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A Review of Low - Cost Natural Adsorbents for Heavy Metal Removal from Wastewater

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Abstract: ***Heavy metal contamination in wastewater, stemming from industrial activities like mining and manufacturing, poses significant environmental and health risks due to the persistence and toxicity of metals such as lead, cadmium, and nickel. This review evaluates the efficacy of low - cost, natural adsorbents—such as eggshells, rice husks, and tea waste in removing these pollutants from industrial effluents. While conventional methods like chemical precipitation and electro dialysis are effective, their high costs and sludge generation limit widespread use. This study synthesizes findings on adsorption as a simple, eco - friendly alternative, detailing the performance of various biomaterials and their potential to address a pressing global challenge.***

Keywords: adsorption, heavy metals, low cost adsorbents, activated carbon, electro dialysis

1. Introduction

Currently heavy metal pollution is a serious threat to the environment. Decades of human activities such as urbanization, industrialization and population growth deteriorate the quality of our environment day by day. Rapid industrialization has led to increase the disposal of heavy metals into the environment and water bodies. The major sources of these heavy metal pollutants are industrial wastewater arises from mining, metal processing, tanneries, pharmaceuticals, pesticides, rubber, plastics and wood products. The industrial effluents containing hazardous materials are discharged to water bodies by the industries without prior treatment. These effluents, containing heavy metals, contaminate water sources via runoff. The heavy metals that are discharged into the wastewater are found to be toxic and carcinogenic and cause serious health hazards to human beings. There are at least 20 metals, which cannot be destroyed. The important toxic metals are Cd, Zn, Pb, Ni, Cr etc. Due to their non - biodegradability and persistence they possess a number of environmental problems accumulated in the food chain, and cause a substantial peril to human health as well as aquatic life [1 - 3]. Hence, for the environmental safety point of view it is indispensable to eliminate these heavy metal pollutants from industrial wastewater.

This review is significant as it highlights affordable, sustainable alternatives to conventional wastewater treatment, offering practical solutions for industries in resource - limited settings and reducing environmental harm from industrial waste.

Metal ion Toxicity:
Heavy metals in industrial wastewater include Pb, Cr, Hg, U, Se, Zn, As, Cd, Ag, Ni, etc. While metal ions like Cd^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} serve as micronutrients in soil - water systems for plants, animals, and humans, excessive exposure can damage central nervous function, the cardiovascular and gastrointestinal systems, lungs, kidneys, liver, endocrine glands and bones [4]. Given below are the ill effects of several metal ions or atom with particulars like tolerance limit and industrial source [5].

Table 1: Sources, tolerance limit and toxic effects of some heavy metals on human health

Metal Ion	Source	Tolerance limit (PPM)	Effect on body system
1. Cd	Industrial waste, Mining Waste, Petroleum refining, Coal Burning, Fertilizers, Paint etc.	0.01	Kidney damage, blood pressure, destruction of tissue and red blood cells etc.
2. Cr (VI)	Mining of chromite ores, Industrial Waste, Coal Burning, Paint, Petroleum refining, Plup & Paper mills.	0.05	Nausea, Skin, ulcerations, lung cancer, liver damage etc.
3. Hg	Industrial waste, Mining of coal, fertilizers, leather, textiles, plup & paper mills, metallurgy, Pesticides.	0.001	Paralysis of nerve & brain, visual disturbance, dysphasia, atakia and death.
4. Pb	Sewage, industrial effluents, paints, fertilizer, glass, textiles, Petroleum refining.	0.1	Anemia, Kidney disease, Nervous disorder, endocrine disruption, degrade immune function, mental impairment, decrease fertility and cancers etc.
5. Cu	Industry, coal burning, fertilizers, paint, petroleum refining etc.	0.05	Genetic diseases.
6. As	Industrial waste, mining and ore processing, textiles, coal burning, fertilizers, leather, glass, metallurgy etc.	0.05	Depressed growth and increased mortality.
7. Zn	Industrial, fertilizers, leathers, metallurgy, mining & ore processing, paint, textiles etc.	5.0	Vomiting, diarrhea, Lung diseases, Kidney diseases, blood pressure etc.
8. Ni	Coal burning, fertilizers, metallurgy, pulp &b paper mills, textiles.	_	Liver diseases.

Although it is difficult to remove heavy metals at their low concentration from wastewater, there are numerous methods have been currently employed and proposed to remove and recover the metals from our environment and from wastewater [6]. These methods include chemical oxidation and reduction, membrane separation, liquid extraction, adsorption, ion exchange, electrolytic treatment, electro precipitation, coagulation, flotation, evaporation, hydroxide and sulfide precipitation, crystallization, ultra - filtration, electro dialysis etc [7]. However, these methods differ in their effectiveness and cost and are regarded as ineffective for such purposes. Chemical precipitation, reverse osmosis, ultra - filtration, electro chemical deposition etc. become inefficient when contaminants are present in trace concentration [8] and are not economically feasible for industries because of their relative high costs [9]. Therefore, there is a need of an alternative to investigate a low cost method, which is effective and economic. Adsorption is one of the alternatives for this purpose [10] and is an effective purification and separation method used in water and industrial wastewater treatments [11]. Various research groups investigated the removal of heavy metals from wastewater by using adsorption technique by using low - cost adsorbents. For instance, the adsorption of toxic waste from industrial waste water using agricultural waste and industrial by products has been immensely examined by Basu et al, 2006 [12]. They used fish scales for the removal of lead and cobalt ions from aqueous solution. Their research showed fish scales provide a far better alternative to chemical adsorbents due to their inexpensive and nontoxic nature. Different concentrations of lead nitrate and cobalt chloride were prepared. In this experiment, the core holder was packed with the adsorbent and consolidated with a vibrator. The porous medium was saturated with the solvent before injecting the cobalt solution at specific flow rates. In lead solution, the medium was saturated with the influent concentration before injection. Effluent samples were collected at regular time intervals at the outlet. The solutions of both the lead and cobalt ions were analyzed with an atomic absorption spectrophotometer. The pH of the solution before injection was observed to be in range of 7.0–7.3. The effluent pH was observed to stabilize between 6.1 and 6.4 for all the runs. This clearly indicates the excess amount of protons released into the bulk phase during the sorption process. This novel adsorbent has some distinctive features that allow a decrease of pH of approximately 0.6–0.9 from an initial pH of 7. Babel et al, 2003 [13] reviewed the technical feasibility of various low cost adsorbents for heavy metal removal from contaminated water. Several researchers have worked on inexpensive materials, such as chitosan, zeolites and other adsorbents, which have high adsorption capacity and are locally available instead of commercial activated carbon. Given below is the description of various conventional methods such as chemical precipitation, coagulation or flocculation, ion exchange, ultrafiltration, electro dialysis, adsorption etc. [14], which are used for removal of heavy metal ions from wastewater.

