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Use of Low Cost Cellulosic Biopolymer Based Adsorbent for the Removal of Toxic Metal Ions from the Aqueous Solution

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INTRODUCTION

Global urbanization and industrial development has led to various kinds of environmental pollution. Among them water pollution has become a cause of great concern for the sustenance of life. Water pollution due to toxic heavy metal ions has become a more serious environmental problem, as it creates significant problems for both human beings and aquatic life (1-2). Heavy metals ions and their derivatives are potential pollutants in water due to their stability, mobility and their non-biodegradable nature (3). These heavy metals such as Cd, Pb, Cr, Cu, Hg, Zn, and Ni, etc., tend to accumulate in the food chain (4). Ions of copper (Cu$^{2+}$), nickel (Ni$^{2+}$) cadmium (Cd$^{2+}$), lead (Pb$^{2+}$), and zinc (Zn$^{2+}$), which are frequently present in the wastewaters beyond their permissible limit, are quite hazardous and can cause various diseases as well as chronical alterations in the nervous system and disorders of living organisms (5). Therefore, such toxic water resources need to be made free from the toxic ions. So in order to achieve this method like precipitation, ion exchange, adsorption, membrane processes, activated carbon, reverse osmosis, and solvent extraction have been used by various researchers (6).

Among these various methods adsorption is emerging as a cost effective, efficient, environmentally-friendly, and an alternative technique to conventional technologies (7). Due to high cost of activated carbon and other conventional methods, recently scientists have been paying attention towards cellulosic materials as low cost eco-friendly adsorbents to remove the toxic ions form polluted water. The primary advantages of using cellulose fibers as adsorbents are their easy availability, low cost, eco-friendly nature, regenerable and reusable behavior, and minimization of toxic sludge (8). Further, cellulosic fiber represents a huge reservoir of renewable biomass with an annual production estimated to $18 \times 10^{10}$ tons (9). Cellulosic materials for removal of toxic metal ions includes agricultural wastes such as tea and coffee waste, saw dusts, pinus bark, coconut husk, modified cellulosic materials, corncobs, sugarcane bagasse, agave bagasse and different agricultural by-products (10-15). Among various cellulosic materials Abelmokus esculentus fiber containing cellulose, hemicelluloses, and lignin as major constituents and is obtained from the agriculture waste. This fiber has not been studied so far for the purpose of removal of toxic metal ions from the polluted water resources. Therefore, in the present work attempts have been made to determine potential of low cost alkali treated Abelmokus esculentus cellulosic fiber for the removal of toxic heavy metal ions from waste water. For the study, four heavy metal ions copper(II), zinc(II), cadmium(II), and lead(II) were selected and batchwise adsorption on NaOH treated Abelmokus esculentus cellulosic fibers has been carried out. The effect of physico-chemical key
parameters such as the solution pH, the initial metal concentration, contact time, and temperature has been also studied.

MATERIALS AND METHODS
Preparation of Adsorbent
Abelmoschus esculentus cellulosic fibers extracted from stem of okra plant were freed from impurities by using the method reported in literature (16). The dried fibers were then ball milled to a particle size of 60 μm. The fibers were then suspended in 2 M sodium hydroxide solution for two hours. The alkali solution was filtered off and the fibers were washed thoroughly with distilled water until the pH of the wash was close to neutral. The alkali treated fibers were dried at 70°C for 12 hours and then stored in a vacuum desiccator.

Preparation of Adsorbate
For metal adsorption experiments, the stock solutions of Cu(II), Zn(II), Cd(II), and Pb(II) were prepared by dissolving an accurate quantity of copper sulfate (CuSO₄ · 5H₂O; Merck India), zinc nitrate (Zn(NO₃)₂ · 2H₂O; Loba Chemicals) and cadmium nitrate (Cd(NO₃)₂ · 2H₂O; Qualigens fine chemicals) and lead nitrate (Pb(NO₃)₂; Merck India) in double-distilled water.

