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Removal of Pb(II) and Zn(II) metal ions by carbonaceous material obtained from industrial waste lignin

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ABSTRACT
The aim of this research work is to investigate the performance of low cost metal ion adsorbent obtained from pyrolysis of industrial waste lignin. Lignin is a major waste product from pulp and paper industry and its disposal is a matter of environmental concern. From the utilization point of view this waste has been converted into low cost adsorbent after appropriate treatments. The industrial waste lignin was subjected to thermal degradation in N2 atmosphere at 450-5000C to obtain a porous carbonaceous residue (char). The char was characterized by proximate analysis, SEM, and FTIR spectroscopy. Biosorptive studies of Zinc and Lead were carried out through various parameters such as pH, adsorbent dosage and contact time. The results showed the efficient removal of Zn2+ and Pb2+ ions by the char obtained from industrial waste lignin. This study indicates that lignin on appropriate treatment has the potential to become an effective and economical adsorbent for removal of toxic metal ions from waste water.

Keywords - About carbonaceous material, toxic metal ion**,** adsorption, degradation

I. INTRODUCTION

Overgrowth in population, industrialization, agricultural and domestic activities of humans have affected the environmental system, resulting in drastic problems such as global warming and the generation of waste water containing high levels of pollutants. These inorganic micropollutants are non-biodegradable, highly toxic and have a carcinogenic effect. They can accumulate in water, soil, plants and living tissues, thus becoming concentrated throughout the food chain. The main sources of heavy metal contamination are metal plating, mining operations, tanneries, radiator manufacturing, smelting, alloy industries and storage battery manufacturers[1]. These would endanger public health and the environment if discharged improperly. As water of good quality is a precious commodity and available in limited amounts, demands for water are increasing geometrically. Therefore, alternative sources of water are required and waste water treatment may serve this purpose. Waste water mostly contains heavy metals like Aluminium, Chromium, Manganese, Cobalt, Nickel, Zinc, Copper, Lead and Mercury etc. Among all Zinc and Lead are most important because of their high toxicity. Lead even at extremely low concentration can cause brain damage in children[2]. Hence the presence of these toxic metal ions in ground water, surface water and other water resources should be

monitored. If their amount exceeds than the prescribed limit, proper treatment for removal of these metals is needed. Zinc is essential in small quantity but when exceeds the prescribed limit it has also detrimental effect on human health. The various methods used to remove metal ions from waste water includes chemical precipitation, ion exchange, membrane process and adsorption[3]. Among various water treatment technologies, adsorption onto activated carbon is in the front line due to its universal nature. Activated carbon is the best adsorbent able to capture inorganic as well as organic pollutants that contaminate water resources.

Although activated carbon is effective in removal of metal ions from waste waters, it is expensive and requires chelating agents to enhance its performance, thus increasing treatment cost[4]. For this reason, a lot of work has been carried out on extensive search for low cost and efficient sorbents. These low cost sorbents includes industrial or agricultural waste products such as waste slurry, lignin, straw and nut shells, sawdust and bark[5-7]. Lignin is a polymeric natural product arising out of enzyme initiated dehydrogenative polymerization of primary precursors[8] e.g. coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. Lignin is present in large quantities in the cell walls of terrestrial plants and is the main binding agent for fibrous plant components typically comprising from 16-33% of plant biomass[9]. Every year about 50 million tons of lignin is generated by the paper industries all over the world[10], but less than 10% of it is utilized and mostly get consumed as fuel by paper industry itself. As huge amount of lignin is discharged, it causes a serious environmental problem. Lignin has an aromatic, three dimensional polymer structure with apparent infinite molecular weight, also it contains several functional groups such as methoxyl, hydroxyl-aliphatic and phenolic, carboxyl etc[11]. As lignin has high carbon content (about 55-60%) and molecular structure similar to bituminous coal, it can be effectively considered as a precursor for activated carbon and its use as adsorbent[12].The present study was undertaken to investigate the adsorption of two heavy metals Zinc and Lead on the carbonaceous material obtained from industrial waste lignin.

