimentation basins and clarifiers.

Filtration Technology: filtration technology is an essential component of treatment applications for drinking water and waste water that include microfiltration, ultra filtration, nanopathy, and reverse osmosis. This was examined for the elimination of metal ions. For a given water treatment function, each membrane method is most suitable.

Chemical treatment: One powerful approach to remove the colour is by the chemical treatment of metal ions in wastewater by coagulating/floculant. The procedure includes addition to the metal ions waste fluid and produces flocculation of materials such as aluminium (Al3+), calcium (Ca2+) or ferric ion (Fe3+). The technique has also been utilized in addition to the other agents. Sometimes two might be added in order to improve the procedure.

Oxidation: oxidation is a way to use oxidizing chemicals to clean waste water. Two kinds of chemical oxidation and aided UV oxidation are usually employed in the treatment of effluent, notably of those derived from the initial treatment, such as chlorine, hydrogen peroxide, fenton reagents, ozone or permanganate (sedimentation). They are one of the most often utilized decolourization techniques since they need minimal amounts and quick reaction times.

Methodological electrochemistry: Electrochemical methods are also employed in colour removal as a tertiary treatment. Decolourization may either be accomplished using non-soluble anode electro-oxidation or electric coagulation with consumable substances. Several anode materials, such as iron, boron doped diamond electrode polymers, etc., were effectively utilized for electro-degradation of metal ions under varied experimental circumstances. The 83–100 percent colour removal was found in direct red 80 by three distinct electrodes: iron, chromium-doped polypyrrol, and diamond-doped electrode boron.

Advanced Process Oxidation (AOP): Advanced processes Oxidation (AOPs) require more than one simultaneous use of oxidation, since often a single system of oxidation is insufficient to decompose metal ions totally. These reactions are known as advanced oxidation procedures, including techniques such as reagent oxidation, ultra violet (UV) photolysis and sonolysis, all involving the rapid generation of hydroxy-free radical which is highly reactive.

Biological treatment: The most frequent and common approach of treatment of metal ions wastewater is biological treatment. Many species were employed for the colouring of various metal ions and for mineralizing them. The technique has significant advantages, such as being very affordable, minimal operating expenses and no toxicity of the final products of full mineralization. Aerobic, anaerobic or mixed aerobic-anaerobic processes are available.

Mechanism of adsorption

The process for adsorbing metallic ions (solutes) on the porous solid adsorbent comprises four phases as reported by McKay et al. The following are the different steps in the adsorption process:

- Transportation or migration of solvents to the adsorbent surface from the bulk of the solution.
- Solution molecules are moved or distributed across the interface/boundary layer into the surface and the external adsorbent surface area is adsorbed.
- Migration in the interior pores of the adsorbent of solution molecules.

Activated carbon adsorption

Activated carbon (AC) for the removal of water and wastewater contaminants is widely utilised as an adsorbent. Determined and published in a literature was the elimination of organic, dyes and inorganic (metal ions) compounds by AC. AC adsorption suffers from numerous drawbacks, such as difficulties in acquisition of the AC, despite its excellent adsorption capability and process cost. Commercial carbon (CAC) costs are substantial. The costly, impractical chemical and thermal regeneration of wasted CAC contributes to further costs.

Low Cost Adsorbents

When it comes to heavy metal removal, adopting low-cost adsorbents such natural materials, agricultural waste, or industrial byproducts is more encouraging in the long run because of the abundance of low-cost adsorbent materials already on hand. A commercially viable adsorbent must have high selectivity to facilitate rapid separations, favourable transport and kinetic characteristics, thermal and chemical stability, mechanical strength and resistance to fouling, regeneration capacity and low solubility in the liquid it is in contact with, as well as the ability to regenerate itself. Compared to other heavy metal removal techniques, the adsorption process provides a number of benefits. [6] The adsorption technique has a number of advantages over other processes, including being economical, selective for metals, regenerative, eliminating harmful sludge formation, and effective [6]. Adsorbents generated from a variety of natural and man-made sources have been used to remove heavy metals from waste water. Agriculture waste, industrial wastes, natural materials, and biopolymers modified for adsorption are the most common adsorbents.

