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Removal of Heavy Metals from Aqueous Solutions

by Using Low Cost Materials

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ABSTRACT

Fresh water is already a limiting resource in Egypt and many parts of the world. Pollution of freshwater decreases the supply of usable water and increases the cost of purifying it.one of the Major water pollutants are heavy metals. They can affect human health. The Solution to this pollution is treating of the polluted water. There are many ways to treat polluted water but the most effected one is adsorption. The use of low cost materials as adsorbent was used as a replacement for costly methods for removing heavy metals from aqueous solutions.

Removal of heavy metals ions from aqueous solutions by different adsorbents such as Sawdust, Mirabilis Jalapa, Ash, Rice Husk Ash, Nile Rose Plant etc… These materials were used as untreated, treated and modified materials. The equilibrium adsorption level was determined as a function of the solution PH, temperature and contact time.

Adsorption isotherms of heavy metals ions on adsorbent were determined and correlated with common isotherm equations such as Langmuir and freundlich models. Chemical modified materials exhibit higher adsorption capacities than unmodified forms. Many chemicals have been used in modification as acids, bases, organic compounds, etc… Some of the treated adsorbents show good adsorption capacities for Cd, Cu, Pb, Zn and Ni.

1. INTRODUCTION

1.1 General Introduction

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination, high ambient air concentrations near emission sources, or intake via the food chain [1].

Heavy metals are nowadays among the most important pollutants in source and treated water, some of these are cumulative poisons capable of being assimilated, stored and concentrated by organisms that are exposed to low concentration of these substances for long periods or repeatedly for short periods [2].

Heavy metal removal from aqueous solutions has been commonly carried out by several processes: chemical precipitation, Coagulation/ flocculation, solvent extraction, ion-exchange, reverse osmosis or adsorption. However, most of them do not lead to a satisfactory depollution considering the operational costs [3].

Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. Gopalratnam *et al*. (1988) found that 80% removal of Zn, Cu, and Pb, and up to 96.2% removal of oil from industrial wastewaters by using a joint hydroxide precipitation and air floatation system [3].

Electro dialysis (ED) is a membrane process, during which ions are transported through semi permeable membrane, under the influence of an electric potential. The membranes are cation- or anion-selective, which basically means that either positive ions or negative ions will flow through.

Cation-selective membranes are polyelectrolytes with negatively charged matter, which rejects negatively charged ions and allows positively charged ions to flow through [3].

Coagulation and flocculation are an essential part of drinking water treatment as well as wastewater treatment. Coagulation is the chemical reaction which occurs when a chemical or coagulant is added to the water. The coagulant encourages the colloidal material in the water to join together into small aggregates called "flocs". Suspended matter is then attracted to these flocs. Flocculation is a slow gentle mixing of the water to encourage the flocs to form and grow to a size which will easily settle out. Randtke *et al.* (1997) reviews the basic mechanisms involved in the removal of organic contaminants by coagulation. Kuo *et al.*(2001) studied the effects of initial pH and turbidity, alum and pre ozonation doses, and flocculation time on the removal of dissolved organic matter during alum coagulation [3].

Ultrafiltration is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron. Typically, ultrafiltration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. It is a pressure-driven purification process in which water and low molecular weight substances permeate a membrane while particles, colloids, and macromolecules are retained. The primary removal mechanism is size exclusion, although the electrical charge and surface chemistry of the particles or membrane may affect the purification efficiency [3].

In the reverse osmosis process cellophane-like membranes separate purified water from contaminated water. RO is when a pressure is applied to the concentrated side of the membrane forcing purified water into the dilute side, the rejected impurities from the concentrated side being washed away in the reject water. Applications that have been reported for RO processes include the treatment of organic containing wastewater, wastewater from electroplating and metal finishing, pulp and paper, mining and petrochemical, textile, and food processing industries, radioactive wastewater, municipal wastewater, and contaminated groundwater.[3] ,[4]

1.2. Adsorption by Suitable Adsorbents

It can be an effective technique for the removal of heavy metals from wastewater. Because of its simplicity and cost effectiveness. [4] Adsorption is commonly used technique for the removal of metal ions from various industrial effluents.[4] Over the recent years, a growing research interest has been prompted into the production of low cost alternatives to the commonly used expensive adsorbents. In our previous work we investigated the removal of metal ions from their aqueous solutions using many low cost adsorbents [3]

1.3. Adsorption isotherms

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase, since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents and so are critical for design purposes; therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation. Adsorption equilibrium can be described by a variety number of isotherm models. These models describe the solute-adsorbent interactions. The most applied are the Langmuir and the Freundlich models [5]

2.3.1. Langmuir isotherm equation

The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface [5]

The Langmuir isotherm is defined as:

$$q_e = (q_m b C_e)/(1+b C_e) \tag{1}$$

where, q_e and Ce are the adsorbate concentration in liquid and adsorbent at equilibrium, respectively, and q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent and b is the adsorption equilibrium constant that is related to the apparent energy of adsorption.

