Synthesis, characterization and application of nano adsorbent procure from pitheocellobium dulcewood

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Abstract

In this research nanoparticles have been prepared utilizing a lignocellulosic precursor pitheocellobium dulce. A porous nano adsorbent Zinc chloride Activated Carbon of Pitheocellobium Dulce wood (ZACPDW) has been prepared by simple pyrolysis method. The nanoparticle is characterized using ultimate analysis, Particle size analysis,SEM, TEM and FTIR. This nano adsorbent is subjected to chemisorption of Lead(II) ions and Cadmium(II) ions from industrial effluents. The batch work studies of lead and cadmium removal from aqueous solution also examined. This process was carried out with the effect of various operating variables mainly adsorbent dose, pH, and agitation time. The nano adsorbent ZACPDW has shown the optimum pH value for Pb(II) ion removal is 4.0 and Cd(II) ion removal is 6.0 from aqueous solutions. From this analysis it is evident that the new nano particle ZACPDW synthesized can be employed as low cost adsorbent for the removal of Lead and Cadmium ions from various industrial effluents.

Keywords: *Pitheocellobium Dulce; Zinc Chloride; Nano particle; FTIR; SEM; TEM.*

I. INTRODUCTION

Recently, novel porous materials have attracted much attention [1] because of their wide ranging potential applications in catalysis, adsorption and nanotechnology. Characteristics such as large surface area, Potential for self assembly, high specificity, high reactivity and catalytic potential make nanoparticles excellent candidates for water treatment applications [2]. Heavy metal contamination in water sources is recognized as a priority problem in environmental protection [3]. Water pollution due to disposal of heavy metals continues to be a massive problem worldwide. Among various heavy metals lead and cadmium are well known toxic elements with greatest potential hazard to humans and the environment. Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain. A severe exposure to Lead has been associated with sterility, abortion, stillbirths and neonatal deaths [4]. Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, Itai- Itai, bone lesions, cancer and hyper tension in humans [5]. Various techniques have been employed for the removal of heavy metals. Out of them adsorption is the most often involved technique. Activated carbons are the most widely used industrial adsorbent for removing pollutants due to their uniquely powerful adsorption properties and the ability to readily modify their surface chemistry [6]. The properties result from its adequate pore size distribution, high surface area, and broad range of surface functional groups \are responsible for its adsorptive properties, which are exploited in removal of heavy metals[7].Among the numerous dehydrating agents, Zinc Chloride in particular is the most widely used chemical agent in the preparation of activated carbon[8]. The objective of present work is to investigate the use of nanoadsorbent ZACPDW for the adsorption of Pb(II) and Cd(II) from aqueous solutions with different parameters.

II. METHODOLOGY

A. Preparation of ZACPDW

Local available Pitheocellobium Dulce wood was collected and washed with distilled water for three times to remove the water soluble impurities. Then dried in an oven at 120°C for a period of 10hours to remove the moisture and other volatile impurities. The washed wood was cut into 22.5 to 38.6mm pieces. The wood pieces were sundried for 20 days. They were ground and sieved into particle size of 50 to 100μm. The dry powder of the precursor is subjected to chemical activation with Zinc chloride. 30g of $ZnCl_2$ is dissolved in 100ml of distilled water and 10g of the dried precursor powder was well mixed with this. This mixture was stirred vigorously for 90 minutes at 65°C. After mixing the slurry was subjected to vacuum drying at 100°C for 30 hours. The resulting Zinc chloride impregnated samples were Kept in a silica crucible and heated to the final carbonization temperature at 610 ±5°C for a time of 45 minutes [9]. The products were washed sequentially with 0.5N HCL, hot water and finally with cold distilled water to remove residual organic and mineral matters. Then this carbon was dried at 110°C for 180 minutes. After this the ZACPDW is collected in air tight containers for experimental use.

B. Characterization with Equipments

The ZACPDW is characterized using ultimate analysis and the results are shown in Table.1. Scanning Electron Microscope JSM-6090 JEOL JAPAN is used to viewed the surface texture and topology of ZACPDW at an accelerated voltage of 10kV. The size of the Nano adsorbent was found out with the help of particle size analyzer. Transmission Electron Microscope (TEM) studies are carried out on the ZACPDW using a model JEOL-2010 microscope with an accelerating voltage of 100kV. Fourier Transform Infrared Spectroscopy (JASCO FT/IR-670 Plus) studies were carried out to determine the type of functional groups responsible for heavy metal adsorption. The vibrational frequencies were scanned in the spectral range of 4000 to 400 cm^{-1} and are shown in Fig.1.