1) Chemical Precipitation:

Chemical Precipitation technique involves the addition of chemical reagents to metals to form precipitate, then separation of the precipitated solids from the water. Adding coagulants such as alum, lime, iron salts, and other organic polymers achieve precipitation of metals.

2) Coagulation / flocculation

Coagulation is the chemical reaction process in which a coagulant is added to the water in order to form flocks. The colloidal materials in water are joined together and converted into small aggregates of flocks. Then the suspended matter is attracted to these flocks and easily settles out.

3) Ion exchange

In this technique heavy metal ions held electrostatically on the surface of a strong base anion exchange resins and are exchanged for ions of similar charge in the solution from the resin.

4) Membrane filtration

In this technique heavy metal ion is separated from water by using a semi permeable membrane. Pressure difference is the driving force for the separation. The removal efficiency depends on the pore size in the membrane and the particle size of metal ion species. Pre oxidation step improves the removal efficiency. Various types of membrane filtration techniques are mentioned in Table - 2 [15].

Table 2: Various types of membrane filtration

Membrane process	Operating Structure	Operation range (μm)
Microfiltration	Macro pores (>50 nm)	0.08 - 2.0
Ultra filtration	Mesopore (2 - 50 nm)	0.005 - 0.02
Nano filtration	Micro pore (< 2nm)	0.0001 - 0.001
Reverse osmosis	Dense (<2nm)	0.0001 - 0.001

5) Electro dialysis

Electro dialysis is a membrane process, in which ions are transported through semipermeable membrane, under the influence of an electric potential. The membranes are cation or anion - selective. Cation - selective membranes are polyelectrolyte with negatively charged matter, which rejects negatively charged ions and allows positively charged ions to flow through.

6) Adsorption

Adsorption occurs when a gas or liquid solute accumulates on an adsorbent's surface, forming a molecular or atomic film of the adsorbate. Adsorption is a commonly used technique for the removal of metal ions from industrial effluents and suitable for wastewater treatment because of its simplicity and low - cost [16 - 18]. Some commonly used adsorbents are activated carbon [19 - 22], clay [23 - 24], zeolites [25], chitosan [26], chitin [27] silica, fly ash [28] etc. Other low cost adsorbents have been investigated which includes microbial biomass, peat, compost, leaf mould, palm press fiber, coal, sugarcane, bagasse, straw, wool fiber and by products of rice mill, soyabean and cottonseed hulls [29 - 32]. Coal and straw are inexpensive but ineffective. Peat moss has been found as very effective in adsorbing heavy metals. Muhammad et al 1998 [33] used slow sand filters to remove heavy metals. Quek et al 1998 [34] used the sago processing waste, which is both a waste and a pollutant to adsorb lead and copper ions from solution. Mahavi et al. (2005) [35] utilized tea waste to adsorb heavy metals (Cd, Pb, Ni) from industrial wastewater. About 94 - 100% removal of lead, 86% for Ni and 77% for Cd were achieved using tea waste. The adsorption ability of tea waste were investigated for the removal of Cu (II) and Cd (II) from single and binary aqueous system by Cay et al 2004 [36]. Malkoc and Nuhoglu et al,

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2005 [37] investigated the removal of Ni from aqueous solution using tea factory waste (TFW). The effect of adsorbent dose, initial metal concentration, solution PH, agitating rate and temperature on the adsorption of nickel on TFW were studied. Malkoc et al, 2006a [38] studied the feasibility of TFW as an adsorbent for the removal of chromium in fixed bed. Their study indicated that the TFW can be used as an effective and environment friendly adsorbent for the treatment of chromium in aqueous solutions. Malkoc et al, 2006 b [39] investigated the fixed - bed adsorption of Ni (II) ions from aqueous solutions using TFW. The bed depth service time (BDST) model and the Thomas model were used to analyze the experimental data and the model parameters were evaluated. Thermodynamics and kinetic studies were carried out to find out the potential of TFW as an adsorbent for the removal of chromium. Amarasinghe etal, 2007 [40] used the tea waste as a low cost adsorbent for the removal of Cu and Pb from waste water. Batch experiments were conducted to determine the factors affecting adsorption and kinetics of the process. Wasewar et al. studied the adsorption of zinc onto Indian TFW [41 - 43]. Singh et al [44] used the rice husk carbon as a new low cost adsorbent for treatment of water containing Cr (VI). The rice husk carbon is a low cost by product from a rice mill and is activated using H_3P0_4 (40%). The stock solution of Cr (VI) is prepared by dissolving 2.828gm of potassium dichromate in 1 lt of demineralized water. Batch mode experiments were done. The effect of various parameters like adsorbent dose, pH, and contact time were studied. The characteristics (RHC) were reported as FTIR. The adsorption of Cr (VI) was found to be maximum (93 - 94%) at low values of PH (nearly 2) for the carbon dosage of 1000 mg/l and nearly 100% for carbon dosage of 1200 mg/l. Bishnoi et al. [45] used the rice husk and activated alumina as the adsorbents of Cr (VI) from synthetic solutions. The maximum removal of Cr (VI) occurred at pH 2 by activated rice husk and at pH 4 by activated alumina. The amounts of Cr (VI) adsorbed increased with increase in dose of both adsorbents and their contact time. Freundlich isotherm was applied. Jayakumar et al. [46] used the activated carbons prepared from marine green algae for adsorption of Pb (II) ions. This was investigated with the variation in the parameters of pH, contact time, Pb (II) ion concentration and the adsorbent dose. The Langmuir, freundlich and tempkin models have been applied. Results showed that the adsorption process was better described by the Langmuir model.

Mofty et al [47] used the clay Attapulgite as an adsorbent for removal of toxic metal ions such us Co, Ni, Pb, Cd from waste solution. Adsorption depletion tests were performed as a function of solid to liquid ratio, conditioning time, heavy metal ion concentration and PH to identify the mode and extent of interactions in the system. Conditioning time data confirm that ion exchange is nearly complete after 30seconds indicating the fast kinetics of the ion exchange process. Solid to liquid ratio data suggest that optimum ratio is 50g/lt. The adsorption isotherms constructed as function of heavy metal concentration and pH reveal that adsorption of metal ions increase in the order of Co<Ni<Cd<Pb.

Bohli et al [48] used olive stone activated carbon (COSAC) as adsorbent for the removal of bivalent cationic metals like Pb (II), Cd (II), Ni (II) And Cu (II). The investigation results show that the removal efficiency of heavy metal ions by COSAC decreases in the order Pb (II) > Co (II) > Ni (II) > Cu (II).

Gupta et al [49] used sawdust a biodegradable adsorbent for removal of Cr (VI) from aqueous solution. The batch experiments are carried out to investigate the effect of the significant process parameters such as initial PH, change in PH during adsorption, contact time, adsorbent amount and the initial Cr (VI) concentration. The maximum adsorption is obtained at an initial PH of 1. The value of PH increases with increase in contact time and initial Cr (VI) concentration. The equilibrium data for the adsorption of Cr (VI) on sawdust is tested with various adsorption isotherm models such as Langmuir, Freundlich, Redlich – Peterson, Koble - Corrigan, Tempkin etc. The Langmuir isotherm model is found to be the most suitable one for the Cr (VI) adsorption using sawdust and the maximum adsorption capacity obtained is 41.5 mg/g at a pH value of 1.