A linear form of equation (1) is:

$$1/q_e = 1/q_m b.\ 1/C_e + 1/q_m \tag{2}$$

Isotherm parameters q_m and b can be obtained by plotting $1/q_e$ against C_e.

1.3.2. Freundlich isotherm equation

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies [5]. The Freundlich isotherm is defined as:

$$q_e =\ K_f\ C_e^{1/n} \tag{3}$$

with its logarithmic linear form:

$$\log q_e = \log K_f + 1/n \log C_e \tag{4}$$

where K_f and n are the Freundlich constants, the K_f constant is an indicator of the adsorption capacity of the adsorbent while n indicates biosorption intensity. The $\log q_e$ versus $\log C_e$ plot allows the determination of the Freundlich constants.

1.4. Mechanism of Adsorption

There are two principal modes of adsorption of molecules on surfaces, namely physical adsorption (physisorption) and chemical adsorption (chemisorption).

The basis of distinction is the nature of the bonding between the molecule and the surface. Physical Adsorption: the only bonding is by weak Van der Waals - type forces. There is no significant redistribution of electron density either in the molecule or at the substrate surface [6].

Chemical Adsorption: a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character. There is a possibility that the molecules can decay [6]

Four interaction forces are important:

☐ London-Forces (molecular forces between two anti - polar substance).

☐ Keesom-Forces (forces from the interaction between permanent dipoles).

☐ Debey-Forces (by induced dipoles).

☐ Chemical interaction forces (charge-transfer-interaction) [6].

The use of low-cost adsorbents has been investigated as a replacement for costly current methods. Natural materials or waste products from certain industries with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost.

In general, an adsorbent can be assumed as "low cost" if it requires little processing, is abundant in nature, or is a by- product or waste material from industry [22]. Some of the reported low-cost adsorbents include bark, tannin-rich materials, lignin, chitin, chitosan, peat moss, moss, modified wool and cotton. Insoluble starch xanthates have been found to be very useful to remove heavy metal ions from solutions [23] . Agricultural waste materials such as spent grain, polymerized onion skin , rice husks [24], bark, maize cobs, wheat bran and sawdust have been studied to investigate their effectivities in binding heavy metal ions.[7][25]

The adsorption of heavy metals by these materials (low cost materials) might be attributed to their proteins, carbohydrates, and phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions [7].

2. Literature Survey on Some Low Cost Materials Used to Remove Heavy Materials

2.1. Rice Husk Ash (RHA) and Nile Rose Plant

Rice milling generates a by product known as rice husk. This surrounds the paddy grain. During milling of paddy about 78% of weight is received as rice, broken rice and bran. Rest 22 % of the weight of paddy is received as husk. This husk contains about 75 % organic volatile matter and the balance 25 % of the weight of this husk is converted into ash during the firing process, is known as rice husk ash (RHA). So for every 1000 kg of paddy milled, about 220 kg (22 %) of husk is produced, and when this husk is burnt in the boilers, about 55 kg (25 %) of RHA is generated.

Nile rose plant (water hyacinth plant). The water hyacinth Eichhornia crassipes is considered the world's worst invasive aquatic weed. In Africa, it was first recorded in the 1890s from the River Nile in Egypt, but since then become widespread throughout the continent. The plant thrives in still and slow-moving water-bodies that have become nutrient-enriched through eutrophication, and dense mats of water hyacinth now blanket many of Africa's dams, lakes, rivers and canals. This plant causes water loss through evaporation, obstruction of navigation and fishing, and blockage of irrigation and drainage systems [2].

The present study was undertaken to evaluate the effectiveness of both rice husk and Nile rose plant in the removal of Cr^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} from a mixed metal ions solution by adsorption. Laboratory batch experiment and isotherm studies were conducted to determine the adsorption efficiency of husk and Nile rose plant. The effect of contact time, pH, and initial concentration of adsorbate and adsorbent dosage on adsorption were studied. A case study was also performed to examine the feasibility of using the investigated adsorbents for treating real electroplating wastewater.

The results obtained in this study clearly demonstrated the potential use of rice husk and Nile rose plant for the removal of Cr (III), Cu (II), Zn(II), Cd (II) and Pb (II) from mixed metal ions aqueous solutions. The following conclusions can be drawn based on the investigation: ´ The kinetic studies indicated that equilibrium in the adsorption of Cr (III), Cu (II), Zn(II), Cd (II) and Pb (II) on the rice husk and Nile rose plant was reached in 90 min of contact between the rice husk and Nile rose plant and the aqueous solution. The optimum pH corresponding to the maximum adsorption was found to lie between 4.5 and 6.5.The extent of adsorption for metals increased along with an increase of rice husk and Nile rose plant dosage. The experimental data were best fitted by the Temkin isotherm ´ Rice husk and Nile rose plant showed good removal efficiencies in treating the electroplating wastewater, so that they can be considered as cheap materials that can be used as neutralizing agents in the treatment processes [2].

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 0.99. 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].