II. MATERIALS AND METHODS

All the chemicals used are of AR grade. Sample solutions were prepared by dissolving required amount of Lead Acetate and Zinc Sulphate salts (Merck) in distilled water. The concentration of the solutions prepared was in the range of 48mg/L and 66.5mg/L for Lead and Zinc respectively.

A. Biosorbent preparation

The adsorbent material used is the carbonaceous residue obtained from pyrolysis of solid lignin in Nitrogen atmosphere. Industrial waste solid lignin was subjected to thermal degradation at 500^0C for 3 hrs. The carbonaceous residue obtained was ground and sieved to get a particle size of 300 microns (Industrial standard sieves). Then it was treated with 10% NaOH solution to remove the traces of undegraded lignin and then washed with distilled water and dried at 110^0C. The char obtained was used to study the removal of Lead and Zinc metal ions.

B. Characterization of Char

The physiochemical characteristics like moisture content, ash content and elemental analysis of adsorbent were determined. For morphological characteristics, scanning electron micrograph of the adsorbent obtained from industrial waste lignin was carried out. The sample was also characterized with FTIR spectra using Perkin Elmer spectrophotometer.

C. Adsorbent Dosage

Adsorption of Lead and Zinc solution by the different adsorbent dosage (0.5-2g/50ml) was carried out for 60 mins. Different adsorbent doses were agitated with 50ml of standard lead and zinc solution for 60 mins separately with constant stirring. Then the solutions were filtered through sintered glass funnel and analyzed for the amount of Pb(II) and Zinc(II) ions uptaken which was quantitatively determined by the difference between the initial and final concentration of Pb and Zn solutions respectively by AAS.

D. Ph Studies

In order to investigate the effect of pH on metal ion adsorption, the pH of metal ion solutions was adjusted to different value ranging from 1 to 7. pH was measured using a pH meter. pH adjusted solution and 1g of adsorbent were used in batch experiments conducted for 60 mins. The uptake studies were carried out separately for Lead and Zinc and the solutions were analyzed for % adsorption by AAS. The pH value at which the maximum Lead and Zinc removal occurs was optimized.

E. Contact time

50ml of Lead Acetate and Zinc Sulphate solution each(pH=5) and 1g of adsorbent were agitated separately at different time intervals. Then the solutions were analyzed for the amount of Pb(II) and Zinc(II) ions uptaken by AAS.

F. Adsorption Studies

Equilibrium sorption studies were performed to provide the maximum metal adsorption capacities of the carbonaceous material. The biosorption equilbria are described with adsorption isotherms of Langmuir and Freundlich types. Since the adsorption isotherms are important to describe how adsorbates will interact with adsorbents and so are critical for design purposes, therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation. The sorption data obtained was analyzed by Freundlich and Langmuir isotherms.

III. RESULT AND DISCUSSION

Characterization of adsorbent

The physiochemical characterization like moisture content, volatile matter content, ash content, and fixed carbon of adsorbent was determined. Moisture determined is 2.41% and that of ash is 12.84%. Moisture content, though does not affect the adsorption power, but dilutes the adsorption and therefore requires the use of additional adsorbents. The ash content gives an idea about inorganic constituents associated with carbon. The % of volatile matter determined is 24.65 and the fixed carbon is 60.1%.The elemental analysis of the carbonaceous material obtained from industrial waste

lignin was carried out by CHN analysis it shows C- 65.34%, H- 3% and N- 1.49% The carbonaceous material prepared by pyrolysis of industrial waste lignin was analyzed by scanning electron micrographs as shown in Fig.1.
SEM is widely used to study the morphological features and surface characteristics of the adsorbent material. In the present study, SEM of carbonaceous material reveals surface texture and porosity.

