Adsorption of chromium (III) ion on biosorbents prepared from *Leucaena leucocephala* tree

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**Abstract.** Biosorbents (fiber, treated fiber, and charcoal) from the *Leucaena leucocephala* tree were prepared in this study. The potential of the biosorbents as metal capture (removal percentage %R) for chromium (III) (Cr³⁺) from aqueous solution was examined. The concentrations of the Cr³⁺ solutions were measured before and after the adsorption to investigate the %R using atomic absorption spectrometry (AAS). Moreover, the specific surface area (A) of the biosorbent samples was evaluated after measuring the adsorbed acetic acid onto the samples. From the results, A and %R were found in the order of charcoal > treated fiber > fiber. The highest values of A and %R were about 423 m²g⁻¹ and 97%, respectively. This finding suggested the high potential of *Leucaena* charcoal usage as chromium ions capture compared to fibers and treated fibers.

1. **Introduction**

Adsorption is the phenomenon that occurs due to the adhesion of the solute (adsorbate) on the adsorbent material surface whereas sorption is the term that expresses both adsorptions as well as absorption. That depends on the nature of both adsorbate and adsorbent substances, the adsorption is named physical or chemical adsorption based on the way of the attachment. It could be via weak intermolecular forces or chemical bonding. Several isotherm models have been developed to study the phenomenon such as Freundlich [1], Langmuir [2], Brunauer–Emmett–Teller (BET) [3], Temkin [4], Redlich-Peterson [5], and Dubinin-Radushkevich (D–R) [6,7] isotherms. Adsorption and sorption are widely used in different applications as catalysts [8-11], chromatography [12], pharmaceutical industry applications [13], and water treatments [14-21].

Biomaterials and activated carbon have been proven to be an effective adsorbent for the removal of a variety of pollutants from water, such as heavy metals [14,16] and dyes [15,18] from aqueous solutions. They are extensively used for adsorption owing to the high surface area, electrical charge, ease of fabrication steps and surface modifications, eco-friendly, high-efficiency, renewable, and low-cost starting materials [14-18,22,23]. Therefore, there is a growing research interest in the preparation, development, and investigation of the adsorbents from renewable biomaterials which are mainly industrial, plant materials, and agricultural by-products.

*Leucaena leucocephala* is a species of the *Fabaceae* family (Subfamily: *Mimosoideae*), it is commonly known as *Leucaena*. The tree is native to Southern Mexico and Northern Central America,
now it is widespread in over 35 countries. It is fast-growing (reaching up to 3-15 m in height) and a long-lived perennial legume, *Leucaena* is used in numerous applications such as wood products \[24-26\]. Bu Hajar and Mukassabi \[27\] examined the capability of *Leucaena* seeds to germinate under different low watering regimes and their ability up to which level of dryness to grow and establish successfully. The area of study was in Libya and it was concluded that *Leucaena* seed under such very dry conditions had more germination potential than that concluded in the literature \[27\]. *Leucaena* in Libya grows as a wild tree in several regions of the country. Nevertheless, it is not yet applied in Libya for the different applications and not reported in scientific or industrial researches database.

In this study, twigs of *Leucaena leucocephala* tree were collected from Benghazi city, Libya and it was used for preparation different biosorbents. The specific surface area \((A)\) of the biosorbents was estimated. Moreover, sorption percentage (the removal \(\% R\)) of chromium (III) ion from aqueous solution was examined using Atomic Absorption Spectrometry (AAS).

2. Experimental

2.1. Estimation of specific surface area

Twigs of *Leucaena leucocephala* tree were chopped into small pieces and washed with distilled water, then they were partially burned in an oven at 200 °C. The dried samples were ground as a powder and divided into three parts, one part labelled as fiber (F). The second part was treated with NaOH solution (4%), it was labelled as treated fiber (TF). The third part was burned to obtain charcoal and labelled as (Ch). The three samples were washed with distilled water several times, dried at 100 °C, and finally kept in a desiccator until used. Chemicals used in this study are sodium hydroxide (NaOH), acetic acid (CH\(_3\)COOH), phenolphthalein indicator, and chromium (III) nitrate \([\text{Cr(NO}_3\text{)}_3.9\text{H}_2\text{O}]\).

2.2. Estimation of specific surface area

The estimation was carried out with a series of different concentrations \((0.05, 0.1, 0.2, 0.3, 0.4, 0.5 \text{ mol L}^{-1})\) of the acetic acid solution and a fixed amount of the biosorbents \((m)\) as well as the volume of solution \((V)\). The solutions were shaken at 23 ±1°C for 30 min and then filtered. The concentration of the acetic acid solutions was determined before \((C_i)\) and after \((C_f)\) the addition of the biosorbents. The titration was conducted against NaOH using phenolphthalein as an indicator.