Table 1. ZACPDW Characterisation

S.NO	***Characteristics***	***ZACPDW***
1	Particle Size(nm)	13 - 48
2	Carbon(%)	44.2
3	Hydrogen(%)	6.2
4	Nitrogen(%)	2.3
5	Sulphur(%)	0
6	Moisture content (%)	3.5
7	Ash content (%)	2.1
8	Volatile matter(%)	11.5

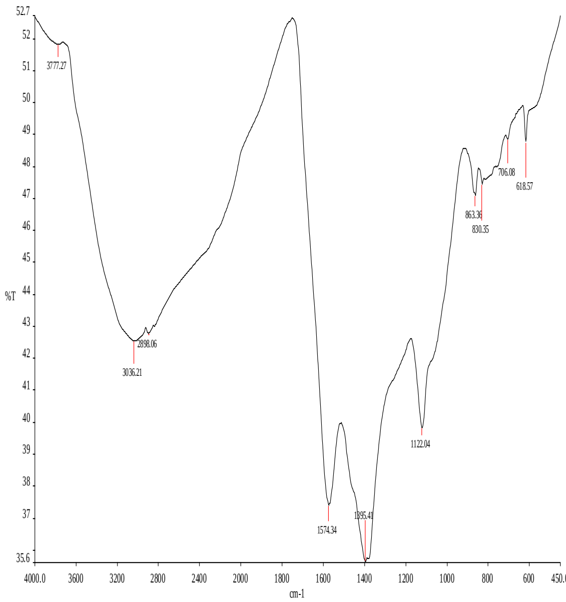


Fig.1. FTIR Spectra of ZACPDW

C. Chemicals and reagents

All the chemicals used in these experiments were of Analytical grade. A stock solution of Lead having 1000ppm concentration was prepared. The sample AR Grade Lead Nitrate was dried in an oven for 2 hours to remove moisture. Then 1.599g of this sample was taken and was dissolved in 1000mL of double distilled water in a volumetric flask. This solution was acidified with 3mL of nitric acid to prevent hydrolysis [10]. From this solution the working solutions for batch work were prepared on dilution. $3CdSO_4.8H_2O$ (MERCK) was used as the source of Cd(II) and all of the solutions were made in distilled water. The solutions of Cd(II) were prepared from a stock solution containing 100mg/L of Cd(II).

D. Adsorption Experiments

Batch adsorption experiments were conducted at desired pH value, contact time, and adsorbent dosage using ZACPDW in a 150mL capped reagent bottle containing 50mL of test solution on an electrically thermostatic shaker. After reaching equilibrium, the mixture was filtered through Whatmann filter paper. Then the concentrations of lead(II) and Cadmium(II) ions in filtrate were determined by Atomic Absorption Spectrophotometer (AAS). The percentage removal of Pb (II) and Cd(II) were calculated by using the equation

$$\%Removal = [(C_{initial} - C_{final}) / C_{initial}] \times 100$$

The batch work studies were carried out with six different pH values, six different time intervals and seven different adsorption dosages. All the batch experiments were carried out in duplicate and the values reported are the average of two readings.

Table 2.Heavy Metal Analysis of Industrial Effluents				
Sample	***Ni mg/L***	***Zn mg/L***	***Pb mg/L***	***Cd mg/L***
EPI	1.6	5.1	0.91	0.14
DM	1.7	3.09	0.83	0.09
BC	3.8	2.3	1.2	0.26

E. ZACPDW in Treatment of Industrial Effluents

The efficiency of nano adsorbent is further examined using three industrial effluents which are collected from an Electro Plating Industry (EPI), a Dyeing Mill (DM) and a Battery Company (BC) from nearby areas. These are previously subjected to heavy metal analysis. The results are displayed in **Table.2.** After this, all the three samples were treated with the ZACPDW at favorable conditions found out in the batch work.

III. RESULT AND DISCUSSION

A. Biosorbent Characterization

The nanoadsorbent ZACPDW is chemically analysed and their results are scheduled in Table.1. The moisture, sulphur and ash contents are very low in the sample but the carbon content is more in ZACPDW. These properties lead to strong adsorption capacity. The particle size is less than 50μm in adsorbent which confirms its nano particle size. The adsorbent is highly active due to its particle size in nano level.