Singha et al [50] used nine natural adsorbents for removal of Cr (VI) from aqueous solutions and these are rice straw, rice bran, rice husk, hyacinth roots, neem bark, saw dust, teak wood, neem leaves, coconut shell etc. Various physico - chemical Parameters such as pH, initial metal ion concentration, and adsorbent dose level and equilibrium contact time were optimized in batch adsorption technique. A detailed FTIR study of adsorbents and Cr (VI) loaded adsorbents at the optimized condition was carried out to identify the different functional groups that were responsible for the adsorption. The important functional groups like hydroxyl, alkene, aromatic nitro, carboxylate anion, silicon oxide, sulphonic acid etc. were present in the natural adsorbent and were responsible for the chemical adsorption of Cr (VI) from aqueous solutions.

Ong et al [51] used activated sludge and powdered activated carbon (PAC) as adsorbent for removal of Cu, Cd, Ni, Zn, and Cr from synthetic solution. The results showed that activated sludge and PAC had a higher adsorption capacity than dried sludge. However, PAC showed a better adsorption capacity for Cu, Zn, and Ni than activated sludge.

A basic investigation on the removal of Cu (II) and Ni (II) ions from metal solution by cross linked chitosan - g - acrylonitrile copolymer was conducted in a batch adsorption system by Ramya et al [52]. Graft copolymerization was confirmed by FTIR, X - ray, DSC and SEM measurements. The influence of different experimental parameters such as PH, adsorbent dosage and contact time were evaluated. A pH 5.0 was found to be an optimum pH for Cu (II) adsorption; meanwhile PH 5.5 was an optimum PH for the adsorption of Ni (II) onto crosslinked Chitosan –g – acrylonitrile copolymer. The Langmuir adsorption isotherm model was applied. The maximum adsorption capacities of Cu (II) and Ni (II) ions were 230.79 and 358.54 mg/g respectively. Results showed that cross linked chitosan - g - acrylonirile copolymer is a favorable adsorbent for the removal of Cu (II) and Ni (II).

Annadurai G. et al [53] have worked on removal of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} in low concentration range of 5 – 25 mg/L using low cost banana and orange peel wastes and examined at 30° C. Under comparable conditions, the amount

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of adsorption decreased in the order of Pb^{2+} >Ni^{2+} >Zn^{2+} > Cu^{2+} >Co^{2+} for both adsorbents. The amount of adsorption was increased with increasing pH and reached a plateau at pH > 7, which was confirmed by Zeta potentials. The removal of Pb^{2+} up to 7.97 mg /gm of banana peel at pH 5.5 was appeared to be better.

Cong Liu et al [54] have analyzed on biosorption of Cu, Zn & Pb on watermelon rind in well stirred batch system. The optimal pH for removal of Cu, Zn & Pb was found to be 5.0, 6.8 and 6.8 respectively. Watermelon rind was in favour of Pb and it could remove up to 99% Pb between pH ranges of 5 to 6.8 when concentration was lower than 100 mg/L. The biosorptive capacity of watermelon on Cu, Zn & Pb was 6.281, 6.845 and 98.063 mg/gm respectively. NaOH was found to be suitable eluent for desorption and desorption reached as high as 99% of those three metals. Thus, watermelon was found to be having high uptake capacity as well as reusable.

U. Rafique et al [55] have studied on low - cost biomaterial such as fruit peel of lemon (Citrus Limonum), banana (Musa acuminate) and peel composite for remediation of heavy metals in industrial effluents like Pb, Cd, Ni &Cu. Application of fruit peels and composite adsorbent showed optimum removal of metals at pH 6 - 6.5 and included concentration of 30mg/L. The adsorption process removed Pb most effectively showing maximum removal (88%) in comparison to other metals. The results also proposed that banana peel as more effective adsorbent.

M. Kanyal et al [56] have studied on heavy metal (Cu & Pb) removal using household waste as an absorbent like banana peel and pumpkin peel. The effect of various parameters such as agitation speed and contact time was studied and good results were obtained at pH 7, 100rpm and 90 mins of contact time. The results indicated the biosorbents are cheap and efficient for toxic metal removal from waste water.

FENG Ning - Chuan et al [57] have prepared a modified orange peel with NaOH & $CaCl_2$ as an adsorbent for removal of heavy metal Cu, Pb and Zn. The adsorption behavior of Cu^{2+}, Pb^{2+} & Zn^{2+} on modified orange peel (SCOP) was studied by varying parameters like initial concentration of metal ions. Equilibrium was well described by Langmuir equation with the maximum adsorption capacities for Cu^{2+}, Pb^{2+} & Zn^{2+} at 70.73, 209.8 & 56.18 mg/gm respectively. Based on the results obtained in batch experiment, break through profile were examined using a column packed with scope for the separation of small concentration of Pb^{2+} from an excess of Zn^{2+} followed by elution tests. Ion exchange with Ca^{2+} neutralizing the carboxyl groups of the pectin was found to be predominant mechanism.

Bernard et al [58] have studied the adsorption of Pb, Fe, Cu and Zn from industrial electroplating wastewater by orange peel activated carbon. The ability of activated carbon produced from orange peel (AOP) to adsorb Pb (II), Fe (II), Cu (II), and Zn (II) ions from electroplating industrial wastewater has been investigated through batch experiment. Batch adsorption studies were conducted to examine the effects of contact time, adsorbent dosage and pH on adsorption of Pb (II), Fe (II), Cu (II), and Zn (II) from the wastewater. The results obtained shows that, the adsorption of metal ions were contact time, adsorbent dosage and pH dependent. The optimum contact time, adsorbent dosage and pH were found to be at 60 min, 1 g and pH 6 respectively; for the activated carbon used (AOP). Kinetic study shows that pseudo - second - order reaction model best described the adsorption process. The goal for this work was to develop inexpensive, highly available, effective adsorbents from orange peel as alternative to existing commercial adsorbents.

Tahiruddin N S M et al [59] have worked on the adsorption of Lead in aqueous solution by a mixture of activate charcoal and peanut shell. In this research, charcoals and peanut shells were used as low - cost adsorbents, which are abundant in nature, or are a by - product or waste material from another industry. The experiments were conducted using batch adsorption method. The effect of contact time, initial metal concentration, dose and pH on the simultaneous adsorption of lead was studied. The experimental results concluded that the better adsorption efficiency was obtained within 30 minutes of contact time. Furthermore, the adsorption of lead is higher when using a mixture of charcoal and peanut shell as adsorbent compared to the single adsorbent of charcoal. The maximum removal of lead on the charcoal and peanut shell was achieved when pH is 4 which is about 98.57%. The surface morphology of charcoal and peanut shell before and after the adsorption process was observed under Field Emission Scanning Electron Microscopy (FESEM).