2.2-Biochars Derived from Anaerobically Digested Biomass

This study examined the ability of two biochars converted from anaerobically digested biomass to sorb heavy metals using a range of laboratory sorption and characterization experiments. Initial evaluation of DAWC (digested dairy waste biochar) and DWSBC (digested whole sugar beet biochar) showed that both biochars were effective in removing a mixture of four heavy metals (Pb^{2+}, Cu^{2+}, Ni^{2+}, and $Cd2^+$) from aqueous solutions. Compared to DAWC, DWSBC demonstrated a better ability to remove Ni and Cd. Further investigations of lead sorption by the two biochars indicated that the removal was mainly through a surface precipitation mechanism, which was confirmed by batch sorption experiments, mathematical modeling, and examinations of lead-laden biochars samples using SEM–EDS, XRD, and FTIR. The lead sorption capacity of the two biochars was close to or higher than 200 mmol/kg, which is comparable to that of commercial activated carbons [9].

2.3. Mirabilis Jalapa

Mirabilis jalapa (chandrakantha) leaves were used as a biosorbent for the removal of toxic metals ions cadmium (II), chromium (VI) and lead (II) from water. The physiochemical properties of the developed biosorbent were studied using FTIR. The efficiency of this developed biosorbent was tested using batch experiments under controlled conditions such as a function of pH, contact time, initial metal concentration and the optimization amount of biosorbent. The residual metallic ion concentrations of cadmium (II), chromium (VI) and lead (II) were determined using AAS. The biosorption capacity of *Mirabilis jalapa* was found to be pH dependent and the percentage removal of cadmium (II), chromium (VI) and lead (II) was increased with increasing adsorbate solution pH and a maximum value was reached at an equilibrium pH = 6 for cadmium(II), pH = 5.5 for chromium(VI) and pH 4.5 for lead (II) respectively. The equilibrium time required for the saturation loading of cadmium (II), chromium (VI) and lead (II) in the biosorbent was found to be about 120 min. The obtained equilibrium biosorption data was fitted to the linear forms of Freundlich

isotherms. The results proved the efficiency of *Mirabilis jalapa* leaves powder as biosorbent for the removal of metal ions and it can be used for the development of an efficient, clean and novel technology for waste water treatment.[10]

2.4. Ash

The influence of different factors on the sorption capacity of ash and modified ash as low-cost sorbents obtained by different methods was investigated. The synthesis of new ash-based materials was carried out at ambient temperature (20 $^{\circ}$C), 70∘C, and 90∘C, respectively, in an alkaline medium with NaOH concentrations of 2 M and 5 M, respectively, corresponding to a mixture with solid/liquid ratios of 1: 3 and 1: 5, respectively. The prepared materials (sorbents) were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), X-ray diffraction, and BET surface measurement. Adsorption isotherms were determined using the batch equilibrium method. The results showed that these types of new materials displayed a good capacity to remove copper, nickel, and lead ions (29.97 mg of Cu2+ per g of sorbent, 303 mg of Ni2+ per g of sorbent, and 1111 mg of Pb^{2+} per g of sorbent) from aqueous solutions. The modified materials were prepared using an alkaline attack (a recognized method used in previous studies), but Romanian ash from a thermal power plant was studied for the above purpose for the first time. Hence, the factors which affect the sorption capacity of the prepared low-cost sorbents were determined and their behaviour was explained, taking into account the composition and structure of the new materials [11].

2.5. Sawdust

The removal of copper ion presents in industrial waste water using the local sawdust. Adsorption column was utilized in the removal process at constant temperature. The effect of the concentration of copper ion in the range (100-500) mg/L was studied. Increasing the inlet ion concentration increases the slope of the breakthrough curve. The effect of bed height in the range of (10-30) cm on copper ion adsorption from wastewater was studied. The increase in bed height increases the break

point values. The effect of flow rate in the range (0.5-1.5) cm^3/sec on copper ion adsorption also was studied. Increasing the flow rate decreases the breakthrough time. The best operating conditions in this work for copper ion adsorption are 100 mg/L of feed, 30 cm bed height and 0.5 cm3/sec feed flow rate. It was found that the equilibrium relation agrees with Langmuir & Freundlich equations. Finally accumulation adsorption of copper ion at different operating conditions was calculated [12].

2.5.1. Sawdust of Walnut

The adsorption of lead, cadmium and nickel from aqueous solution by sawdust of walnut was investigated. The effect of contact time, initial metal ion concentration and temperature on metal ions removal has been studied [7]. The sawdust of walnut was obtained commercially and used for the preparation of adsorbent. It was washed with distilled water to remove surface impurities and dried at 100°C for 24 h, ground to increase the surface area. The adsorbents were used as raw materials.

