



Removal of Hg (II) metal ions from environmental water samples using chemically modified natural sawdust

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Abstract

In the present study, chemically modified natural saw dust (CMSD) sorbent was prepared via refluxing reaction between citric acid and sawdust. Then, the as prepared CMSD was characterized using scanning electron microscopy (SEM) and FT-IR. The adsorption capability of CMSD towards Hg(II) was significantly increased because of the introduction of carboxylic groups on CMSD's surface during the modification, and the adsorption capability was linearly reliant on carboxylic sites level to some extent. The prepared CMSD was employed for removal of Hg(II) from different samples. Sorption parameters which include pH, temperature, contact time and sorbent and metal ion concentrations were evaluated to determine the best conditions for sorption of Hg(II) onto CMSD sorbent. In addition, the sorption uptake of CMSD was 80 mg g⁻¹. The prepared CMSD was successfully applied to remove Hg(II) from environmental water samples with recovery % , more than 95%.

Keywords: Mercury, chemically modified natural saw dust (CMSD); heavy metal ions; solid phase extraction

1. Introduction

Remediation of aqueous systems polluted with heavy metals is gaining higher consideration since additional data on their poisonous actions to human being and the environmental impact becomes identified. Moreover, raised human growth is considered as placing pressure on water resources and global industrialization is releasing major amounts of pollutants which contaminate the water supplies all over the world. Among the most common heavy metals, there is mercury which is introduced into natural water sources mainly from the urban wastes, oil refining, discharges of the chloride manufacturing industries and manufacture of paints, plastic and batteries.

Separation methods that discard the damaging metal ions from industrial streams and contaminated water are frequently required [1-6]. Multiple approaches including solid phase extraction, precipitation, membrane processes, as well as ion-exchange were utilized to eliminate the pollution arising from harmful metal ions [7-24]. One of the most important natural biopolymer is cellulose. Natural cellulose does not give valuable results if used as a metal scavenger without modification. Therefore, some chemical and

physical modifications must be made to provide some new functional groups, which enable the natural cellulose for the removal of some hazardous metal ions. Chemical modification by insertion of some carboxylic and imino-groups as metal scavenger [25-35] sulphonic acid groups [36], succinyl group [37, 38] and recently the selective oxidation of two neighboring hydroxyl groups (O-H) to give dialdehyde cellulose [39], have been reported. On the other hand, native cellulose possesses reduced sorption ability thus many modifications via introduction of a novel ligand centers into its surface were performed to enhance the sorption capability. Recently, biosorption is efficiently employed to prevent heavy metals from pollution of aqueous solutions. Many low-charge biosorbents were assessed for their ability to remove heavy metals from water. Sugarcane bagasse is considered one of the main biosorbents. Sawdust is a biomaterial chiefly formed of cellulose (45%), hemicellulose (30%) and lignin (30%) [40]. It is a bio waste of wood industry and its accumulation is considered a serious contamination and major health problems. In recent times, utilization of sawdust from various classes of wood to remove heavy metals from watery solutions has gained more

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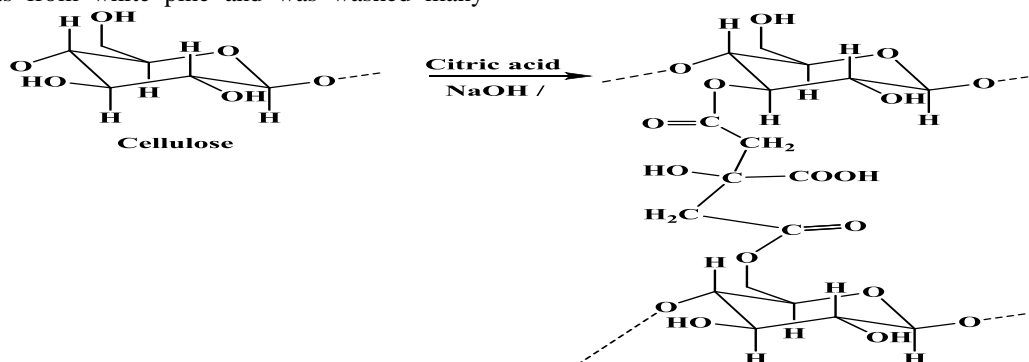
consideration. The adsorption load of sawdust for heavy metals may be improved through modification of its physicochemical characteristics.