Characterization of Adsorbent
Functional groups present in raw and treated cellulosic fiber were determined by the Fourier transform infrared (FT-IR) spectroscopy. Spectra were recorded with a spectrometer using KBr pellets with a scan resolution of 4 cm⁻¹ in the range of 4000–500 cm⁻¹.

To determine the crystallinity of the treated samples under different conditions, the sample (powder) was dispersed onto a stub and placed within the chamber of analytical X-ray powder diffractometer (Philips 1710 X-ray diffractometer). Generator intensity was 40 kV, generator current was 50mA. The sample was then scanned from 5 to 50°, in step of 2 degree/minute.

Thermogravimetric analysis of the raw and alkali treated fibers was carried out at a heating rate of 10°C/min over a temperature range of 40 to 800°C using a Linseis L81-II TGA instrument. The surface morphologies of cellulosic fiber before and alkali treated fibers were studied using FEI Quanta 450 SEG Scanning electron microscopy machine at very high magnification.

Adsorption Experiments
Batch experiments were carried out by immersing 50 mg of chemically modified fiber in a 50 ml of metal ion solution taken in stoppered Erlenmeyer flasks. The flasks were gently agitated in an electrically thermostated reciprocating shaker at 150 ± 2 rpm for 180 minutes. At the end of the experiments, the mixtures were separated by filtration using Whatman filter paper no.41. The metal ion concentration before and after the adsorption process was calculated using the method as reported in the literature (17-18). All experiments were conducted in triplicate and mean values were used. The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution. The adsorption amount (q) and removal percentage (%E) were calculated by the Eqs. (1) and (2):

\[ q = \frac{(C_0 - C_e) \times V}{W} \]  
\[ \%E = \frac{(C_0 - C_e)}{C_0} \times 100 \]

where q is the adsorption amount in mg/g, W is the weight of the adsorbent (g), V is the volume of solution (L), and C₀ and Cₑ are the initial and equilibrium concentrations of metal ions in solution. The pH measurements of all aqueous samples were performed following standard methods with pH meter manufactured by Eutech Instruments.

RESULTS AND DISCUSSION
The alkali reaction between cellulosic fiber and sodium hydroxide aqueous solution was shown as below:

\[ \text{Cellulosic fiber-OH} + \text{NaOH} \rightarrow \text{Cellulosic fiber-O}---\text{Na}^+ + \text{H}_2\text{O} \]

When cellulosic fiber was treated with aqueous alkali solution, hydrolysis reactions of polyoses occur, consuming a larger amount of alkali and hindering access of hydroxide ions to cellulose. The alkali treatment results in solubilization of hemicelluloses and pectin embedded in the cell wall of fiber, leaving behind a material with exposed active binding sites for adsorption of metals. The dissolution of especially hemicelluloses and pectin during the treatment of cellulosic fiber with the NaOH solution actually led to shrinkage of the material. This shrinkage of cellulosic fibers may also change the amount of exposed lignin and other cell wall components that may affect the heavy metal ion adsorption capacities of the cellulosic fibers. There is also the possibility of deprotonation of biofibers which may lead to adsorption of toxic metal ions on negatively charged functional groups in the modified adsorbent (19). It was suggested by many researchers that the adsorption capacity get improved by the dissociation of hydrogen ions bonded to hydroxyl, carboxyl, and other groups, which concomitantly offered a negatively charged surface (20). Kapoor and Vijayaraghavan have reported that NaOH might increase the net negative charge on the surface of the biomass by solubilizing surface lipids and by removing base-soluble tannin due to peeling of end-groups, alkaline hydrolysis, degradation, and decomposition of dissolved polysaccharides (21). This peeling is an advantage for new moieties and improves the adsorption process by liberating new adsorption sites.
Characterization of the Adsorbent