LITERATURE REVIEW

Sabino De Gisi and Mchele Notarnicola, et al (2016) The properties and adsorption capacity of low-cost waste water treatment sorbents have been investigated by Sabino De Gisi. In this connection, the objective of the study was to update the literature on using low cost wastewater adsorbents, carefully stressing both adsorption and adsorption capacity features. Low cost adsorbents were classified into five groups for this purpose. I waste for agriculture and the household, (ii) industrial bi-products, (iii) waste (iv) soil and ore, marine materials, (v) new low cost sorbents. After discussion of adsorption methods, the affinity of sorbents in removing different contaminants their usage in real wastewater, prices and concerns for their reuse was considered [7].

Gonzalo Montes – Atenas and Sven L.M. Schroeder (2015) Sustainable natural heavy metal adsorbing agents have been investigated; pine bark sorption. The metal retention mechanism characterised by scanning electron microscopy (SEM), diffuse infrared reflectance Fourier transforms and photoelectron spectroscopy x-rays (XPS), pulp density > 1.5gl-1 is almost 100% Pb(II) removed from aqueous solutions containing 100mgl-1 Pb(1) Adsorption of lead has been evalued (II). Adsorption rates rose with pulp density while, due to obstruction of adsorption sites, adsorption capacity decreased at high density. It was estimated that the effect of washing and activating sulphuric acid is less significant than in earlier research on metal sorption [8].

Olivella and Villaescusa, et al (2015) In aquatic settings, Sen investigated heavy metal removal utilising bark as a biosorbent. A review of the biosorptone of heavy metals solution on several bark species, including the characterization of the bark structure and chemistry, is gathered. The author said. The results show that biosorption is becoming more important for the objectives of bark recovery. Promising results for heavy metal absorption utilising different bark species have previously been achieved. These values are equivalent to commercially active carbon values. Bark offers a cost advantage compared to carbon activated and may be utilised without pretreatment. Bark thus provides a green option for the removal of heavy metals from industrial waterways. A short overview is provided on the chemical structure and content of several bark species. There are suggestions to enhance screening for particular heavy metal ion sorption for bark species [9].

Hala Ahmed Hegazi (2013) has researched the removal by agricultural and industrial waste as adsorbents of heavy metals from waste water. The aim of this research is to explore the use possibilities for the removal of heavy metals from waste water using less costly adsorbents. For the disposal of heavy metals in waste water the EL – AHLIA firm wastes water for the electroplating sectors as an actual case study were utilised for the agricultural and industrial waste bi products such as rice husk and fly ash [10].

Rakesh Kumar and Aparna Sharma et al (2012), Biosorption of heavy metal ions by modified waste tree bark material has been investigated in Rakesh Kumar. In this study the bark was adsorbed by chromium (VI) with parameter change such as the concentration of adsorbed adsorbent impact of the time and pH-effect temperature effect [11].

Omar, Elshafei, et al (2011) Omer et al examined heavy metals removal properties from wastewater via low-cost adsorbents. The adsorption behaviour in this study was examined with regard to Cu2+ and Zn2+ ions of several cheap adsorption agents, such as peanuts husk charcoal, fly ash and nature zeolite, to evaluate its use for the purification of metal waste water in metals. Parameters such as pH, period of contact and starting metal concentration were examined for this batch technique. The pH of metal ion solutions was influenced by the various adsorbents employed between pH 4 to pH11 in the absorber levels of metal ions [12].

Demcak et al (2011) the investigation was performed using wood materials on the elimination of heavy metals from model solutions. The renowned tree's sawdust and bark were used in adsorption tests to remove copper and zink cations from Model Solutions at a starting concentration of 10mg. L-1. L-1. Infrared spectroscopy was not used to evaluate hemicellulose, cellulose, or lignin structures; instead, the FTIR was used to identify functional groups. When it comes to the ionisation of copper and zinc (II), the popular sawdust efficiency was about 80.0 percent from aquatic model solutions. In models, which have presumably been generated by exchanging ions between sorbents ions and solution ions, changes in the pH values were also detected [13].

Tajal and his co-workers (2009), Have been examined as a substitute for existing costly technologies for the removal of cadmium from aqueous solutions and wastewaters, Nut shells and their changed sample of low-cost active carbon. Sulfurized carbon (SAC) and commercial activated carbon (CAC) have both been used to study cadmium adsorption on activated carbon (SPAC and SCAC). For a variety of characteristics, we looked at things like contact time, initial concentration, and pH. In order to test the Freundlich and Langmuir models, adsorption data were collected on carbon that had been manufactured as well as carbon that had been purchased commercially. In comparison to Langmuir, they were more suitable with Frendlich isotherm [14].