The present work aims to enhance the adsorption capacity of sawdust for Hg(II) from watery solutions through modification of sawdust surface. Such process was conducted by refluxing approach and utilizing citric acid solution. The carboxylic groups were attached to sawdust surface throughout the process of modification. In addition, the modification degree, solution pH and temperature effects on adsorption capacity of sawdust for Hg(II) were assessed accurately and the adsorption mechanism of Hg (II) on CMSD was as well explained.

2. Experimental

2.1. Materials

The sawdust which was used through the current study was from white pine and was washed many



Scheme 1 Synthesis of CMSD sorbent

2.3. Instrumentation

FT-IR spectra were obtained by using a Shimadzu 5800 Fourier transform FT-IR spectrometer for the different steps of modification of the natural cellulose to produce modified cellulose (CMSD) by using KBr-pressed discs. To prove the change in the morphological structure of natural and modified one, FEI Quanta 200 environmental scanning electron microscope (Czech Republic) was utilized. Samples were grind well and underwent coating with gold previously by utilizing scanning electron microscope. The amount of uptake of Hg²⁺ was studied with the aid of Agilent's 5100 ICP-OES (Agilent technologies, Australia).

2.4. Sorption studies using batch method

Adsorption experiments were conducted at adjusted pH and 25 °C by vibrating 0.1 g of CMSD with 50 mL of Hg (II) metal ion solution at concentration 80ppm for 6 hours using 220 rpm vibration in pH range (2-6) and time 6 hours. The uptake value (q) was determined using equation (1)

$$q_e = (C_i - C_f) V/W \quad (1)$$

times by using deionized water (DIW) for dust removal. After that it underwent drying in an electric oven at approximately 70 °C for 12 h. Thus, it was milled via an analytic mill and sieved to a mean particle diameter of 0.2 mm. All used chemicals were used as attained, Citric acid and sodium hydroxide were purchased from Sigma, United Kingdom. DIW was utilized during the experiment.

2.2. Synthesis of chemically modified Sawdust (CMSD)

Firstly we take 3 g of the washed sawdust sample and put it in a rounding flask (500 ml) and add (100 ml) of prepared citric acid and (3 ml) of sodium hydroxide (0.1 M) using stirrer device at 80 °C and leave the reaction for (12 hours). Leave the sample until it cools to room temperature, filter the sample, wash it with DIW and dry it in an oven at 50 °C for 8 hours.

Where C_i (ppm) is the initial concentrations of metal ions in solution and C_f (ppm) is the terminal concentration of metal ions in solution following solid phase extraction, W (g) is the weight of the modified cellulosic saw dust and V (L) is the volume. For assign of some thermodynamic parameters, the initial concentration of metal ions was 50 mg L⁻¹ the studying temperature was getting around 35 °C for 6 h.

3. Results and discussion

3.1. Assignment of polymeric samples

3.1.1. Scanning electron-microscope

By studying the variance in morphological structure of the natural and CMSD after modification by SEM, as presented in Fig. 1a, the surface of raw dust was more regular and homogeneous than CMSD [41]. Moreover, the surface is more irregular in cases of CMSD (Fig. 1b). Through previous results, it is possible to conclude the occurrence of interaction between of the citric acid with raw dust to form CMSD.