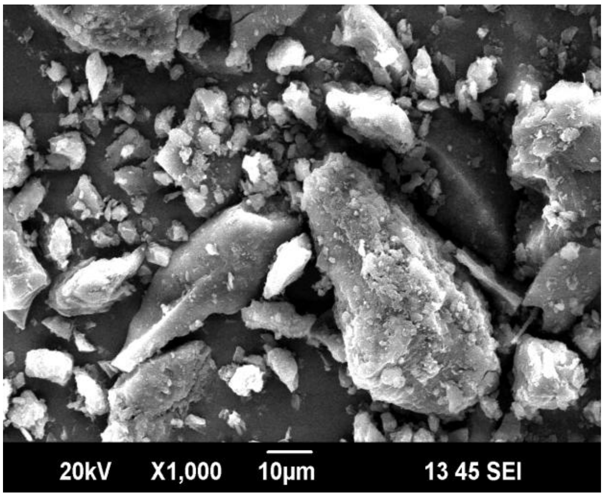

Fig.1.SEM photomicrograph of carbonaceous material

The FTIR spectra of pure lignin showed some characteristics features which are helpful for structural investigations[13]. Fig. 2. shows the FTIR spectrum of purified lignin. The broad peak at 3413 cm^{-1} represents OH Hydrogen bonded. The peak at 2927 cm^{-1} can be assigned to CH stretching in methoxyl group, methyl and methylene group. Vibrations frequency at 1713 cm^{-1} can be assigned to Unconjugated carbonyl/ carboxyl stretching. The peak at 1458cm^{-1} represents C-H deformation combined with aromatic ring and peak at 1426 cm^{-1} represents Aromatic skeletal vibrations. The peak at 1217 cm^{-1} and 1119 cm^{-1} can be assigned to Syringyl ring breathing with C-O stretching and C-O stretching for Secondary alcohols, aliphatic ether, aromatic C-H in plane deformation respectively. The peak at 1034 cm^{-1} represents Aromatic C-H in plane deformation guiacyl type and C-O stretching for primary alcohol.

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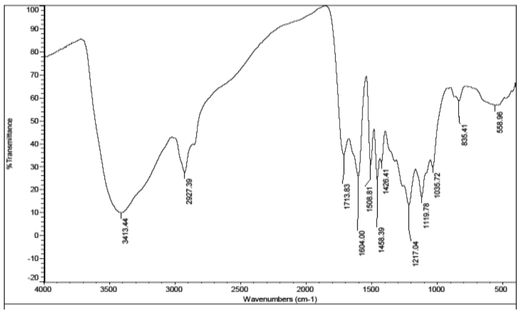

Fig.2. FTIR spectra of pure lignin

Similarly the adsorbent was characterized by FTIR spectroscopy to analyze the functional groups responsible for heavy metal adsorption. Fig.3. Shows that, after degradation / pyrolysis, the decrease in the band intensities is visible in all regions and only some peaks are presented in the FTIR spectrum. For example, a visible intensity was recorded at 1100 cm^{-1} for the char obtained from industrial waste lignin.