The equilibrium time was found to be of the order of 60 min. Kinetics fit pseudo first-order, second-order and intraparticle diffusion models, hence adsorption rate constants were calculated. The adsorption data of metal ions at temperatures of 25, 45 and 60°C have been described by the Freundlich and Langmuir isotherm models. The thermodynamic parameters such as energy, entropy and enthalpy changes for the adsorption of heavy metal ions have also been computed and discussed. Ion exchange is probably one of the major adsorption mechanisms for binding divalent metal ions to the walnut sawdust. The selectivity order of the adsorbent is Pb(II) = Cd(II) >Ni(II). From these results, it can be concluded that the sawdust of walnut could be a good adsorbent for the metal ions from aqueous solutions.[7]

2.5.2. Modified Red Pine Sawdust

The adsorption of Cr(VI) from aqueous solutions on sawdust (SD), base extracted sawdust (BESD) and tartaric acid modified sawdust (TASD) of Turkish red pine tree *(Pinus nigra),* a timber industry waste, was studied at varying Cr(VI) concentrations, adsorbent dose, modifier concentration and pH. Batch adsorption studies have been carried out. Sawdust was collected from waste timber industry and modified with various amount of tartaric acid (TA) (0.1–1.5 M). The batch sorption kinetics has been tested and the applicability of the Langmuir and Freundlich adsorption isotherms for the present system has been tested at 25±2 ◦C. Under observed test conditions, the equilibrium adsorption data fits the linear Freundlich isotherms. An initial pH of 3.0 was most favorable for Cr(VI) removal by all adsorbents. Maximum Cr(VI) was sequestered from the solution within 120 min after the beginning for every experiment. The experimental result inferred that chelation and ion exchange is one of the major adsorption mechanisms for binding metal ions to the SD. Percentage removal of Cr(VI) was maximum at the initial pH of 3.0 (87.7, 70.6 and 55.2% by TASD, BESD, and SD, respectively). Adsorption capacities range from 8.3 to 22.6 mg/g for SD samples.

BESD was prepared by stirring 50 g of (SD) in 1000mL of 0.1M NaOH at room temperature at 180 rpm. The product was filtered, washed with four-time larger volume of distilled water than volume of solution for modification was, and was dried at 50 ◦C, overnight. Drying at 50 ◦C was chosen because high drying temperature might cause a decrease of the number of cellulose based OH− groups on the lower SD moisture content. Modification with tartaric acid (TA) was carried out using the method reported by Wong et al. (2003). 0.1 g (SD) and 0.7mL of 1.2M TA was mixed in a container. TA modified sawdust samples were dried 80 ◦C for 24 h then the material was heated at 90 $^{\circ}$C for 90 min and rinsed with distilled water in a ratio of 0.1 g TASD to 5mL distilled water. The adsorbents were further modified by changing the tartaric acid concentration (0.1–1.5 M). The modified sawdust was then washed to neutral pH and dried at 50 $^{\circ}$C 40h [13].

Table 1. Comparison of the adsorption capacities of SDs with various low-cost adsorbents.

| Adsorbent	pH	Temperature (°C)	Adsorption capacity (mg/g)
Grafted silica	5.5	20	16.57
Fly ash	6.5	30	1.39
Bagasse fly ash	4.0	30	2.40
Tree fern	–	20	13.90
Chitosan	3.5	–	2.83
Lemma minor L.	4.0	20	69.00
Prawn shell	6.0	25	92.40
River bed sand	6.5	25	0.15
Pumice	8.0	20	0.06
Pumice/composite	8.0	20	0.27
SD[a]	3.0	20	5.50
BESD[a]	3.0	20	10.10
TASD[a]	3.0	20	10.72

2.5.3. Modified *Pinus Sylvestris* Sawdust

The study describes the adsorptive removal of Pb(II) ions from aqueous solutions by raw sawdust (R-SD) and sawdust modified with urea (U-SD) or thiourea (TU-SD). Adsorption experiments were carried out using a batch technique. The influences of solution pH, contact time, initial lead concentration, and adsorbent dose on the removal efficiency have been investigated. Langmuir and Freundlich adsorption isotherms fit well in the experimental data and their constants were evaluated. The results obtained in this study showed that sawdust modified with urea or thiourea has higher removal efficiencies (97.0-98.3%) for removal of Pb(II) from aqueous solutions in the Pb(II) concentration range of 10-50 mg/L compared to those of raw sawdust (86.7-95 %) used in this study. The results of treatment of some polluted water samples showed that the amount of lead reduced from 1.10 ± 0.02 mg/L to 0.55 ± 0.02; 0.46 ± 0.02 and 0.36 ± 0.02 by application of raw sawdust (R-SD), urea modified sawdust (U-SD) and thiourea modified sawdust (TU-SD), respectively. These facts suggest that the raw and modified sawdust present high potential to remove heavy metals from wastewaters.