Castro R S D et al [60] have worked on banana peel for adsorption of Copper and Lead from river water. That article reports on an investigation into the ability of minced banana peel to extract lead and copper ions from water and the parameters involved in this process. The kinetics of copper and lead uptake reached equilibrium in 10 min and the extraction of metals ions was favorable above pH 3. The medium was characterized by FTIR, which showed absorption bands of carboxylic and amine groups at 1730 and 889 cm^{-1} respectively. The adsorption isotherm fitted by Langmuir's model showed maximum adsorption capacities of 0.33 and 0.20 mm or g - 1 (or 20.97 and 41.44 mg g - 1) for Cu (II) and Pb (II), respectively. Minced banana peel was applied in the pre concentration system and showed approximately 20 - fold enrichment factor and the column was reused for 11 cycles without loss in the percentage of recovery. The proposed method was applied in the determination of Cu (II) and Pb (II) in a sample of raw river water and was validated by comparison with a standard reference material.

Kursunge H et al [61] have studied on the use of waste orange peel as an adsorbent for adsorption of Cu (II) from aqueous solution after effectively extraction of value added component pectin. Four parameters affecting adsorption were studied are pH (2.6, 4.3, 5.2, 6.8, 7.6), contact time (20, 40, 60, 80, 100 min), initial concentration (100, 200, 400, 600, 800, 1000 ppm) and adsorbent dosage (0.1, 0.2, 0.4, 0.6, 0.8, 1.0 gm.). The optimized parameters for maximum adsorption capacity was found to be concentration of 100 ppm at pH 6 to 7, contact time 60 to 100 min and adsorbent dosage of 1 gm. for 20 ml copper solution for both adsorbents. Maximum % removal of Cu (II) for pectin extracted orange peel was found 80.95% while for fresh orange peel it is 87.30%. The kinetics

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study was done by fitting the equilibrium data to Langmuir, Freundlich and Tempkin adsorption isotherm. It was found that Langmuir isotherm fitted well and most appropriate to describe adsorption kinetics. The adsorption of Cu (II) for both adsorbents follows pseudo second order kinetics and rate of adsorption is controlled by film diffusion.

Mahmoud M M. et al [62] have worked a batch adsorption of Cd (II) onto orange peel, a residue of the fruits processing industry. Equilibrium isotherms, kinetic data, and thermodynamic parameters have been evaluated. Equilibrium data fit well with Langmuir isotherm model. The kinetic data were found to follow the pseudo - second - order model. The negative **Δ**H° value indicates the exothermic nature of the adsorption process. Orange peel was shown to be a promising adsorbent for Cd (II) removal from aqueous solutions.

Ugbe F. A et al [63] have worked on the adsorption of Cr (III) ion from aqueous solution using orange peels as adsorbent. Batch equilibrium technique is used. The research is significant as it's aimed at investigating the suitability of orange peel, a waste product as adsorbent for the adsorption of Cr (III) ions from aqueous solution. Orange peel as an adsorbent is resource - saving and has an environmental friendly behavior. Adsorption experiment was conducted using a constant Cr (III) ion concentration of 0.1 M, adsorbent dose of 2.5 g and a temperature of 30˚C at varying solution pH of 2, 4, 7, 9 and 12 respectively with pH of 2 having the highest adsorption and therefore it was selected for use in the adsorption isotherm experiment. Adsorption isotherm experiment was conducted at varying temperatures (30˚C, 40˚C, 50˚C, 60˚C), concentration (0.1 M, 0.2 M and 0.3 M) Cr $(NO_3)_3$. Thermodynamic parameters such as ΔG, ΔH, and ΔS were calculated from the experimental data which showed that the adsorption process is feasible, spontaneous and followed physic - sorption mechanism $9H_2O$ and adsorbent dosage (1 g, 1.5 g and 2 g) respectively. The experimental results were tested using Langmuir, Freundlich, and Temkin adsorption isotherm models. The experimental data best fitted the Freundlich isotherm model. The experimental results revealed the suitability of orange peel which is a waste product as effective adsorbent for the sorption of Cr (III) ions from aqueous solution.

Husoon Z. A et al [64] have studied using less expensive and much frequently available materials orange and lemon peels to remove copper and lead from industrial waste - water. Three forms of these peels (fresh dried small pieces and powder) were used. Also other factors such as pH and temperature were examined for probable effects on biosorption. Current data showed that both orange and lemon peels are capable of removing copper and lead ions at significant capacity. Furthermore, lemon peels had higher capability than orange peels and the form of peel powder of both orange and lemon showed higher capacity than fresh and dried pieces where lemon powder has shown biosorption capacity of 72.5% and 71.3% for lead and copper respectively while orange powder had bioremoval percentage of 56.7% of lead and 34.5% for copper. In case of fresh lemon peels, these figures were 70.9% for lead and 62.2% for copper but fresh orange peels gave much less percentage (48.7of lead and 29.6% of copper). Regarding dried peels which showed the lowest values, but again, lemon peels were significantly better than those of orange. These values of lemon were 58.0% for lead and 57.1% for copper but for orange peels, the biosorption percentages reached 37.2% and 23.7% for lead and copper respectively. However, biosorption capacity of both fruit peels at different forms was significantly affected by various levels of both pH and temperature. The optimum pH and temperature values for better bioremoval capacity for all treatment within this study were 5 and 40 C° for pH and temperature respectively. Based on above, current data found that lemon peels are more efficient than the orange peels as biosorbents materials.

Jamil R. Memon et al. [65] have studied on the use of banana peel, a commonly produced fruit waste, for the removal of Cd (II) from environmental and industrial wastewater. The banana peel was characterized by FT - IR and scanning electron microscopy (SEM) coupled with energy dispersive X - ray (EDX) analysis. The different parameters, viz. - pH, contact time, initial metal ion concentration and temperature were investigated. The Langmuir adsorption isotherm was used to describe partitioning behavior for the system at room temperature. The binding of metal ions was found to be pH - dependent with the optimal sorption occurring at pH 8. Kinetics of sorption followed the pseudo - first - order rate equation with the rate constant k, equal to 0.13±0.01 min−1. Thermodynamic parameters viz. Gibbs free energy at 303K (−7.41±0.13 kJ mol−1) and enthalpy (40.56±2.34 kJ mol−1) indicated the spontaneous and endothermic nature of the sorption process. Using flame atomic absorption spectrophotometer (FAAS), we can remove Cd (II) ions from environmental and industrial wastewater samples.

Jamil Anwar et al. [66] have worked on the adsorption of cadmium (II) on peels of banana has been studied by using flame atomic absorption spectroscopy for metal estimation. Concerned parameters like adsorbent dose, pH, contact time and agitation speed were investigated. Langmuir, Freundlich and Temkin isotherms were employed to describe adsorption equilibrium. The maximum amounts of cadmium (II) adsorbed as evaluated by Langmuir isotherm, was 5.71 mg per gram of powder of banana peels. Study concluded that banana peels, a waste material, have good potential as an adsorbent to remove toxic metals like cadmium from water.