OBJECTIVES OF THE STUDY

- To analyze the Comparative study of Mercury (II) ions adsorption onto various low cost adsorbents: isotherms, kinetic & thermodynamic studies.
- To analyze the Novel low cost adsorbents for the removal of Cadmium (II) ions from polluted aqueous solution.
- To analyze the Preparation, Characterization and Application of new low cost adsorbents.

RESEARCH METHODOLOGY

Materials & Methods for First Objective

Bark will be gathered locally and cleaned before usage of the SPJC, SHRSC and SPGC waste plant material. The concentrated Sulphuric Acid (Sp.gr. = 1.82) grade LR (purity: 98.3 percent) has been utilized. SD Fine Chemicals (India) obtained further chemical chemicals and reagents of chemical pure quality (AnalaR). Figure 1 revealed the presence of SPJC, SHRSC and SPGC.

Preparation of activated carbon

Sweet sulfuric acid (500 ml) and maintained at ambient temperature (30 ±1OC) during 24 hours, will be then carboled and sulfonated in the hot air oven at a temperature of 90 OC at a temperature of 90 OC. Sweet acid (500 ml) were then heated for 6 hours. It will be then refrigerated, washed with distilled water many times and then dry at 70OC for 12 hours with DD (double distilled) for removal of surplus free acid (checked with solution BaCl2). The samples have been dried (250–300μm) and are kept for further characterization, by using Jayant sieves (India). Tests of the SPJC, SHRSC and SPGC samples were identified.

Spectral analysis

Activated carbohydrocarbon produced and loaded with Hg (II) will be evaluated by the use of the KBr wave number pellet model SII, Vega3 Tescan Model Scanning Electron Microscope (SEM), SII Model 6000 Gravimetric analysis (TGA) and differential thermal analysis (TGA) by Shimadzu FT-IR spectrometer (DTA).

- Batch adsorption studies
- Regeneration studies

Thermodynamics study

In 303K-333K, the Thermodynamic Equilibrium Consistent (lnKC) of Hg2+ reaction were achieved using 40 ml of 180 ppm Hg2+ ion stock solution. In Van't Hoff's, Van't Hoff, and Gibbs's Helmholtz equations thermodynamic parameters (few G, ten H, and fewer S) were determined.

Materials & Methods for Second Objective

Flora bark such as SPJC, SHRSC and SPGC have been gathered in the immediate vicinity and cleansed before usage. The concentrated Sulphuric Acid (Sp.gr. = 1.82) grade LR (purity: 98.3 percent) has been utilised. SD Fine Chemicals (India) obtained further chemical chemicals and reagents of chemical pure quality (AnalaR).

Preparation of activated carbon

The gathered bark of the superplant materials, alone (each 500g), had been slashed into small parts, then carbonized, suffocated and stored in a hot air oven for 24h at ambient temperature (30 ± 1OC). The samples have been dried (250–300μm) and are kept for further characterization, by using Jayant sieves (India). SPJC, SHRSC and SPGC were the seven samples indicated.

Spectral analysis

With a SHIMADZU MODEL FT-IR spectrometer, FT-IR free spectral data and CD(II) loaded SPJC were acquired with a KBr pellet at 400 to 4000 cm−1 wave number.

Morphological analysis

The Vega3 Scanning Electron Microscope (SEM) will be examined as morphological analysis. The samples were produced using a little quantity of grid on a carbon-coated copper grill, an excess solution will be released using a blotting paper and afterwards the SEM film will be allowed to dry by placing it under a mercury lamp for five minutes.

Structural analysis

A X'Pert Pro Material Research diffract metric system has been used to control the produced adsorbent. The pattern of X-ray diffractions (XRD) will be analyzed using drop-coated adsorbent foils on glass plate and worked at the scanning range of 200 - 900, with a time constant of 2 s, CuK-α and amplitude μ = 1,5418 Å with 40 kV voltage and 30 mA current, with a characterizing radiation range of 0.050 /min.

Thermal analysis

In order to find out thermal deterioration of samples utilizing a SII MODEL 6000 thermal analyzer, thermal gravimetrical analysis (TGA) and differential thermo analyse (DDA) were employed. These analyzers were then utilized to evaluate the free SPJC adsorbents loaded by Cd(II).