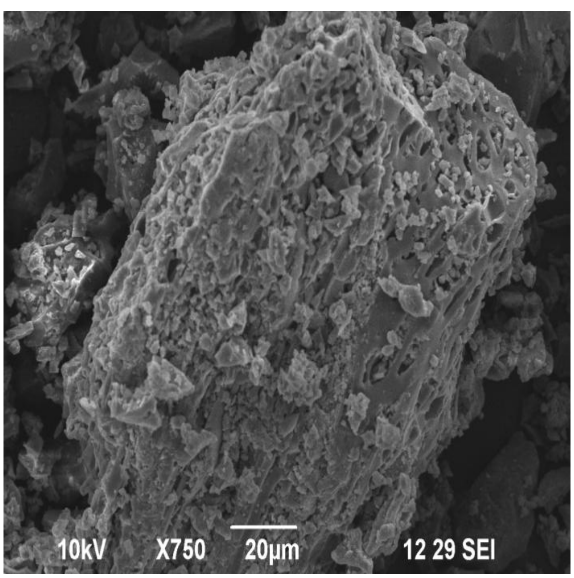


Fig.2. SEM Morphology of ZACPDW

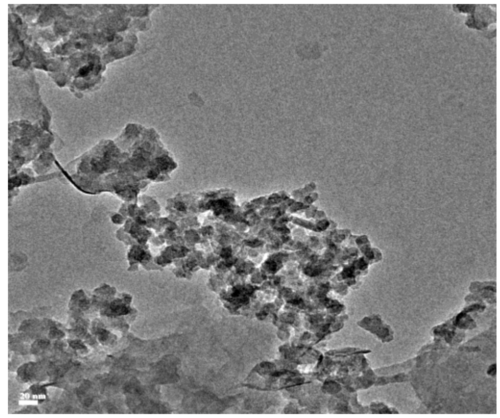


Fig.3. TEM of ZACPDW

B. Spectral analysis of ZACPDW

Fourier Transform Infrared analysis was conducted to confirm the existence of amine, carboxyl and other functional groups. As presented in **Fig.1,** in the FTIR analysis of ZACPDW there are 10 peaks found such as 3777,3036, 2898, 1574, 1335, 1122, 869, 830, 706, 618/cm. The spectrum showed the peak at 1574/cm indicating the carboxyl groups,1335/cm showing –C=O stretching , peak at 1122/cm corresponding to ether linkage, peak at 3036/cm shows –OH stretching, 2898/cm refers –CH stretching and the peaks at 869/cm,830/cm,706/cm all indicates –CH groups out of plane[11].

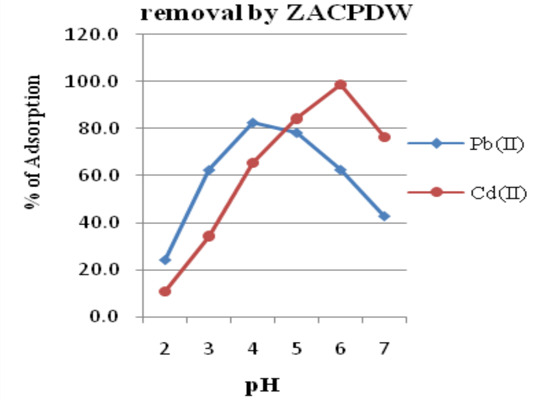
The Scanning Electron Microscope result of the nano adsorbent is given in **Fig.2.** On observation, SEM shows highly porous morphology for the novel ZACPDW. It reveals that there are voids elongated deeply inside the surface of the adsorbent. The zinc chloride activation process in ZACPDW leads to corrode the surface of carbonaceous material and introduce micro, macro and meso pores. The observation of Transmission Electron Microscopy frame of ZACPDW can be viewed in **Fig.3** in its agglomerated form. This is a very good evidence for the nano particle size of the prepared material. All these features enable the nano adsorbent very active.

C. Adsorption Experiments

1) Optimum pH studies

The hydrogen ion concentration (pH) influences the adsorption yield of the novel ZACPDW. The pH value is varied between 2.0 to 7.0 at constant adsorption dosage of 1.0g of adsorbent with constant contact time 75 minutes and the percentage of adsorption is determined. It is found that for Pb(II) the optimum adsorption occurs at pH 4 and for Cd(II) the optimum adsorption occurs at pH 6. It is clearly visible in Fig.4.

Fig.4.Effect of pH on heavymetal removal by ZACPDW



2) *Optimum Dosage Studies*

The percentage removal of Lead(II) and Cd(II) at contact time75 minutes and pH is equal to five with adsorbent dosage from 0.25g to 1.75g shows a very good linear increase in percentage of adsorption since contact surface of adsorbent particles is increased. The effect of adsorbent dosage is shown in Fig.5. For Pb(II) ions the optimum adsorption reached at 1.5g of the adsorbent. But for Cd(II) ions it reached well in advance at 0.5g .

3) *Optimum Time Studies*

1.0g of ZACPDW is taken and the pH is maintained at 5. In these conditions, the contact time varied between 15 to 90 minutes and the percentage of adsorption is monitored. The effects are given at **Fig.6.** At 75 minutes, optimum removal of both the metal ions occurs on the nano adsorbent. After this time it is almost constant throughout the experiment.