The sawdust, originating from Pinus sylvestris, was first sieved (20-30 mesh), then washed with distilled water, and dried in an oven at 80° C, until constant weight (raw sawdust, R-SD). Next, 15 g of R-SD was mixed in a beaker with 1000 ml of 0.25 M urea (U) or thiourea (T) solution, and allowed to soak for 24 hours. Then, the mixture was filtered o remove the adsorbent, which was washed several times with distilled water to provide neutral pH. The adsorbents were then oven-dried at 80° C for 2 h. The sawdust treated with urea is denoted (U-SD) and that treated with thiourea is denoted (T- SD). The materials were kept in an airtight container for further use [14].
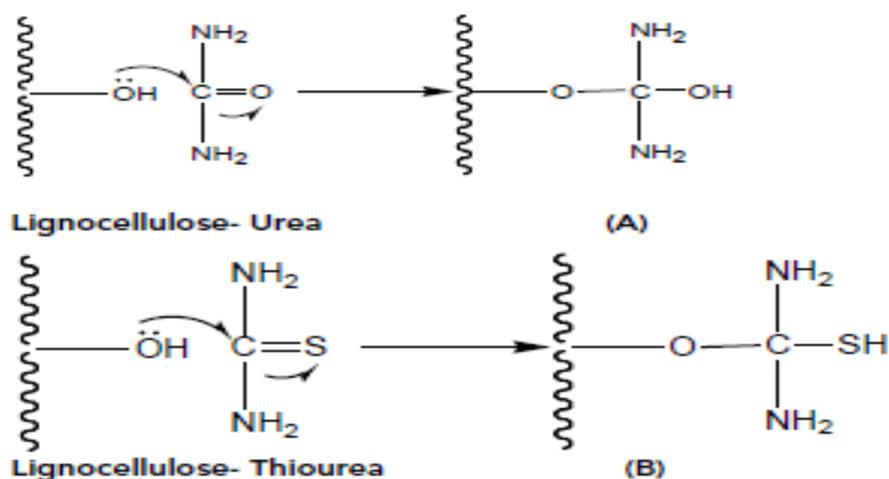
Figure 1. Modification of sawdust by urea (A) and thiourea (B)
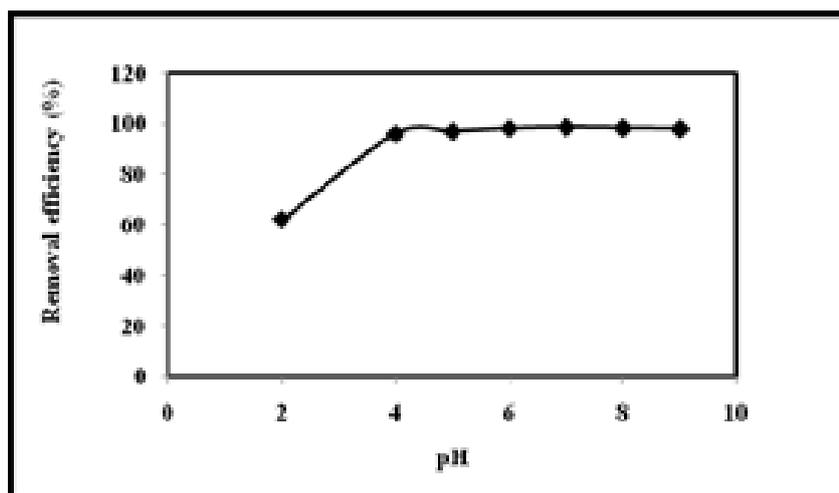
Figure 2. Effect of pH on the adsorption of Pb(II) ion on raw sawdust (initial concentration = 30

mg/L, contact time =90 min, adsorption dosage = 20 g/L).
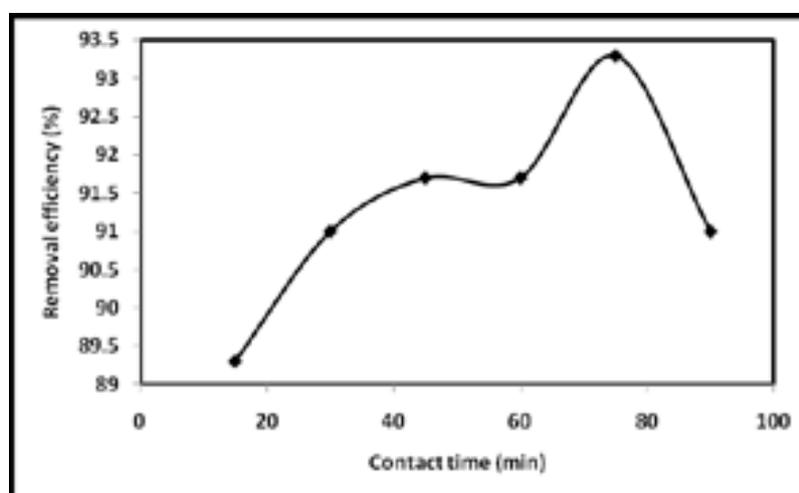
Figure 3. **Effect of contact time on the adsorption of Pb(II) ions (initial concentration = 30
mg/L, adsorbent dose = 20g/L and pH 6)**

pH	Sorbent dose (g/L)	Initial concentration (mg/L)	Removal efficiency (%)		
			R-SD	U-SD	TU-SD
6-7	20	10	95.0	97.0	97.9
		20	93.5	97.5	97.6
		30	89.4	97.7	97.6
		40	86.7	97.9	97.9
		50	86.7	98.3	98.2

Table 2. Removal efficiency (%) of Pb(II) ions using raw sawdust (R-SD), urea modified sawdust (U-SD) and thiourea modified sawdust (TU-SD).