- Regeneration studies

Thermodynamics study

A 40ml of 210ppm Cd(II) ion stock solution of 303K-3 333K were used to estimate the thermodynamic equilibrium constants (lnkC) of a reaction between Cd(II) and adsorbents. Thermodynamic parameters (ΔG, ΔH, and ΔS) were calculated by using Van't Hoff isotherm, Van't Hoff and Gibbs Helmholtz equation.

Materials & Methods for Third Objective

The flora resources used in the current study are freely given in Tamil Nadu, India, such as SPJC, SHRSC and SPGC. The concentrated sulphuric acid grade LR (purity: 98.3 percent) will be utilized for activated carbon production. (Sp.gr. = 1.82). The other chemicals and reagents from SD Fine Chemicals, India were chemically pure.

In the current investigation, three adsorbents were weighted to 300g alone. Three adsorbents were progressively carbonized, sulfonated and retained at room temperature (30 ±1 °C) for 24 hours with the conc.H2SO4 addition. These adsorbents were then heated to 90OC for 6 hours in a water bath.

Characterization of the samples

For recent investigation, the spectrum of FT-IR (SHIMADZU MODEL FT-IR spectrometener) has been utilized by utilizing the KBr pellet ratio of 1:200 to the wave numbers range from 400 to 4000 cm−1 to evaluate before and after Ni (II) adsorption of the three adsorbents. SEM examined the sound structure of the free and loaded Ni (II) adsorbents (Vega3 Tescan SEM instrument). The thermal degradation of free and Ni (II) loaded adsorbents will be detected using the TGA and DTA (SII MODEL 5000 thermal analyzer).

Batch, Regeneration and thermodynamic studies

Lots of produced 3 adsorbents in 250 mL glass bottle containing Ni (II) solutions of varying concentrations (30-2,80 mg/L) have been supplied for load adsorption studies. Mixtures using a remi-rotator water bath shaking machine at different temperatures (303-333k) were raised at 200 to balance. In subsequent intervals such as 10, 20, 30, 40, 50, 60, 70 and 80 minutes, shaking time will be adjusted to detect balance. Links behind the Ni (II) ion concentration in the aqueous media were measured by use of conventional literature titration methods. With the assistance of the following equation the balance adsorption capacity of adsorbents (qe) will be calculated:

$$q_e = (C_o - C_e) \times \frac{V}{M}$$

The percentage removal of heavy metal will be calculated by using equation.

Percentage removal = $(C_O - Ce)$ x100/ CO

In the current research, 10% (w/w) of NaCl as the eluting agent will be examined in adsorbent desorption level.

$$\%\ \text{of Regeneration level} = \frac{\text{Amount of Ni (II) ions desorbed}}{\text{Amount of Ni (II) ions adsorbed}} \times 100$$

Constants in thermodynamic equilibrium (ln KC) between Ni(II" and adsorbents are achieved by employing Ni(II) ion 303K, 313K, 323K and 333K 40 mL of 230 ppm stock solution. Thermodynamic factors (ΔG, ΔH, and ΔS) were calculated by Van't Hoff isotherm, Van't Hoff and Gibbs Helmholtz equation.

CONCLUSION

Water loses its limpidity due to the problem of pollution. Our current enhanced practice gives us comfortable existence but is failing to preserve our cherished environment's living decency, So quick action must be taken in order to reduce water contamination effectively. Many procedures have been used to remove heavy metals from industrial effluents such as solvent removal, electrolysis, precipitation, coagulation, division from the membrane, ion exchange, and adsorption. Adsorption is both efficient and cost-effective among the methods. The sludge-free characteristic of adsorption by activated carbon is prevalent in industry. Commercial Activated Carbon is an industry-specific benchmark adsorbent. But it is extremely difficult to adapt to industrial applications because of its highly costly nature. Thus the research and creation of superior alternatives to CAC for low-cost activated carbon from cheaper and local waste products is important. Several research hands used several low cost adsorbents in industrial wastewater for removing heavy metals. Although this approach involves additional investigation, the adsorption of heavy metals from contaminated water solutions must be well suited. In addition, the current research suggests the relevance of low-cost chemical-activated carbon from low-cost source substances as agricultural waste to be analyzed and their adsorption capability compared to CAC.

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