**FT-IR Analysis**

Figure 1 shows the FT-IR spectra of raw and NaOH treated cellulose fiber. The characteristic IR bands for lignocellulosic materials, as *Abelmoschus esculentus* cellulose fiber, can be divided into four regions: the broad hydroxyl bands (3200–3600 cm\(^{-1}\)), the stretching bands of CH, CH\(_2\), and CH\(_3\) (2800–3000 cm\(^{-1}\)), the stretching bands of carbonyl groups (1550–1750 cm\(^{-1}\)), and the fingerprint region (below 1550 cm\(^{-1}\)) in which the assignment of IR peaks is not clear because of the complex interaction of their vibration systems. The absorption band at 1733 cm\(^{-1}\) is attributed to the absorption of ester functional groups of hemicelluloses. The intense peak at 1054 cm\(^{-1}\) along with the weak peak at 1250 cm\(^{-1}\) and the shoulder at 1162 cm\(^{-1}\) are C–O stretching vibrations of ethers and alcohols (22). Three strong absorption peaks at 1600, 1512, and 1470 cm\(^{-1}\) correspond to typical aromatic ring vibrations of the phenylpropane skeleton. On treatment with alkali solution, the characteristic bands of lignin and hemicelluloses disappear and absorbance was changed as can be noticed in Fig. 1. The removal of a large chunk of hemicelluloses can be attributed to the disappearance of bands at 1738 cm\(^{-1}\) corresponding to C=O stretching of ester group present in the hemicellulose and similarly the removal of lignin can be identified by the decrease/disappearance of bands 1604, 1252 cm\(^{-1}\) (23) aromatic skeletal vibrations of C=O stretch, respectively. The absorbance of the band at 1377 cm\(^{-1}\) which corresponds to deformation vibration of C–H was decreased due to removal of lignin (24).

**X-Ray Diffraction Analysis**

The crystallinity index (CrI) of raw fiber and NaOH treated fiber was calculated from an X-ray diffraction (XRD) pattern obtained using X-ray powder diffractometer (Philips 1710 X-ray diffractometer). CrI was calculated using the intensity values corresponding to the diffraction of the crystalline structure and the amorphous fraction, according to the Segal method (25):

\[
\text{CrI}\% = \frac{I_{200} - I_{am}}{I_{200}} \times 100
\]

I\(_{200}\) is the intensity of the crystalline peak at the maximum at \(2\theta\) between 22\(^{\circ}\) and 23\(^{\circ}\) and I\(_{am}\) is the intensity at the minimum at 2\(\theta\) between 15\(^{\circ}\) and 18\(^{\circ}\). Figure 2 shows the XRD pattern of raw and NaOH treated cellulose fiber. The crystallinity index of raw fiber and NaOH treated fiber were 48.45\% and 55\%, respectively. This shows that the crystalline nature of the fiber increases on NaOH treatment.

**Thermogravimetric Analysis**

Figure 3 shows the TG scans of the samples. In case of raw fiber, the initial decomposition temperature (IDT) and...
final decomposition temperature (FDT) were 230°C and 466°C respectively. Raw fiber exhibited two stage decomposition with (67%) weight loss in 230–334°C range and second stage decomposition in 335–466°C range. The former stage was attributed to dehydration and volatilization processes. The second stage decomposition was attributed to the degradation of cellulose and lignin. In case of NaOH treated fiber, the IDT and FDT were 223°C and 510°C, respectively. NaOH treated fiber also exhibited two-stage decomposition with (48%) weight loss in 223–342°C range and second stage decomposition in 342–510°C range with 34% weight loss. From the above, it is clear that the treated fibers show higher thermal stability than raw fiber, perhaps due to the removal of oils and hemicelluloses from the fiber surface.

Morphological Studies

Surface morphology of both raw and treated fiber was studied through scanning electron microscopy. It can be observed from SEM micrographs (Fig. 4) that the surface of the alkali modified cellulosic fibres was more rough and porous than that of raw fiber. This could be due to leaching out of waxy layer and hemicelluloses from the fiber surface. In case of alkali treated fiber after adsorption of metal ions, the pores on the surface of the treated fiber got filled with these metal ions from aqueous solution.