D. ZACPDW in Treatment of Industrial Effluents

Table.3. represents the result of heavy metal analysis of all the three Industrial effluents. They are subjected for Lead (II) and Cadmium(II) removal at

Fig.5. Effect of ZACPDW dosage on heavy metal removal

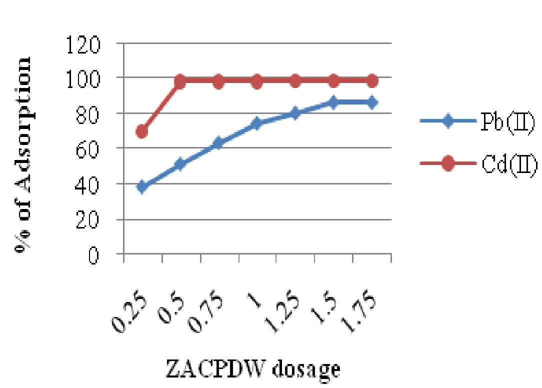
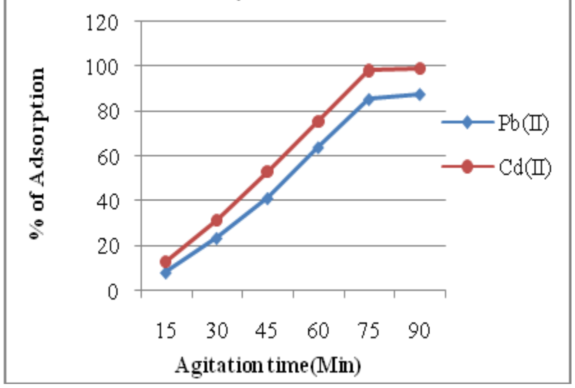


Fig.6. Effect of agitation time on heavymetal removal



Optimized conditions found out from batch work which is about 1.0g of ZACPDW, pH equal to 5 and at contact time 75minutes. The inferences are clearly shown in Fig.7. The nano adsorbent offer more than 80% of Lead (II) adsorption and offer more than 90% of Cadmium(II) adsorption. From this it is obvious that ZACPDW is a better adsorbent for cadmium and lead removal.

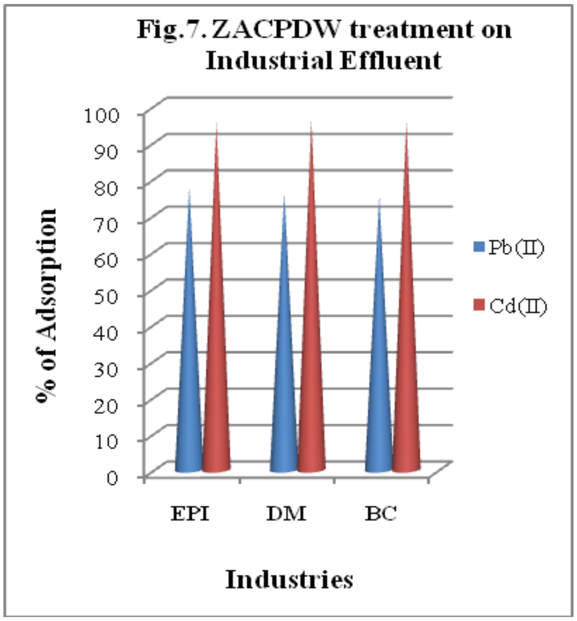
IV. CONCLUSION

The main findings of the present study are summarized as

- Zinc chloride Activated Carbon of Pitheocellobium Dulce Wood (ZACPDW) nano particles are synthesized and it was well confirmed by SEM, TEM and Particle size analysis.
- The synergistic effect of pH, adsorbent dose and agitation time on the removal of Pb(II) and Cd(II) adsorption by the nano adsorbent ZACPDW is examined.
- Lead and Cadmium ions were adsorbed onto the ZACPDW very rapidly within the first 75 minutes.The maximum adsorption of Pb(II) ion is at 1.5g/L of ZACPDW and the same

Table 3. Adsorption percentage of Pb(II) and Cd(II) from Industrial effluents by ZACPDW

Heavy Metals	***Industrial Effluent Samples***		
	EPI	***DM***	***BC***
Pb(II) ions	84.2%	87.8%	80.8%
Cd(II) ions	95.1%	98.6%	92.4%



- is 0.5g/L for Cd(II) removal from dilute solutions.
- The favourable pH condition for Lead removal is slightly acidic(4) and for Cadmium the optimal pH is neutral(6).
- All the batch experiments and the industrial effluent treatment suggest that the ZACPDW is an effective adsorbent for the Cadmium removal. It may be used for Lead removal also.

On the whole, in the adsorption process using ZACPDW, the Cadmium heavy metal performs better than the Lead heavy metal. The precursor used in this work is easily available because it is a common plant which is indigenous in India. The use of ZACPDW as an adsorbent for Cd(II) seems to be an economical and worthwhile alternative over conventional methods.

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