2.5.4. Modified Holly Sawdust

The removal of divalent nickel from aqueous solutions on modified holly sawdust was studied at varying contact times, pH, initial divalent nickel concentrations and adsorbent dose. Results showed the removal efficiency by increasing of pH increased and decreased with initial nickel divalent concentration. By increasing pH from 2 to 12 (equilibrium time= 240 min, adsorbent dose= 0.6g/100 mL, divalent nickel concentrations= 60 mg/L), the removal efficiency increased from 17.47 % to 81.76 %. Also removal efficiency was decreased from 98 % to 19.3 % by increasing of initial divalent nickel concentrations from 20 mg/l to 100 mg/L. Also the results showed the removal efficiency was increased by increasing of adsorbent dose and contact time. By increasing of adsorbent dose from 0.2 g/100CC to 1 g/100CC, the removal efficiency increased from 32.78% to 99.98%. The removal efficiency increased from 34.7% to 83.67% by increasing of contact time from 5 min to 240 min. Experimental equilibrium and kinetics data were fitted by Langmuir and Freundlich isotherms and pseudo-first-order and pseudo-second-order kinetics models, respectively. The results show that the equilibrium data follow Langmuir isotherm and the kinetic data follow pseudo-second-order model. The obtained maximum adsorption capacity was 22.47 mg/g at a pH 7.

The results show that the modified holly sawdust can be used for the treatment of aqueous solutions containing nickel as a low cost adsorbent.

Holly sawdust from a timber mill in the city of Hamadan was washed with deionized water and dried at sunlight. The sawdust washed several times with distilled water and then decolorized with 1% formaldehyde in the ratio of 1:5 (sawdust: formaldehyde, w/v) at 50 ℃ for 4hr. The sawdust was filtered out, washed with deionized water to remove free formaldehyde and then activated at 80 0C in a hot air oven for 24hr. Then one part of as-prepared sawdust was mixed with one part of concentrated sulfuric acid and heated in the oven for 24hr at 150 0C. The heated material was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid [27].The obtained material was dried in an oven at 105 0C for 24hr, and sieved in the size range of 70 mesh ASTM. The specific surface area (BET) of the modified sawdust was determined as 365 m2/g by Research Institute of Petroleum Industry (RIPI) [15].

2.6. Peat Moss

Presence of lead, a heavy metal in the environment has been a serious concern especially with rapid industrialization which has created new uses for lead. The acute toxicity of lead to aquatic Life and humans and the stringent effluent standard to be met by industries as specified by regulatory organizations has necessitated the development of innovative, effective and economical methods for treating lead-bearing wastewater. An adsorption process using an inexpensive adsorbent such as peat moss is an attractive option for the removal of lead from wastewater.

Batch kinetic studies indicated that peat was effective in removing *95.5%* of lead. The equilibrium time was determined to be 2 h and optimum pH range was found to be 5.5 to 6.0 [16].

2.7. Sugar Beet Pulp Carbon

Sugar beet pulp was carbonized at different temperature to convert into an effective adsorbent, namely, sugar beet pulp carbon (SBPC) to be used for the removal of Cu(II) ions from aqueous solutions. The parameters affected the adsorption yield such as pH, contact time, adsorbent dosage and initial Cu(II) concentration were optimized. The optimum pH was determined as 5.5, and it was found that the adsorption reached equilibrium state in 120 min. Equilibrium data were fitted to both Langmuir and Freundlich adsorption models in the concentration range studied. The maximum adsorption capacities of Cu(II) ions were 12.24, 13.44 and 14.81mg/g for SBPCs obtained at 300, 400 and 500°C, respectively. The adsorption of Cu(II) ions were analyzed using Lagergren pseudo first-order kinetic model. The results showed that the Cu(II) adsorption process followed the first order rate expression and the adsorption rate constants decreased with increasing carbonization temperature [17].

2.8. Soybean Hulls and Sugarcane Bagasse

Study the efficiency of removing copper ions and Zinc ions from Copper Chloride and Zinc Chloride, using naturally based adsorbents like soybean hulls and Sugarcane Bagasse respectively. Batch adsorption studies show that the modified Soybean hulls show a great ability for extracting metallic ions from wastewater samples as compared with the Sugarcane bagasse. For Soybean Hulls the experiment was divided into two parts. In the first part, the time to heat soybean hulls that were soaked in citric acid was determined. In the second part the factors affecting copper ion adsorption by soybean hulls were determined to be initial concentration and pH of the solution, ratio of soybean hulls to copper chloride solution and size of soybean hulls. The results showed that the Soybean hulls and sugarcane bagasse were found to be an attractive low cost alternative for the treatment of wastewater. A good efficiency to remove toxic metal ions was achieved by usage of such by-product.

The maximum removal of copper will occurs at pH-4 and at 70° Celsius and the contact time is 360 min. After pH-7 there is slightly a decrease in adsorption and below pH-7 very less copper is removed [18].