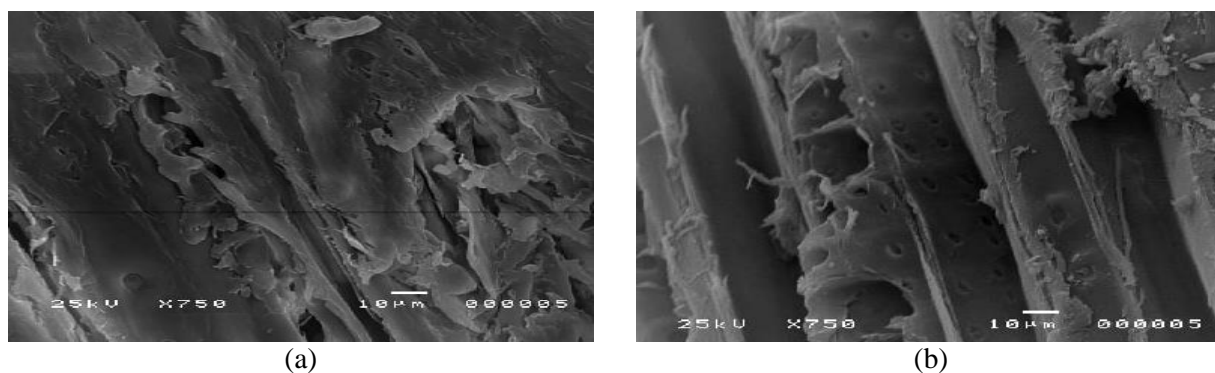


Figure 1 SEM images of (a) sawdust, (b) CMSD

3.1.2. Infrared spectra

The FTIR spectra of native and CMSD was studied to prove the process of modification as presented in Fig. 2. The basic spectra of character of natural cellulose could be seen in (Fig. 2). There are some basic peaks that distinguish cellulose for example a certain peak at $1080\text{--}1160\text{ cm}^{-1}$ which represents the stretching vibrations of (C-O), the certain peak at $1300\text{--}1450\text{ cm}^{-1}$ denotes bending vibrations of O-H, in addition to $3450\text{--}3200\text{ cm}^{-1}$ [42, 43] which denotes stretching vibrations of O-H. The organic acid was bounded to wood components through an esterification reaction among the OH of the wood components and one COOH of the organic acid which has 2-3 COOH groups, and following reaction one or two COOH groups remain free to be bounded to the heavy metal cations.

3.2. Optimization of Hg(II) by CMSD from aqueous solution

3.2.1. Influence of pH

The Influence of medium acidity on Hg(II) uptake was evaluated and represented in Fig. 3. It can be observed that there is slight increase in the uptake of Hg(II) as pH rises in a range of pH 2–6, at pH > 6, the metal ions leave of the solution because of development of colloidal precipitate of Hg(OH) but not because of the adsorption of free Hg(II) ions. Such conclusion was summarized from the evaluation of Hg(II) precipitation as a function of pH [44]. The major uptake value was reported at pH 6 (natural). This might be related to the existence of free lone pair of electrons on O2 atoms of carboxylic group appropriate for coordinate with metal ions giving the corresponding resin-metal complex