Adsorption Studies

Effect of pH

The solution pH affects the adsorption of metal ions from aqueous solution. The effect of pH on the adsorption of metal ions by the NaOH treated cellulosic fiber has been presented in Fig. 5. The pH of the aqueous medium not only affects the solubility of the metal ions but also the ionic form in which it will be present in the solution and the type and ionic state of the functional groups at the adsorbent surface (26). At low pH, adsorption sites are more protonated and they are less attractive to metal ions present in aqueous solution and hence low adsorption. With the increase in pH the adsorption of metal ion was found to increase. This could be due to the fact that at lower pH (pH < 4), the concentration of protons competing with metal ions for the active sites was higher (27) but at higher pH (pH > 4), the concentration of protons decreased which result in easy attraction between the metal ions and the adsorbent. The maximum adsorption of metal ions occurred at

FIG. 4. SEM images of (a) Raw fiber (b) NaOH treated fiber (c) NaOH treated fiber with metal ion adsorption.
REMOV AL OF TOXIC METAL IONS

FIG. 5. Effect of pH on the removal of Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) metal ions by NaOH treated fiber adsorbent (initial concentration 200 mg/L; contact time 180 minutes; shaking rate 150 rpm, 25°C).

pH range from 5 to 7. Further pH of maximum adsorption was selected for the other batch experiments.

**Effect of Time and Adsorption Kinetics**

It has been found that adsorption of metal ion increases with increase in contact time as shown in Fig. 6a. From the figure it has been observed that a very rapid increase during the initial stage of adsorption and thereafter the rate of adsorption decreases, beyond 60 minutes. For, Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) the equilibrium time of adsorption was found to be 90, 60, 90, and 60 minutes, respectively. Beyond equilibrium time, no significant change has been found in metal ions removal. In general, about 80% of the total metal ion adsorption was achieved within 60 minutes for different metal–adsorbent systems. Adsorption kinetics plays a very important role in providing insights into the reaction pathways and mechanism of adsorption reactions. The followed kinetic models have been studied to identify the rate and kinetics of adsorption of heavy metal ions. The pseudo-first-order kinetic model proposed by Lagergren can be expressed as (28):

\[
\ln (q_e - q_t) = \ln (q_e) - k_1 t
\]  

(5)

where \(k_1\) is the rate constant of pseudo-first-order adsorption (min\(^{-1}\)) and \(q_t\) is the amount of metal ion adsorbed at time \(t\) (mg/g), \(q_e\) is its value at equilibrium (mg/g). For the pseudo-first-order model rate constant, the straight line plots of \(\ln (q_e - q_t)\) vs. \(t\) have been analyzed. The kinetic constant \(k_1\) and correlation coefficients have been calculated and summarized in Table 1. The pseudo-second-order kinetic model as proposed by Ho and McKay based on the assumption that adsorption follows second-order chemisorption and this can be presented as follows (29):

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \left(\frac{1}{q_e}\right)t
\]  

(6)

The equation constant \(k_2\) (mg/min/g). can be determined from the intercept and the slope of the plot of \(t/q_t\) versus \(t\) and summarized in Table 1. Besides adsorption at the external surface of the adsorbent, there was a possibility of intraparticle diffusion from the external surface into the pore of the adsorbent.

FIG. 6b. The plot of intraparticle diffusion modelling of Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) metal ions by NaOH treated fiber adsorbent (initial concentration 200 mg/L; shaking rate 150 rpm, 25°C).

FIG. 6a. Effect of time on the removal of Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), and Pb\(^{2+}\) metal ions by NaOH treated fiber adsorbent (initial concentration 200 mg/L; shaking rate 150 rpm, 25°C).


TABLE 1

Kinetic parameters for Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ ions adsorption NaOH treated cellulosic fibers

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$K_1$ (min$^{-1}$)</th>
<th>$q_e$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>$4.25 \times 10^{-2}$</td>
<td>16.95</td>
<td>0.9901</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>$6.26 \times 10^{-2}$</td>
<td>17.51</td>
<td>0.9924</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>$3.18 \times 10^{-2}$</td>
<td>28.46</td>
<td>0.9466</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>$4.90 \times 10^{-2}$</td>
<td>54.45</td>
<td>0.9988</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$K_2$ (g/mg min)</th>
<th>$q_e$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>$3.97 \times 10^{-3}$</td>
<td>17.46</td>
<td>0.9925</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>$3.19 \times 10^{-3}$</td>
<td>15.69</td>
<td>0.9936</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>$2.57 \times 10^{-4}$</td>
<td>40.12</td>
<td>0.9963</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>$6.33 \times 10^{-5}$</td>
<td>58.89</td>
<td>0.9945</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$c$</th>
<th>$K_{id}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>3.89</td>
<td>0.987</td>
<td>0.8067</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>5.90</td>
<td>0.76</td>
<td>0.6526</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>12.06</td>
<td>2.082</td>
<td>0.8022</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>21.22</td>
<td>2.905</td>
<td>0.6997</td>
</tr>
</tbody>
</table>