Modifying Soybean Hulls with Citric Acid

Ten grams of soybean hulls with a particle size of 1.5 to 1.8 mm will be taken in 200 ml of 0.1N NaOH. The slurry will be stirred at 300 rpm for 1 hr. and then will rinse with distilled water. The moist hulls will be then added to 200 ml of distilled water and stirred at 300 rpm for 45 min to remove the excess NaOH. This procedure will be repeated for three times to ensure removal of NaOH. The hulls will be then blended with 0.6M of citric acid in a proportion of 1.0 gram of hulls to 7.0 ml acid. The acid/soybean hulls slurry will then be allowed to dry overnight at 50°C. The dried hulls will be heated further up to 120°C for 0, 15, 20, 60, 90 and 120 minutes. The acid-modified soybean hulls were then cleaned by washing with distilled water and filtered. Finally, the modified hulls will be allowed to dry overnight at 50 °C and sieved in the range of 1.5mm to 1.8 mm.[18]

Modifying Sugarcane Bagasse

20 ml of zinc chloride solution and different amount of the dosage of the adsorbent added to the solution and kept into the magnetic stirrer. Then solution is filtered with filter paper. Filtered solution is analysed by an atomic absorption spectrometer (AAS) to know concentration of zinc in solution .solution is treated at different PH, different temperature, and different time of contacts [18].

2.9. Teak Leaves

Using Teak Leaves Powder as adsorbent were carried out to remove copper from waste water. The aim of the present investigation is to study the potential of teak leaves for copper removal and optimize the parameters like contact time, pH and the temperature. Optimum contact time found to be 60 minute as after that desorption also become dominant. As adsorbent dose increases, % removal increases as surface area increases for adsorption. The optimum dose was 2 g/l. Maximum % removal was at 55 0C. The equilibrium adsorption data were fitted to Langmuir and Freundlich

adsorption isotherm models and model parameters were evaluated. We can say both models were suited to the experimental equilibrium data for teak leaves because value of R2 was found to be 0.993 and 0.995 respectively. The results show that Teak Leaves Powder has scope for modification, to use it as low cost adsorbent for adsorption of Cu (II) from aqueous solution.

For Adsorption studies, desired quantities of the chosen adsorbents Teak Leaves powder were mixed with 100 ml of Cu (II) solution in 250 ml conical flasks. The flasks were placed on a magnetic stirrer at 120 rpm and the samples were taken at regular time intervals. The experiments were carried out at different adsorbent dosage (5-25g/l), temperature (30-75°C). The samples were then filter. The Cu (II) content in the supernatant was determined according to the standard methods of analysis using Atomic Absorption Spectrometer at $\lambda = 324.8$ nm. [19].

2.10- Mango Leaves

The potential of mango leaves as a low-cost adsorbent for the removal of Cu(II) ions from aqueous solution was investigated in this study. The influences of pH, contact time, initial metal concentration, agitation rate, particle size and presence of chelating agent were studied in batch experiments at room temperature. The mango leaves used in this study were characterized by FTIR spectroscopy and it was found that O-H, C-H, C=C and C-O stretching were present. Maximum sorption for metal was found to be at pH 5. The adsorption was rapid at the first 5 minutes of contact, with uptake of more than 90%, and equilibrium was achieved in 60 minutes of agitation. Kinetic studies showed good correlation coefficient for a pseudo-second order kinetic model. The uptake was found to increase with higher agitation rate and smaller size of adsorbent. The presence of chelating agent EDTA and NTA suppressed the uptake of Cu(II) ions, with the earlier having a stronger suppressing effect. Langmuir, Freundlich, and BET isotherm models were applied to describe the biosorption of Cu(II) ions onto mango leaves. Langmuir model fitted the equilibrium data better, giving correlation coefficient of 0.9918 and a maximum adsorption capacity of 15.77 mg/g. This indicates monolayer coverage on adsorbent. The results showed that mango leaves have the potential

to be applied as alternative low-cost biosorbent in the remediation of heavy metal contamination in waste water [20].

2.11. The Marine Alga

In general, the mechanism of biosorption is based on a number of metal binding processes taking place with components of the algae cell wall. The algae cell walls can reversibly biosorb metals, and thus function in a similar way to an ion-exchange resin. Thus, the biosorption mechanism can be considered as being dependent on the composition of the algal cell wall. Algal cell walls can be made up with further polysaccharides: mannan, xylan, alginic acid, chitin, ect. These components, along with the proteins present, can provide acid binding sites such as amino, amine, hydroxyl, imidiazole, phosphate and sulphate groups [26]. The biosorption mechanism has been described as not involving van der Waals' forces at the cellulose network of the cell walls, thus both ionic charge and covalent bonding are involved in the metal biosorption process. It is thought that the proteins and polysaccharides are the major components responsible for the biosorption. Covalent bonding could be expected with amino and carboxyl groups and ionic charge bonding with carboxyl and sulphate groups associated with these components. Studies with the micro alga Scenedesmus obliquus indicated that the cell wall behaved like a weak acidic cation exchanger containing various cell wall ligands with different exchange capacities. Detailed studies of the metal-binding capacity of the OM of the E.coli showed that the OM (outer membrane of the cell wall) exhibited certain selectivity, which depended on the metal suitability for various physicochemical roles. For instance, Ca^{2+} stabilised the LPS (lipopolysaccharde) and Mg^{2+} formed part of complexes in LPS and protein. The interaction between soluble metallic ions and the OM followed three physical principles, which regulate cation selectivity of biological membranes:

· Binding is dependent on the free energy difference between the site bound cation and cation-water interaction;

· Free energy of interaction originates from electrostatic forces;

·   The principal electrostatic forces were Coulomb forces.