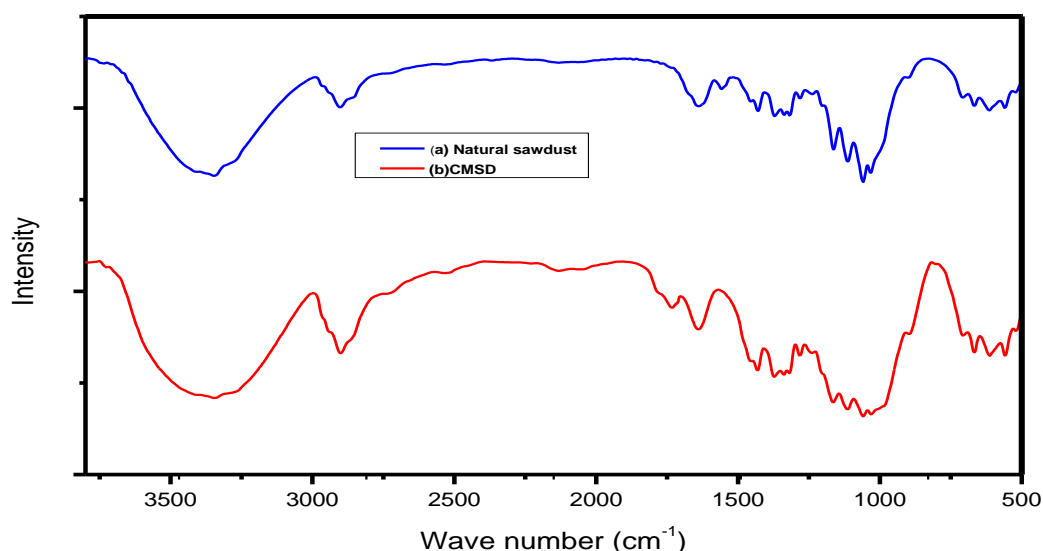


Figure 2 FT-IR spectra of sawdust and CMSD samples

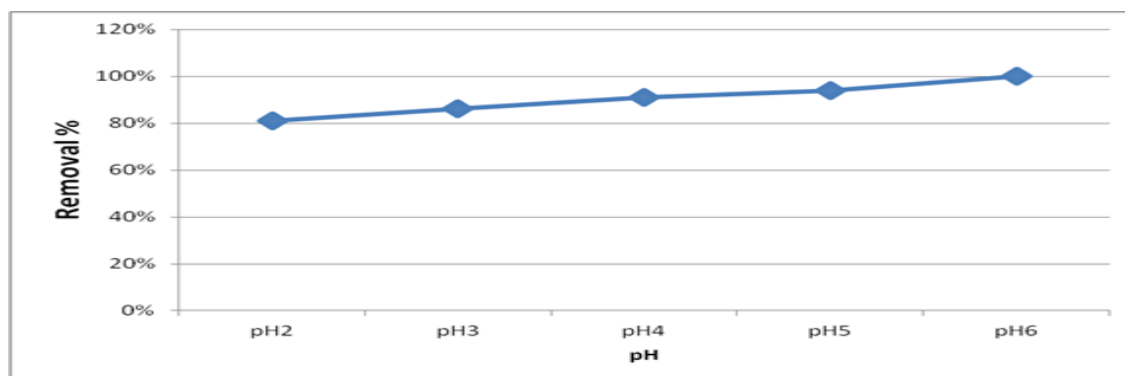


Fig. 3: pH effects on Hg(II) removal by CMSD sorbent (0.1 g), with contact time of 6 hour, centrifugation rate 200 rpm, at 25oC.

3.2.2. The effect of temperature on sorption capacity of metal ions

To evaluate the thermodynamic parameters of the CMSD, the adsorption experiments were performed at different four temperatures and important parameters for instance Gibbs free energy ($\Delta G^{\circ}_{\text{adsn}}$), heat of enthalpy ($\Delta H^{\circ}_{\text{adsn}}$) in addition to entropy of sorption ($\Delta S^{\circ}_{\text{adsn}}$) of metal under study Hg(II) utilizing CMSD were detected. The thermodynamic equilibrium constant (K_c) can be determined as:

$$K_c = C_{\text{adsn}} / C_e \quad (2)$$

Where C_{adsn} is sorbed metal ion concentration on to the active center of the fibers at equilibrium (mg g^{-1}) and C_e is the equilibrium concentration in (mg L^{-1}).

$$\Delta G^{\circ}_{\text{adsn}} = -RT \ln K_c \quad (3)$$

$$\ln K_c = (\Delta S^{\circ}_{\text{adsn}} / R) - (\Delta H^{\circ}_{\text{adsn}} / RT) \quad (4)$$