Satish A. Bhaleraoa et al. [67] have analyzed on the biosorption studies for effective removal of cadmium (II) ions from aqueous solutions using orange rind (Citrus sinensisL. Osbeck). FTIR analysis of biosorbent confirmed that carboxyl, hydroxyl, carbonyl groups were responsible for biosorption of cadmium (II) ions. The SEM represents there is porous structure with large surface area in the orange rind. The effects of operational factors including solution pH, biosorbent dose, initial cadmium (II) ions concentration, contact time and temperature were studied. The optimum solution pH for cadmium (II) ions biosorption by biosorbent was 7.0 with the optimal removal 80.30 %.5 mg/ml orange rind (biosorbent) was enough for optimal removal of 65.15 %. The biosorption process was relatively fast and equilibrium was achieved after 90 minutes of contact. The experimental equilibrium biosorption data were analyzed by four widely used two parameters Langmuir, Freundlich, Dubinin - Kaganer - Redushkevich (DKR) and Temkin isotherm models. Langmuir isotherm model give a better experimental

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data than Freundlich, Temkin and Dubinin - Kaganer - Redushkevich (DKR) isotherm models by high correlation coefficient value (R2 = 0.911). The maximum adsorption capacity determined from Langmuir isotherm was found to be 83.33 mg/g of biosorbent. Simple kinetic models such as pseudo - first - order, pseudo - second - order, Elovich equation and Weber and Morris intra - particle diffusion rate equation were employed to determine the adsorption mechanism. But out of this 4 data, pseudo - second - order kinetic model (R2 = 0.998) was found to be experimental strongest data than other three kinetic models and this suggests that chemical adsorption process was more dominant. Thermodynamic study revealed that the biosorption process was spontaneous, endothermic and increasing randomness of the solid solution interfaces. Orange rind (CitrussinensisL. Osbeck) was successfully used for the biosorption studies of cadmium (II) ions from aqueous solutions and can be applied in waste water technology for remediation of heavy metal contamination.

H. Benaissa et al. [68] have inspected on by using four low - cost materials, namely: eucalyptus bark, maize leaves, grape bunch and banana peel to remove cadmium from synthetic aqueous solutions. Kinetic data and equilibrium sorption isotherms were measured in batch conditions. Kinetics of cadmium sorption depends upon contact time, initial cadmium concentration and sorbent type. The results also showed that the kinetics of cadmium sorption was described by a pseudo - second order rate model. The cadmium uptake of these low - cost materials was quantitatively evaluated using sorption isotherms. Results indicated that the Langmuir model gave a better experimental data than the Freundlich equation within the concentration range studied. A high cadmium sorption was observed by these materials. The eucalyptus bark was the most effective to remove cadmium ions with a maximum sorption capacity about 99.50 mg/g followed by grape bunch (75.59 mg/g), banana peel (69.44 mg/g) and maize leaves (57.84 mg/g).

K. S. Rao et al. [69] have reported on Cadmium, which is known to be toxic for living organism even if it is present in low levels. Generally it is associated with zinc and copper minerals and is produced as a byproduct of these industries. It enters the environment from electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium - nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining industries. Various ways of cadmium removal are: precipitation, ion exchange, solvent extraction and adsorption. The present review specifically describes various types of adsorbents which have been used for removing cadmium from aqueous solutions. General emphasis has been on the utilization of agricultural, industrial wastes and low cost synthetic oxides as adsorbents. In most of the studies batch mode data has been evaluated by determining the kinetic, isothermic and thermodynamic parameters. A number of studies have also addressed the mechanism of adsorption process employing instrumental techniques such as XRD, FTIR, and SEM etc. More attention needs to be given for regeneration/reuse/ safe disposal of the loaded adsorbents wherein the data are insufficient. The engineering aspects also need attention for commercial application of various adsorbents.

Somaia G. Mohammad et al. [70] have investigated on the removal of cadmium (II) from aqueous solution by using low cost, natural and eco - friendly biosorbent of Banana peels Activated Carbon (BPAC). The Activated Carbon was characterized by FTIR, SEM, and TEM with EDX. Various factor affect adsorption parameters such as: effect of pH, amount of the biomass, initial concentrations of Cadmium ion and contact time on the adsorption capacity of the biosorbent were studied. Biosorption experiments were carried out at the temperature of 25°C. The percent removal of Cadmium ions was 98.35% from synthetic wastewater. These results were observed at the optimum dose of 0.8 g at pH 4.0. The removal of Cadmium ions from wastewater is mainly depending on the pH of the synthetic wastewater and the amount of biosorbent dose. The equilibrium adsorption data were fitted to Langmuir adsorption isotherm model and the model parameters were evaluated. The kinetic study showed that the pseudo - second order kinetic model better described the biosorption process. These results demonstrated that the Banana peels could be used as a natural biosorbent for removal of Cadmium from aqueous solution.

Shrimant V et al. [71] have prepared a report on the effective removal of Cd (II) ions from aqueous solutions using Tur Pod (Cajanus Cajan), which is a cost effective biosorbent was carried out in batch system. The effects of operational factors including solution pH, biosorbent dose, initial cadmium (II) ions concentration, contact time and temperature were studied. The optimum solution pH for cadmium (II) ions adsorption by biosorbent was 7.0 with the optimal removal 84.62%. The adsorbent dose 10 mg/ml was enough for optimal removal of 81.25%. The adsorption process was relatively fast and equilibrium was achieved after 90 min of contact. The Cd (II) ion easily eluted from biosorbent loaded with cadmium with acids. The desorption efficiency was found to be 97% (0.1 M nitric acid), 92% (0.1 M hydrochloric acid) and 89% (0.1 M sulphuric acid). The experimental equilibrium biosorption data were analyzed by four widely used two - parameters Langmuir, Freundlich, Dubinin - Kaganer - Redushkevich (DKR) and Temkin isotherm equations. Freundlich isotherm model provided a better fit with the experimental data than Dubinin - Kaganer - Redushkevich (DKR), Langmuir and Temkin adsorption isotherm models by high correlation coefficient value (R2 = 0.8903). The maximum adsorption capacity determined from Langmuir isotherm was found to be 9.2165 mg per g of biosorbent. Simple kinetic models such as pseudo - first - order, pseudo - second - order, Elovich equation and Weber and Morris intra - particulate mixing equation were employed to determine the adsorption mechanism. Results clearly indicates that the pseudo - second - order kinetic model (R2 = 1.000) was found to be correlate the experimental data strongest than other three kinetic models and this suggests that chemical adsorption process was more dominant. Thermodynamic study revealed that the biosorption process was spontaneous, endothermic and increasing randomness of the solid solution interfaces. Tur Pod (CajanusCajan) was successfully used for the adsorption and desorption studies of Cd (II) ions from aqueous solutions and can be applied in waste water technology for remediation of heavy metal contamination.