This possibility has been explored by plotting $q_t$ versus $t^{1/2}$, according to Weber–Morris model \((30)\):

$$q_t = k_{id}t^{1/2} + C \quad (8)$$

where $C$ is the intercept and $k_{id}$ is the intraparticle diffusion rate constant (mg/g h$^{0.5}$) calculated from the slopes of respective plots $q$ vs. $t^{1/2}$ as shown in Fig. 6b. The plot of the metal ion adsorbed quantity against square root of time has been given in Fig. 6b. It can be seen that these plots are multilinear curves over the whole time range, with three distinct regions which indicate that more than one mechanism could govern the adsorption process \((31)\). The initial curve stage relates to the adsorption on external surface. The second region corresponds to the gradual uptake, which reflects intraparticle diffusion as the rate limiting step. The final plateau region indicates equilibrium uptake. This indicates that the mechanism of metal ion adsorption by alkali treated cellulosic fiber is complex and both the surface adsorption as well as intraparticle diffusion contributes to the rate determining step.

In the present study, the experimental equilibrium data of different metal ions on alkali treated fiber was analyzed by the pseudo-first-order and pseudo-second-order kinetic models. Table 1 shows the results of fitting experimental data with pseudo-first-order and pseudo second order study using regres- sional correlation coefficients ($R^2$) calculated using Origin Program 8.0. The kinetic study reveals that the pseudo-second-order model was found to correlate best with our experimental data for metal adsorption from aqueous solutions than other kinetic models studied.

Effect of Temperature and Isosteric Heat of Adsorption

In order to evaluate the effect of temperature, uptake of metals by adsorbent was studied by a series of experiments conducted at the contact time, 120 min, by varying the temperature in the range of 25–60°C. The result has been given in Fig. 7a. It can be seen that the amount of metal ions adsorbed slightly decreases with increase in the temperature, which is indicative of exothermic nature of adsorption process. Decrease in adsorption with the rise in temperature may be due to the increasing tendency to desorbed metal ions from the interface to the aqueous solution \((32)\). Further, the magnitude of heat of adsorption could provide useful information concerning the nature of the surface and the adsorbed phase. The heat of adsorption calculated at constant amounts of adsorbate adsorbed is known as isosteric heat of adsorption ($\Delta H_X$). The heat of adsorption was calculated using Clausius–Clapeyron equation \((33)\):

$$\frac{dlnC_e}{dT} = -\frac{\Delta H_X}{RT^2} \quad (11)$$
Effect of Metal Ion Concentration and Adsorption Isotherm

The effect of different metal ion concentration has been shown in Fig. 8a. From the figure, it has been observed that at low initial concentration (less than 200 mg/L), adsorption capacities of metal ions increased almost proportionally with the increase in the initial metal ion concentrations, suggesting that the adsorption process was highly concentration dependent (34). However, at higher initial concentration (more than 200 mg/L), the increase in metal ion uptake was slow. So, in this case the number of adsorption sites in the adsorbent actually became the limiting factor that controlled the amount of metal ion uptake (35). Further, the Langmuir and Freundlich isotherm models were used for analysis of equilibrium data. The Langmuir isotherm, which describes the adsorption onto specific homogenous sites within an adsorbent and in linear form, can be represented as (36):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$  \hspace{0.5cm} (13)