Where R is ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) the universal gas constant. From the plot of $\ln K_c$ vs $1/T$ as displayed

in Fig.4, we can determine the values of $\Delta H^{\circ}_{\text{adsn}}$ and $\Delta S^{\circ}_{\text{adsn}}$ from the slope ($-\Delta H^{\circ}_{\text{adsn}}/R$) in addition to the intercept ($\Delta S^{\circ}_{\text{adsn}}/R$). The results are presented in Table 1. Through the results obtained of $\Delta G^{\circ}_{\text{adsn}}$ we can conclude that the process of sorption by CMSD is spontaneous at ambient temperature this is obtained from the negative sign of $\Delta G^{\circ}_{\text{adsn}}$. Through the results obtained of $\Delta H^{\circ}_{\text{adsn}}$ we can conclude that the process of sorption by CMSD is exothermic in nature at ambient temperature this is obtained from the negative sign of $\Delta H^{\circ}_{\text{adsn}}$, the lower in the negative charge of $\Delta S^{\circ}_{\text{adsn}}$ values we can conclude that arrangement tendency of the metal ions in the surface of CMSD. Many systems displayed a similar behavior [45]. By drawing a relationship between $\ln K_c$ vs $1/T$, we observed that metal ions' adsorption reduced by raising the temperature of the system. This is because of the weak interaction between the ions and the active center of carboxylic group of CMSD.

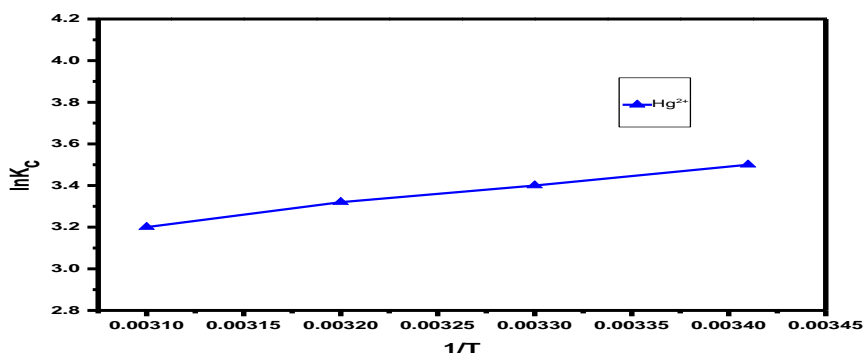


Fig 4: Plot of $\ln K_c$ as a function of $(1/T)$ absolute temperature for the sorption of target metal ions Hg(II) .

Table 1 Thermodynamic studies for the sorption of Hg(II) ions on CMSD

System	K _c			-ΔG ^o _{ads} (kJ/mol)			ΔH ^o _{ads} (kJmol ⁻¹)	ΔS ^o _{ads} (Jmol ⁻¹ K ⁻¹)
	293 K	303 K	313 K	293 K	303 K	313 K		
Hg ²⁺ - CMSD	300	288	275	19.2	17.31	15.95	-31.09	- 44.96

3.2.3. The effect of sorbent concentration

The influence of the concentration of the cellulosic saw dust on mercury ions uptake were obtained by placing (0.1,0.025 and 0.05 g) of CMSD in a series of flasks containing 50 ml 80 ppm of Hg(II) metal solution at definite pH 6. The contents of the flasks were shaken on the equilibrated shaker at 200rpm and 25 °C for 5 and 6 h. After adsorption, the residual concentration of metal ion were determined it shown

that 0.1 g of CMSD at 6 h is sufficient for complete adsorption of mercury ions as shown in Fig. 5.

3.3. Desorption and reusability studies

3.3. 1. Desorption study

The effect of different mixture volumes of nitric acid was studied as following (3-5 ml) of 0.1M nitric acid and for metal ions' desorption. The acquired information (Table2) shows that 5 mL of 0.1 M nitric acid was adequate for entire elution of the metal ions with a recovery exceeding 95%.