N. Azouaou et al. [72] have published about on the ability of some vegetable wastes, released in the nature, to remove cadmium from aqueous solution by adsorption. The selected adsorbents used are - orange barks, olive cores and olive wastes as they are abundant in Algeria. The process of adsorption is affected by several parameters, such as - contact time, adsorbent mass, initial concentration of cadmium, initial pH of the solution and particle size of the adsorbent. The results obtained showed that the orange barks are more competitive with maximum capacity of adsorption of 31.01 mg g - 1than the olive cores (12.56 mg g - 1) and the olive wastes (6.55 mg g - 1). Adsorption on the orange barks and the olive cores is well represented by the Langmuir isotherm and adsorption on the olive wastes obeys to the Freundlich model. The kinetic study showed that for the three adsorbents the process of adsorption is of the pseudo second order with a coefficient of correlation equal to 1.

Jassim M. et al. [73] have found a new and cheap method to remove heavy metal such as cadmium from aqueous solutions by use the seed shell of water melon plant (Citrulluslanatus), four experiments were done to demonstrate the effectiveness of watermelon seed shell to remove cadmium analyzed by FAAS. The first experiment was done to determine the effects of time on the adsorption process and the results show that the adsorption of cadmium increases with contact time. In the second experiment the results show that the removal efficiency (R) increases from 42.83 at concentration 0.5 mg/l of the adsorbent to 43.75 at concentration 2.5 mg/l of the adsorbent. The third experiment was carried out to determine the effect of initial concentration of the cadmium on the adsorption process. The results show that at initial concentration of cadmium 10 mg/l, the adsorbent was able to remove the adsorbate completely and at concentration 60 mg/l the removal efficiency was decrease to 40.9. For the last experiment the effect of pH on the adsorption process was studied, the results show that 47.37 at pH 3 and decrease to 43.01 at pH 11 respectively. Langmuir and freundlich adsorption isotherm models were analyzed and experimental results fit very well with freundlich model than Longmuir model.

Wanna Saikaew et al. [74] have researched on pomelo peel, a natural biosorbent, to remove Cd (II) ions from aqueous solution by biosorption. The experiments were carried out by batch method at 25^0C. The influence of solution pH, initial cadmium ion concentrations and contact times were evaluated. Cadmium ion removal increased significantly as the pH of the solution increased from pH 1 to pH 5. At pH 5, the cadmium ion removal reached a maximum value. The equilibrium process was described well by the Langmuir isotherm model, with a maximum biosorption capacity of 21.83 mg/g. The biosorption was relatively quick, (approx.20 min). Biosorption kinetics followed a pseudo - second - order model. The result showed that pomelo peel was effective as a biosorbent for removing cadmium ions from aqueous solution. It is a low cost material that shows potential to be applied in wastewater technology for remediation of heavy metal contamination.

Mohamed Ahmed Mahmoud et al. [75] have surveyed a batch adsorption of Cd (II) onto orange peel, a residue of the fruits processing industry. Equilibrium isotherms, kinetic data, and thermodynamic parameters have been evaluated. Equilibrium data fit well with Langmuir isotherm model. The kinetic data were found to follow the pseudo - second - order model. The negative ΔH° value indicates the exothermic nature of the adsorption process. Orange peel was shown to be a promising adsorbent for Cd (II) removal from aqueous solutions.

Wanna Saikaew et al [76] had examined the ability of fruit peel wastes; corn, durian, pummelo, and banana, to remove cadmium ions from aqueous solution by biosorption. The experiments were carried out by batch method at 25□C. The influence of particle sizes, solution pH, and initial cadmium ion concentrations were evaluated on the biosorption studies. The result showed that banana peel had the highest cadmium ions removal followed by durian, pummelo, and corn peels at cadmium ions removal of 73.15, 72.17, 70.56, and 51.22% respectively. There was a minimal effect when using different particle sizes of corn peel as biosorbent, while the particle size of the others had no influence on the removal of cadmium ions. The cadmium ions removal increased significantly as the pH of the solution increased rapidly from 1 to 5. At pH 5, the cadmium ions removal reached a maximum value. The equilibrium process was best described by the Langmuir isotherms, with maximum biosorption capacities of durian, pummelo, and banana peel of 18.55, 21.83, and 20.88 mg/g respectively. Fourier Transform Infrared Spectroscopy revealed that carboxyl, hydroxyl and amide groups on the fruit peels surface and these groups were involved in the adsorption of the cadmium ions.

Rifaqat Ali Khan Rao et al. [77] surveyed on Seeds of bottlebrush, a novel plant material, were found to exhibit excellent adsorption capacity over a wide range of Cd (II) concentration. It was characterized by Fourier transform infrared spectroscopy and Scanning Electron Microscopy to support the adsorption of Cd (II) ions. Effect of various parameters like pH, contact time, initial concentration and different electrolytes was investigated using batch process to optimize conditions for maximum adsorption. The adsorbent data were analyzed using Langmuir, Freundlich, Temkin and Dubinin–Redushkeuich isotherm equations at 30□, 40□ and 50□ C. Thermodynamic parameters such as standard enthalpy change (DH), free energy change (DG) and entropy change (DS) were also evaluated and the results indicated that adsorption of Cd (II) are spontaneous and endothermic. Various kinetics models including the Pseudo - first - order kinetics, Pseudo - second - order kinetics and Intraparticle diffusion models have been applied to the experimental data to predict the adsorption kinetics. Kinetic study was carried out by varying initial concentration of Cd (II) at constant temperature and it was found that pseudo - second - order rate equation was better obeyed than pseudo - first - order equation supporting that chemisorptions process was involved.

Inbaraj BS et al. [78] have researched on the fruit of the jack (Artocarpusheterophyllus) is one of the popular fruits in India, where the total area under this fruit is about 13, 460 ha. A significant amount of peel (approximately 2, 714 - 11, 800 kg per tree per year) is discarded as agricultural waste, as apart from its use as a table fruit, it is popular in many culinary preparations. Treatment of jackfruit peel with sulphuric acid produced a carbonaceous product which was used to study its efficiency as an adsorbent for the removal of Cd (II) from

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aqueous solution. Batch experiments were performed as a function of process parameters; agitation time, initial metal concentration, adsorbent concentration and pH. Kinetic analyses made with Lagergren pseudo - first - order, Ritchie second - order and modified Ritchie second - order models showed better fits with modified Ritchie second - order model. The Langmuir - Freundlich (Sips equation) model best defined the experimental equilibrium data among the three isotherm models (Freundlich, Langmuir and Langmuir - Freundlich) tested. Taking a particular metal concentration, the optimum dose and pH required for the maximum metal removal was established. A complete recovery of the adsorbed metal ions from the spent adsorbent was achieved by using 0.01 M HCl.