where $q_e$ is the equilibrium metal ion concentration on the adsorbent (mg/g), $C_e$ is the equilibrium metal ion concentration in the solution (mg/L), $q_m$ is the monolayer biosorption capacity of the adsorbent (mg/g), and $K_L$ is the Langmuir adsorption constant (L/mg) related with the free energy of adsorption.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Metal ion</th>
<th>$\Delta H_x$ (KJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu$^{2+}$</td>
<td>$-3.67$</td>
<td>0.9791</td>
</tr>
<tr>
<td>2</td>
<td>Zn$^{2+}$</td>
<td>$-4.24$</td>
<td>0.9485</td>
</tr>
<tr>
<td>3</td>
<td>Cd$^{2+}$</td>
<td>$-4.5$</td>
<td>0.9822</td>
</tr>
<tr>
<td>4</td>
<td>Pb$^{2+}$</td>
<td>$-5.86$</td>
<td>0.9800</td>
</tr>
</tbody>
</table>

where R represents the molar gas constant (8.314 J/mol K). For this purpose, the equilibrium concentration ($C_e$) at constant amount of the adsorbed metal ions is obtained from the adsorption data at different temperatures. ($\Delta H_x$) is calculated from the slope of the lnCe versus $1/T$ as shown in Fig. 7b. Further, Table 2 shows the enthalpy values and correlation coefficients ($R^2$) values for all metal ions. The calculated enthalpy changes are $-3.67$, $-4.24$, $-4.5$ and $-5.86$ KJ/mol for ions, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$, respectively, indicating that the adsorption process was exothermic in nature.

**Table 2**

Isosteric heat of adsorption for Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ metal ions adsorption by NaOH treated cellulosic fibers

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Metal ion</th>
<th>$\Delta H_x$ (KJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu$^{2+}$</td>
<td>$-3.67$</td>
<td>0.9791</td>
</tr>
<tr>
<td>2</td>
<td>Zn$^{2+}$</td>
<td>$-4.24$</td>
<td>0.9485</td>
</tr>
<tr>
<td>3</td>
<td>Cd$^{2+}$</td>
<td>$-4.5$</td>
<td>0.9822</td>
</tr>
<tr>
<td>4</td>
<td>Pb$^{2+}$</td>
<td>$-5.86$</td>
<td>0.9800</td>
</tr>
</tbody>
</table>
A linearized plot of $C_e/q_e$ versus $C_e$ is obtained from the model and was represented in Fig. 8b. $K_L$ and $q_m$ are computed from the slopes and intercepts of straight lines and presented in Table 3. The isotherm shows good fit to the experimental data. The adsorption capacity of alkali treated cellulosic fiber from the Langmuir isotherm was found to be 19.21, 16.85, 44.42, and 67.24 mg/g for Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$, respectively. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the adsorbate and the adsorbent using the separation factor “$R_L$”, expressed as in the following equation (37):

$$R_L = \frac{1}{1 + K_L C_0}$$  (14)

where $K_L$ is the Langmuir constant and $C_0$ is the initial concentration of metal ion. The value of separation parameter $R_L$ provides important information about the nature of adsorption (Table 4). The value of $R_L$ indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$). Since all $R_L$ values are between 0 and 1, it can be stated that the metal adsorption was favorable for all heavy metal ions studied. The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy and linear form of the Freundlich isotherm can be given as (38):

$$lnq_e = lnK_F + \frac{1}{n}(lnC_e)$$  (16)

where $q_e$ is the equilibrium metal ion concentration on the adsorbent (mg/g), $C_e$ is the equilibrium metal ion concentration.
TABLE 4
Calculated $R_L$ values for Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ metal ions adsorption by NaOH treated cellulosic fibers

<table>
<thead>
<tr>
<th>Metal ion concentration (mg/L)</th>
<th>Cu$^{2+}$</th>
<th>Zn$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Pb$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.3105</td>
<td>0.2937</td>
<td>0.2697</td>
<td>0.3149</td>
</tr>
<tr>
<td>200</td>
<td>0.1838</td>
<td>0.1721</td>
<td>0.1688</td>
<td>0.2080</td>
</tr>
<tr>
<td>400</td>
<td>0.1011</td>
<td>0.1217</td>
<td>0.1040</td>
<td>0.1328</td>
</tr>
<tr>
<td>600</td>
<td>0.0697</td>
<td>0.0846</td>
<td>0.0751</td>
<td>0.0926</td>
</tr>
<tr>
<td>800</td>
<td>0.0532</td>
<td>0.0623</td>
<td>0.0610</td>
<td>0.0740</td>
</tr>
<tr>
<td>1000</td>
<td>0.0431</td>
<td>0.0494</td>
<td>0.0498</td>
<td>0.0559</td>
</tr>
</tbody>
</table>