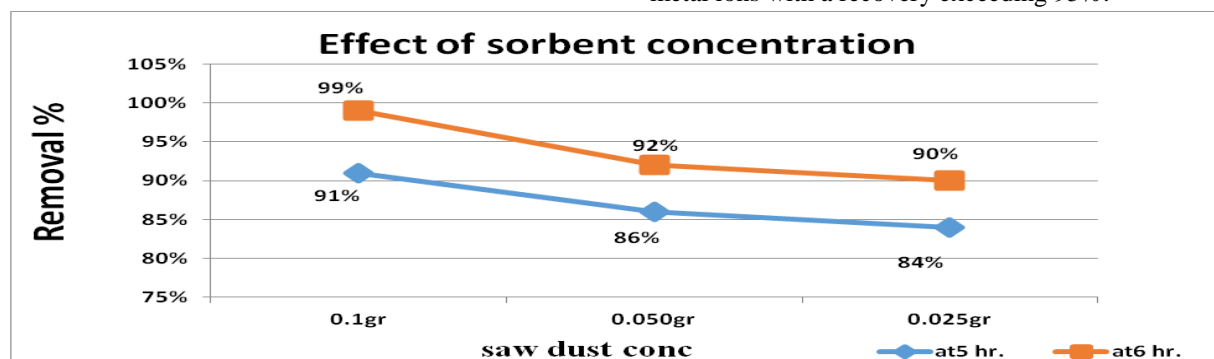


Fig 5: Plot of Removal % of mercury ion vs dose concentration

Table 2 Desorption studies

Eluting agent (0.1M nitric acid) Volume (ml)	Extraction (%)
	Hg(II)
3	87
4	91
5	97.8

3.3. 2. Sorbent reusability

We study five sorption-desorption cycles on CMSD the data were presented in Table 3. It is clear that

modified cellulose kept its sorption capacity following the 5th cycle, that fiber preserve approximately 95% of its initial sorption capacity. of Hg(II) metal ions [46,47].

Table 3 Repeated sorption of Hg(II) (50 ml of 50 mg L⁻¹) by CMSD sorbent (0.10 g), pH 6, shaking time is 6 h, 25 °C, desorption by 5 mL of 0.1 mol L⁻¹ nitric acid.

Cycle number	Recovery (%)
	Hg ²⁺
1	98
2	97
3	96.5
4	95.5
5	95.0

Table 4 Effect of diverse ions

Diverse ions	Tolerance limit (mg L ⁻¹)	% Recovery
K ⁺	1000	98.6
Mg ²⁺	500	98.3
Ca ²⁺	500	97.8
Co ²⁺	50	92.8
Ni ²⁺	50	94.9
Al ³⁺	50	91.9
NO ₃ ⁻	200	92.4
Cl ⁻	1000	98.7
HCO ₃ ⁻	1000	99.8
SO ₄ ²⁻	1000	98.7

3.3.4. The practical applications

Analysis of environmental water samples was performed to determine the accuracy of the suggested approach. The agreement among the spiked and founded quantities with high recovery percentage of

the metal ions which up to value >98%, ensuring the highest precision of the technique and its ability to remove the examined metal ions in real specimens [48]

Table 5 Recovery of Hg(II) from environmental water samples using CMSD

Sample	Ion	Added (µg mL ⁻¹)	Recovery (%)	RSD (%)
Ground water	Hg ²⁺	30	99.06	0.1
Waste water	Hg ²⁺	30	99.9	0.2

4. Conclusion

CMSD chelating fibers were synthesized and identified by efficient techniques. Additionally, the polymeric material CMSD was used in batch method to assess the optimal situations which affects the Hg²⁺ sorption. Regarding the thermodynamic parameters, the sorption processes were exothermic and spontaneous at various temperatures. The kinetics studies of Hg²⁺ metal ions onto CMSD. The adsorption load of modified sawdust for Hg(II) was markedly improved because of the introduction of carboxylic groups on CMSD surface throughout the modification, and it had a linear dependence on carboxylic sites level to some extent.

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