N. Azouaou et al. [79] have reported that the adsorption can be used as a cost effective and efficient technique for the removal of toxic heavy metals from wastewater. Waste materials with no further treatment such as coffee grounds from cafeterias may act as adsorbents for the removal of cadmium. Batch kinetic and equilibrium experiments were conducted to study the effects of contact time, adsorbent dose, initial pH, particle size, initial concentration of cadmium and temperature. Three adsorption isotherm models namely - Langmuir, Freundlich and Dubinin–Radushkevich were used to analyses the equilibrium data. The Langmuir isotherm which provided the best correlation for Cd2+ adsorption onto coffee grounds shows that the adsorption was favorable and the adsorption capacity found was equal to 15.65 mg g−1. Thermodynamic parameters were evaluated and the adsorption was exothermic. The equilibrium was achieved less than 120 min. The adsorption kinetic data was fitted with first and second order kinetic models. Finally it was concluded that the cadmium adsorption kinetic onto coffee grounds was well fitted by second order kinetic model rather than first order model. The results suggest that coffee grounds have high possibility to be used as effective and economical adsorbent for Cd2+ removal

Munusamy Thirumavalavan et al. [80] have published about a viable and cost - effective technology was explored in this present task for removal of heavy metal ions such as Cu2+, Ni2+, Zn2+, Cd2+, and Pb2+ from aqueous solution using three fruit peels such as orange peel (OP), lemon peel (LP), and banana peel (BP). The surface of the LP and lemon peel cellulose (LPC) was chemically modified. All these adsorbents were characterized by FT - IR, BET, and SEM. The widely used Langmuir adsorption isotherms were used to describe the adsorption equilibrium process. The adsorption capacity of metal ions such as Cu2+ and Ni2+ was found to be more than that of other metal ions. Upon comparison of the adsorbents, surface modified LPC (LPCACS) was found to show enhanced adsorption activity. A comparative study of adsorption was carried out with activated carbon (AC) also from which it was inferred that the order of the adsorption capacity is as follows: LPCACS > LPC > AC > LP.

Gurusamy Annadurai et al [81] were prepared low - cost banana and orange peels as adsorbents for the adsorption of dyes from aqueous solutions. Dye concentration and pH were varied. The adsorption capacities for both peels decreased in the order methyl orange (MO) > methylene blue (MB) > Rhodamine B (RB) > Congo red (CR) > methyl violet (MV) >amido black 10B (AB). The isotherm data could be well described by the Freundlich and Langmuir equations in the concentration range of 10–120 mg/l. An alkaline pH was favorable for the adsorption of dyes. Based on the adsorption capacity, it was shown that banana peel was more effective than orange peel. Kinetic parameters of adsorption such as the Langergren rate constant and the intraparticle diffusion rate constant were determined. For the present adsorption process intraparticle diffusion of dyes within the particle was identified to be rate limiting. Both peel wastes were shown to be promising materials for adsorption removal of dyes from aqueous solutions.

Xiaomin Li et al. [82] have worked on the preparation of chemically modified orange peel cellulose adsorbents and its biosorption behaviors of Co (II), Ni (II), Zn (II) and Cd (II). Effects of different chemical modifications on the adsorbent properties including different alkalis saponification (NaOH, NH4OH, and Ca (OH) 2 and different acids (C6H6O7•H2O, H2C2O4, and H3PO4) modification after saponification with NaOH were investigated. The FT - IR spectra showed that there are different functional groups in adsorbents, which are able to react with metal ions in aqueous solution. The maximum adsorption capacities of Ni (II), Co (II), Zn (II) and Cd (II) for SPA, SPA, SCA and SOA were obtained as 1.28, 1.23, 1.21 and 1.13 mol/kg and have increased by 95, 178, 60 and 130% compared to raw orange peel, respectively. Effects of initial pH, initial metal ions concentrations, shaking time and solid/liquid ratio on metal ions biosorption were also investigated. Biosorption equilibriums were rapidly established in about 60 min and the adsorption kinetics followed the Lagergren first - order kinetics model. The Langmuir and Freundlich adsorption isotherms models fitted the experimental data best with regression coefficient (R2) > 0.95 for all the metal ions. Elution efficiencies with different concentrations of HCl were evaluated.

Muhammad Iqbal et al. [83] have analyzed on the Mango peel waste (MPW) as a new sorbent for the removal of Cd2+ and Pb2+ from aqueous solution. The maximum sorption capacity of Cd2+ and Pb2+ was found to be 68.92 and 99.05 mg g−1, respectively. The kinetics of sorption of both metals was fast, reaching at equilibrium in 60 min. Sorption kinetics and equilibria followed pseudo - second order and Langmuir adsorption isotherm models. FTIR analysis revealed that carboxyl and hydroxyl functional groups were mainly responsible for the sorption of Cd^{2+} and Pb^{2+}. Chemical modification of MPW for blocking of carboxyl and hydroxyl groups showed that 72.46% and 76.26% removal of Cd^{2+} and Pb^{2+} respectively was due to the involvement of carboxylic group, whereas 26.64% and 23.74% was due to the hydroxyl group. EDX analysis of MPW before and after metal sorption and release of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and proton H^{+} from MPW with the corresponding uptake of Cd^{2+} and Pb^{2+} revealed that the main mechanism of sorption was ion exchange. The regeneration experiments showed that the MPW could be reused for five cycles without significant loss in its initial sorption capacity. The study points to the potential of new use of MPW as an effective sorbent for the removal of Cd2+ and Pb2+ from aqueous solution.

Ningchuan Feng et al. [84] have studied on equilibrium, thermodynamic and kinetic of biosorption of Pb^{2+}, Cd^{2+} and

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Ni^{2+} ions from aqueous solution using the grafted co - polymerization - modified orange peel (OPAA). Langmuir and Freundlich isotherm models were applied to describe the biosorption of the metal ions onto OPAA. The influences of pH and contact time of solution on the biosorption were studied. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. According to the Langmuir equation, the maximum uptake capacities for Pb^{2+}, Cd^{2+} and Ni^{2+} ions were 476.1, 293.3 and 162.6 mg g−1 respectively. Compared with the unmodified orange peel, the biosorption capacity of the modified biomass increased 4.2 - , 4.6 - and 16.5 fold for Pb^{2+}, Cd^{2+} and Ni^{2+} respectively. The kinetics for Pb^{2+}, Cd^{2+} and Ni^{2+} ions biosorption followed the pseudo - second - order kinetics. The free energy changes (ΔG°) for Pb^{2+}, Cd^{2+} and Ni^{2+} ions in biosorption process were found to be −3.77, −4.99 and −4.22 kJ mol−1, respectively, which indicates the spontaneous nature of biosorption process. FTIR demonstrated that carboxyl and hydroxyl groups were involved in the biosorption of the metal ions. Desorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions from the biosorbent was effectively achieved in a 0.05 mol L^{-1} HCl solution.