Mechanism of Heavy Metal Ion Adsorption by Cellulosic Fibers

The mechanisms of the biosorption process by cellulosic fibers based biomass generally include physico-chemical interactions between metal ions and the functional groups present on the cell surface, such as electrostatic interactions, ions exchange, and metal ion chelation and complexation. The major components of the polymeric component in cellulosic fibers are cellulose and lignin compounds. From the nature of the cellulose fibers which are efficient in capturing heavy metal ions, it can be speculated that cellulose or other phenolic compounds (lignin) are the active ion exchange compounds and that active sites are the hydroxyl and phenolic groups of those compounds. Based on the structure of these compounds, a possible mechanism of ion exchange has been shown in Scheme 1 which shows that a divalent heavy metal ion attaches itself to two adjacent hydroxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ion into solution. Ion exchange mechanism has further been confirmed by the desorption experiments not reported here.

Further, a comparative study of sodium hydroxide treated various lignocellulosic fibers adsorbent for the removal of heavy metal ions from aqueous solution has been shown in Table 5.

CONCLUSIONS

From the above studies it has been observed that mercerization of Abelmoschus esculentus cellulosic fibers results in loss of hemicelluloses and pectin from fiber surface. The adsorption characteristics of the metal ions in aqueous solution depends upon various factors such as pH, time, temperature, and metal

TABLE 5
Comparative studies of sodium hydroxide modified cellulosic fibers wastes as adsorbents for the removal of heavy metal ions from aqueous solution

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Modifying agent</th>
<th>Heavy metal</th>
<th>$q_{\text{max}}$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sawdust (Poplar tree)</td>
<td>Sodium hydroxide</td>
<td>Cu(II)</td>
<td>6.92</td>
<td>(41)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn(II)</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>Cork powder</td>
<td>Sodium hydroxide</td>
<td>Cu(II)</td>
<td>18.8</td>
<td>(20)</td>
</tr>
<tr>
<td>Sawdust (Cedrus deodar wood)</td>
<td>Sodium hydroxide</td>
<td>Cd(II)</td>
<td>73.62</td>
<td>(42)</td>
</tr>
<tr>
<td>Rice Husk</td>
<td>Sodium hydroxide</td>
<td>Cd(II)</td>
<td>20.24</td>
<td>(43)</td>
</tr>
<tr>
<td>Spent grain</td>
<td>Sodium hydroxide</td>
<td>Pb(II)</td>
<td>35.5</td>
<td>(44)</td>
</tr>
<tr>
<td>Imperata cylindrica leaf powder</td>
<td>Sodium hydroxide</td>
<td>Pb(II)</td>
<td>13.50</td>
<td>(45)</td>
</tr>
<tr>
<td>Cone powder</td>
<td>Potassium hydroxide</td>
<td>Cu(II)</td>
<td>26.32</td>
<td>(46)</td>
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<td></td>
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<td>Pb(II)</td>
<td>32.26</td>
<td></td>
</tr>
<tr>
<td>Alfalfa biomass</td>
<td>Sodium hydroxide</td>
<td>Pb(II)</td>
<td>89.2</td>
<td>(47)</td>
</tr>
<tr>
<td>Abelmoschus Esulentus fiber</td>
<td>Sodium hydroxide</td>
<td>Cu(II)</td>
<td>19.21</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
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<td>Zn(II)</td>
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<td>Cd(II)</td>
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<td></td>
<td></td>
<td>Pb(II)</td>
<td>67.24</td>
<td></td>
</tr>
</tbody>
</table>
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REFERENCES