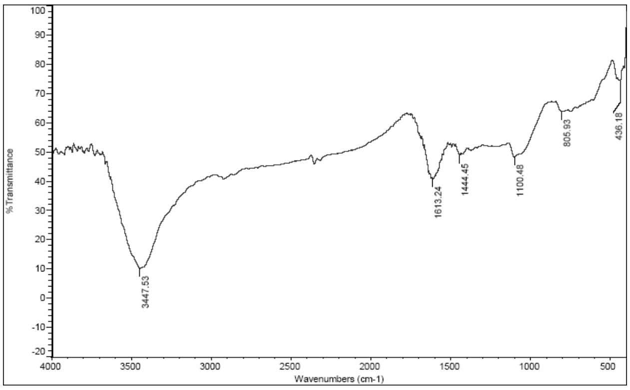

Fig.3. FTIR spectra of carbonaceous material

Effect of adsorbent dose

The effect of adsorbent dose on the removal of Lead and Zinc ions was studied for initial Lead and Zinc concentrations respectively. The uptake studies have been carried out by varying the adsorbent dose, ranging from 0.5 to 2g/50ml for the time interval of 60 mins. Fig.4 shows the effect of adsorbent dosage on the removal of Pb(II) and Zn(II) by the char obtained from industrial waste lignin. The maximum removal of Lead and Zinc was obtained for the adsorbent dose 1g/50ml. The % removal of Lead was 71.66% whereas for Zinc it was 68.75%. However it was observed that after this dose, there was no significant change in the % removal of both Lead and Zinc. It may be due to the availability of the exchangeable sites or surface area on the adsorbents. So 20g/L was considered as the optimum dose for the uptake studies. In the minimum adsorbent dosage level, there will be a low availability of exchangeable sites and ultimately the removal of metal ions at low adsorbent dosage is also minimum. But at maximum adsorbent dosage level (20g/L), there will be a greater availability of exchangeable sites or surface area, hence removal of metal ions at maximum adsorbent dosage is also maximum[14].

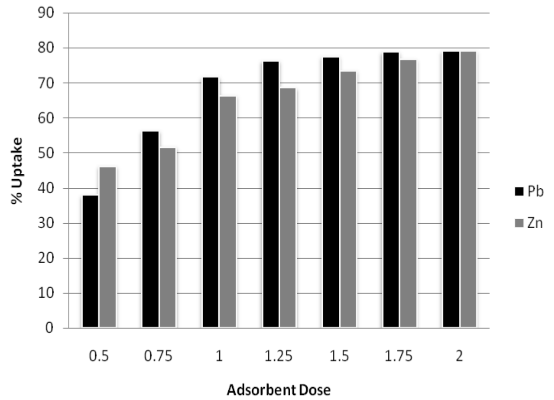

Fig.4. Effect of adsorbent dose

A. Effect of pH

The adsorption of Lead and Zinc was studied at different pH ranging from 1 to 7 and keeping the volume of solution constant under similar conditions. Fig.5. shows that there is practically no removal at pH lower than 3, it may be due to high H^+ ion concentration which may reverse the process of adsorption. There is gradual increase in adsorption with increase in pH from 3 to 6 and the maximum adsorption is at pH 5. It was observed that from pH 7 to 10, there is the formation of the precipitate of $Pb(OH)_2$ and $Zn(OH)_2$. So pH 5 was considered as optimum condition[15].

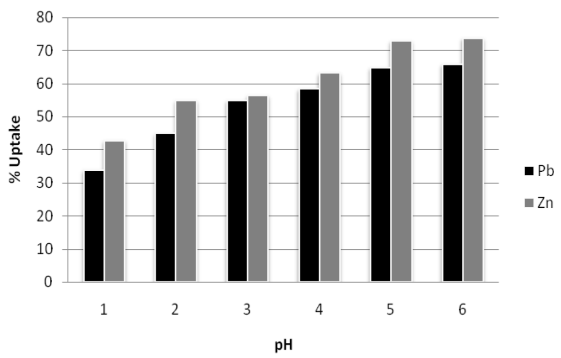

Fig.5. Effect of pH

C. Effect of contact time

Contact time is an important parameter in the adsorption process. The influence of the contact time on the removal of heavy metal ions at different time intervals ranging from 1 hr to 6 hrs was studied, where the volume of the solution kept constant and adsorbent dose 20g/L. In Fig.6. it was observed that there is increase in adsorption with increase in contact time and maximum adsorption takes place at 3hrs. Again after 3 hrs contact time there was no further significant adsorption observed. It may be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. After 3 hrs, the % removal of both Lead and Zinc was decreased due to the decrease in number of adsorption sites and also the Lead and Zinc ion concentration. Normally, the adsorbate forms a monolayer over the surface, which reduces the capacity of adsorbent.