Mohammad Ajmal et al. [85] have reported on adsorption behavior of Ni (II), Zn (II), Cd (II) and Cr (VI) of untreated and phosphate - treated rice husk (PRH) showed that adsorption of Ni (II) and Cd (II) was greater when PRH was used as an adsorbent. Sorption of Cd (II) was dependent on contact time, concentration, temperature, adsorbent dose and pH of the solution. The Langmuir constants and thermodynamic parameters have been calculated at different temperatures. It was found that recovery of Cd (II) from synthetic wastewater by column operation was better than a batch process.

Mohamed R. Lasheen et al. [86] have studied on waste materials from industries, such as - food processing may act as cost effective and efficient biosorbents to remove toxic contaminants from wastewater. This study aimed to establish an optimized condition and closed loop application of processed orange peel for metals removal. A comparative study of the adsorption capacity of the chemically modified orange peel was performed against environmentally problematic metal ions, namely, Cd^{2+}, Cu^{2+} and Pb^{2+} from aqueous solutions. Chemically modified orange peel (MOP) showed a significantly higher metal uptake capacity compared to original orange peel (OP). Fourier Transform Infrared (FTIR) Spectra of peel showed that the carboxylic group peak shifted from 1637 to 1644 cm−1 after Pb (II) ions binding, indicated the involvement of carboxyl groups in Pb (II) ions binding. The metals uptake by MOP was rapid and the equilibrium time was 30 min at constant temperature and pH. Sorption kinetics followed a second - order model. The mechanism of metal sorption by MOP gave good fits for Freundlich and Langmuir models. Desorption of metals and regeneration of the biosorbent was attained simultaneously by acid elution. Even after four cycles of adsorption - elution, the adsorption capacity was regained completely and adsorption efficiency of metal was maintained at around 90%.

Ibrahim Kula et al. [87] have reported on the Cd (II) ions from aqueous solutions by adsorption. As adsorbent, activated carbon prepared from olive stone, an agricultural solid by - product was used. Different activating agent ($ZnCl_2$) amounts and adsorbent particle size were studied to optimize adsorbent surface area. The adsorption experiments were conducted at different parameters such as: adsorbent dose, temperature, equilibrium time and pH. According to the experiments results, the equilibrium time, optimum pH, adsorbent dosages were found 60 min, pH > 6 and 1.0 g/50 ml respectively. The kinetic data supports pseudo - second order model and intra - particle model but shows very poor fit for pseudo - first order model. Adsorption isotherms were obtained from three different temperatures. These adsorption data were fitted with the Langmuir and Freundlich isotherms. In addition, the thermodynamic parameters, standard free energy (ΔG0), standard enthalpy (ΔH0), standard entropy (ΔS0) of the adsorption process were calculated. To reveal the adsorptive characteristics of the produced active carbon, BET surface area measurements were made. Structural analysis was performed using SEM - EDS. The resulting activated carbons with 20% $ZnCl_2$ solution was the best sample of the produced activated carbons from olive stone with the specific surface area of 790.25 m2 g−1. The results show that the produced activated carbon from olive stone is an alternative low - cost adsorbent for removing Cd (II).

Linda Lim et al. [88] have researched on the evaluation of biosorption capability of the core of Artocarpusodoratissimus (Tarap), grown in Brunei Darussalam, towards Cd (II) and Cu (II) ions present in synthetic solutions, and to characterize the surface of Tarap particles. Thermogravimetric analysis and surface titrations were conducted to characterize the surface of dried Tarap core particles. Atomic absorption spectroscopic measurements were conducted to determine the extent of removal of Cd (II) and Cu (II) under different experimental conditions. Mass reductions associated with many exothermic reaction peaks were observed beyond 200°C up to 650°C indicating the combustion of organic matter in Tarap. Dried particles of core of Tarap bear a negative surface charge promoting strong interaction towards positively charged ions, such as Cu (II) and Cd (II). Biosorption of the two metal ions on Tarap, which is relatively high beyond pH - 4, occurs within a short period of exposure time. The extent of biosorption is enhanced by acid treatment of the biosorbent, and further it does not significantly depend on the presence of nonreacting ions up to an ionic strength of 2.0 M.

Asma Saeed et al. [89] have reported on the Papaya wood was evaluated as a new biosorbent of heavy metals. On contacting 10 mg l−l copper (II), cadmium (II) and zinc (II) solutions with 5 g l−1 papaya wood, during shake flask contact time of 60 min, the respective metal removal was noted to be 97.8, 94.9 and 66.8%. Sorption was most efficient at pH 5. Metal ion biosorption increased as the ratio of metal solution to the biomass quantity decreased. Conversely, biosorption/g biosorbent decreased as the quantity of biomass increased. The increase in initial metal ion concentration was associated with steep increase in biosorption at lower concentrations, progressively reaching towards plateau at higher metal concentrations. At equilibrium, the affinity of papaya wood to biosorb metals was in the order of copper (II) > cadmium (II) > zinc (II), which remained the same during the testing of variables of different factors. The biosorption data perfectly fit the Langmuir adsorption isotherms model with 0.99 regression coefficient (r2) for all the metals. The fit on

Freundlich adsorption isotherms model was acceptable but not as good. The biosorption kinetics studies indicated that the data followed the second - order reaction with r2 of 0.99. The first - order reaction was not applicable to the data. The metal - loaded papaya wood was completely desorbed with 0.1N HCl. During repeated biosorption–desorption for five cycles, no loss in the efficiency of copper (II) and cadmium (II) removal from their respective solutions and the metal - loaded biomass was noted. The study points to the potential of a novel use of papaya wood, itself a cause of environmental degradation and otherwise of no utility, for the treatment of wastewaters contaminated with heavy metals.

Ning - chuan FENG et al. [90] have surveyed on the adsorbent prepared by modifying orange peel with sodium hydroxide and calcium chloride. The morphological and characteristics of the adsorbent were evaluated by infrared spectroscopy (IR), scanning electron microscopy (SEM) and N2 - adsorption techniques. The adsorption behavior of Cu2+, Pb2+ and Zn2+ on modified orange peel (SCOP) was studied by varying parameters like pH, initial concentration of metal ions. Equilibrium was well described by Langmuir equation with the maximum adsorption capacities for Cu2+, Pb2+ and Zn2+ of 70.73, 209.8 and 56.18 mg/g, respectively. Based on the results obtained in batch experiments, breakthrough profiles were examined using a column packed with SCOP for the separation of small concentration of Pb2+ from an excess of Zn2+ followed by elution tests. Ion exchange with Ca2+ neutralizing the carboxyl groups of the pectin was found to be the predominant mechanism.

2. Conclusion

This review underscores the effectiveness of natural adsorbents like rice husks and fruit in removing heavy metals from wastewater, offering an economical and environmentally benign alternative to traditional methods. The accessibility and minimal ecological footprint make them promising for industrial adoption, though further research into scalability and adsorbent regeneration could broaden their practical impact.

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