Metal binding occurs though a passive mechanism, which involves electrostatic interaction between the negatively charged groups in the wall and the metallic cation. Most metal binding occurs after initial metal complexation and neutralization of the chemically active site. Binding to the cell walls might proceed through at least a two-step mechanism, for Bacillus subtilis: the first step is the stoichiometric interaction of metal with reactive chemical groups, followed by a second stage in which those same sites nucleate the deposition of more metal as a chemical precipitate, which results in the development of fine-grained minerals. The initial interaction is the "adsorption" phase, but metal retention ability by bacterial walls goes further than their adsorption capacity, since bacterial surface are favorable interfaces for mineral nucleation. Some metals have greater tendency to form precipitates than other. In systems, which include living cells, it is possible that some active uptake or non-specific cation transport system could take place. While the overall metal removal process can be considered as a "sorption" process, metals may in fact be retained by one or more of the above mechanisms. This complication may contribute to the frequent inability of adsorption isotherms to describe experimental data. Adsorption equations may be useful for describing bacterium-metal interaction with certain metals, but this approach may not be adequate when precipitation of metals occurs[28]. The intrinsic composition and structural organisation of the cell envelope (in all its variations, such as cell walls, capsules, S-layer and sheaths) provide bacterial cell surfaces with a high density of negative charge, and result in a great metal-binding capacity. Cell surfaces also provide favorable interfaces for mineral formation by facilitating heterogeneous nucleation processes [21].

3- REFERENCES

[1] http://www.lenntech.com/processes/heavy/heavy-metals/heavy-metals.htm

[2] N.E.T. ABDEL-GHANI and G. A. EL-CHAGHABY, Current World Enviroment, 3(1), 31-38 (2008).

[3] D.Lakherwal, international Journal of Environmental Research and Development, 1 (2014), pp. 41-4.

[4] Slater , 1983; Cartwright, 1985; Ghabris , 1989; Williams , 1990 Yadanaparthi .2009, Kwon ,Gottipati., 2012

[5] O.E.Abdel-Salam, N.A. Reiad, M.M. ElShafei Journal of Advanced Research (2011) 2, 297–303.

 [6] A. Dabrowski , Advances in Colloid and Interface Science 93 Ž2001. 135_224.

[7] B.Yasemin and T.Zeki , Journal of Environmental Sciences 19(2007) 160–166.

[8] J.H.Al-Baidhani and S.T. Al-Salihy, International Journal of Chemical Engineering and Applications, Vol. 7, No. 1, February 2016.

[9] M.Lnyang, B.Gao, Y. Yao, Y.Xue, A.R.Zimmerman, P.Pullammanappallil and X.Cao, Bioresource Technology, (2012).

[10] Sh.A.Begum, Y.Tharakeswar, Y.Kalyan and G.R.Naidu, Journal of Encapsulation and Adsorption Sciences, 2015, 5, 93-104.

[11] M.Harja, G.Buema, D.M.Sutiman and I. Cretescu, Chemical Papers 67 (5) 497–508 (2013).

[12] N. A.Ageena , Eng. And tech. Journal , VOL.28, NO.2 ,(2010).

[13] F.Godea, E.D.Atalay and E.Pehlivan, Journal of Hazardous Materials 152 (2008) 1201–1207.

[14] Indian journal of applied research, VOI.4 , Issue : 7, July 2014.

[15] M. R. Samarghandi, S.Azizian, M. Sh.Siboni, S.J.Jafari, S. Rahimi, Iran. J. Environ Health. Sci. Eng., 2011, Vol. 8, No. 2, pp. 181-188.

[16] A.Akinbiyi, Regina, Saskatchewan,November, 2000.

[17] A. Ozer, F. Tumen, The European Journal of Mineral Processing and Environmental Protection Vol.5, No.1, 1303-0868, 2005, pp. 26-34.

[18] P.Kishor, Patil Vilas S., N.Patil and M.Vijay, *al. IJSRR 2012, 1(2), 13-23*.

[19] A.K.Goswami, S.J.Kulkarni, S.K.Dharmadhikari, M.Phutke, International Journal of Science, Engineering and Technology Research (IJSETR) Volume 2, No 6, June 2013.

[20] O.P.SHEEN, Eng. And tech. Journal May 2011.

[21] F.Petersen, C.Aldrich, A.Esau and BC Qi, WRC Report No 1259/1/05, MARCH 2005.

[22] Bailey , 1999.

[23] Rao, 2000.

[24] Low and Lee, 2000 , Kumar and Dara, 1981.

[25] Khalid and Ahmad,1999, Doris, 2000; Marchetti, 2000; Gloaguen and Morvan, 1997; Duvnjak and Al-Asheh,1998; Ajmal ,1998.

[26] Crist , 1981.

[27] Baral, 2006.

[28] Mullen ,1989.