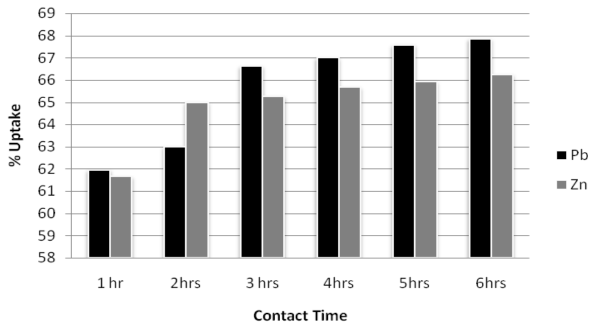

Fig.6. Effect of contact time

D. Adsorption isotherms

Adsorption equilibrium data which express the relationship between mass of adsorbate adsorbed per unit weight of adsorbent and liquid phase equilibrium concentration of adsorbate are represented by adsorption isotherms and provides important design data for adsorption system. The equilibrium data for removal of Lead and Zinc in the present investigations were analyzed using Freundlich[16] and Langmuir[17] adsorption model.
The adsorption data were fitted to the linear form of Freundlich equation (See Fig. 7)

$$\mathrm{Log}q_e = \log K_f + \frac{1}{n} \log C_e$$

Where K_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity respectively.

The adsorption data was also investigated by Langmuir adsorption model

$$\frac{1}{q_e} = \frac{1}{\theta^0 b} - \frac{1}{C_e} + \frac{1}{\theta^0}$$

Where q_e is the amount of metal ion adsorbed per unit weight of the adsorbent (mg/g), C_e is the equilibrium concentration of the metal in aqueous solution (mg/L), θ^0 and b are the Langmuir constants related to the capacity (mg/g) and energy of adsorption (L/mg) respectively.

The linear plots of 1/qe versus 1/Ce (See Fig. 8) suggest the applicability of the Langmuir model for the investigated system, showing formation of monolayer coverage of the adsorbate at the outer surface of the adsorbent.

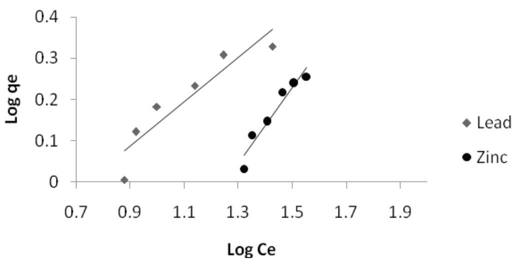

Fig.7. Freundlich isotherm for the adsorption of Pb and Zn onto char

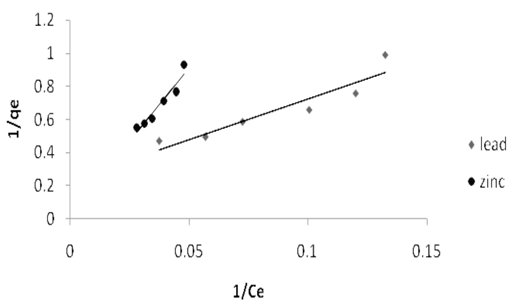

Fig.8. Langmuir isotherm for the adsorption of Pb and Zn onto char

The essential characteristic of Langmuir isotherm may be expressed in terms of dimentionless equilibrium parameter, R using the following equation[18]

$$R = \frac{1}{1 + bC_0}$$

The values of R for all the species lie between 0 and 1 showing favorable uptake of metal ions on the adsorbent.

IV. CONCLUSION

The carbonaceous material obtained from industrial waste lignin had been used to investigate the removal of two metals Pb(II) and Zn(II) ions in aqueous solutions. The highest adsorption occurs at pH 5 for both metal ions. The results obtained from the equilibrium isotherm adsorption studies of two metal ions Pb(II) and Zn(II) were analyzed in two adsorption models namely: Freundlich and Langmuir equations, indicated to be well fitted to both isotherm models. Therefore the technique for preparation of the carbonaceous material from industrial waste lignin showed its potential to be employed as an effective adsorbent in removal of Lead and Zinc ions and would be useful for waste water treatment techniques for the removal of other toxic metal ions and other organic species. Finally it provides a good quality of fuel as a supplement (0calorific value over 5400 kcal/kg) Thus utilization of the lignin in this way is promising and minimizes the disposal problems and converts the waste into useful raw materials and finally ends up as an energy source.

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