The Langmuir equation \[2\] was used to calculate \(A\) of the adsorbents. The general formula of Langmuir isotherm is:

\[
Y = \frac{K C_e}{(1 + K C_e)}
\]

where \(K\) is a Langmuir adsorption constant, and \(C_e\) is the equilibrium concentration (here \(C_e = C_f\)). In this study, \(Y\) is the fraction of surface covered by adsorbed molecules \((Y = N/N_m\), where \(N\) represents the number of moles that adsorbed at \(C_e\), and \(N_m\) is the number of moles of adsorbed which required to form a monolayer). After making the substitution and rearranging the equation, the Langmuir isotherm becomes in the linear form:

\[
\frac{C_e}{N} = \frac{C_e}{N_m} + \frac{1}{K N_m}
\]

From the above equation, a linear plot of \(C_e/N\) values versus \(C_e\) is drawn and \(N_m\) represents the reciprocal of the resulted straight-line slope. The specific surface area was calculated by the following equation \[28\]

\[
A = N_m \times N_a \times 10^{-20}
\]

where \(A\) is the specific surface area \((\text{m}^2 \text{g}^{-1}); \alpha\) is the occupied surface area of one molecule of acetic acid =21 Å\(^2\); \(N_a\) is Avogadro’s number.
2.3 Determination of the removal percentage of chromium (III) nitrate

The experiment was conducted by measuring the concentration of the chromium solution (25 ml) before ($C_i$, 0.5503 mg L$^{-1}$) and after ($C_f$) the addition of the biosorbents (0.244 g). Erlenmeyer flasks containing the biosorbent and the solution were shaken at room temperature (23 ± 1°C) for a period of 30 min and then filtered. Atomic Absorption Spectrometry (AAS) (Model novAA 350, Analytik Jena, Germany) was used to determine the concentration.

3. Results and discussion

Figure 1 illustrates the linear Langmuir isotherm equation with the experimental data for the sorption of acetic acid onto the biosorbents (F, TF, and Ch). The samples showed very high positive values of the correlation coefficient ($R^2$), above 0.9, suggested that the adsorption process follows Langmuir isotherm and a monolayer type of adsorption. The highest value of 0.9943 was recorded for the TF, whereas lower values were recorded for F and Ch due to the impurity on the fiber surface and the surface porosity, respectively. Moreover, the results show that the $N_m$ of the F surface was increased after the treatment and the highest value of $N_m$ was reported for the Ch. Accordingly, $A$ values of the biosorbents are about 82, 87, and 423 m$^2$ g$^{-1}$ for F, TF, and Ch, respectively. The results are comparable with that reported for activated carbons prepared from Leucaena leucocephala biomass by Wan Ibrahim et al. 2019 [20], however, the method of measurement was different. The study showed that the adsorption process of cadmium was best fitted to Langmuir isotherm and the BET surface areas were determined as 185, 595, and 776 m$^2$ g$^{-1}$ for the NaOH:char ratios of 1:1, 2:1, and 3:1, respectively [20].

![Figure 1. Langmuir Linear plots [C$_e$/N values versus the equilibrium concentration (C$_i$)].](image)

The removal percentage (% $R$) of Cr$^{3+}$ and the metal uptake capacity (amount of adsorbed Cr$^{3+}$ in mg/g, mg metal per gram adsorbent) using F, TF, and Ch were calculated according to the following equations:

$$% R = \frac{C_i - C_f}{C_i} \times 100$$

(4)

$$Q = \frac{C_i - C_f}{m} \times V$$

(5)
where $C_i$ and $C_f$ are the initial and final concentrations (mg L$^{-1}$), respectively. $Q$ is the (mg/g), $V$ is the volume of the metal solution in the flask (L) and $m$ is the dry mass of biosorbent (g).

The removal percentage ($\% R$) and the metal uptake capacity ($Q$) are illustrated in Figures 2 and 3, respectively. $\% R$ and $Q$ of Cr$^{3+}$ were slightly increased after treatment, while they were increased significantly using Ch compared with the results of F and TF. The high potential of Ch is due to its high $A$ value compared to the other samples which reflects its porous structure of the surface. Moreover, the adsorption of metals on different adsorption surfaces is dependent on their hydration energies and electronegativity [21]. The values of $\% R$ was about 89, 92, and 97%, for F, TF, and Ch, respectively. The maximum adsorption capacity ($Q$) of Cr$^{3+}$ ions was obtained as $5.45 \times 10^{-2}$ mg/g for the Ch.

**Figure 2.** Removal percentage ($\% R$) of chromium (III) nitrate using fiber (F), treated fiber (TF), and charcoal (Ch).

**Figure 3.** The uptake capacity ($Q$) of chromium (III) nitrate onto fiber (F), treated fiber (TF), and charcoal (Ch).

4. **Conclusion**

Three different biosorbents were produced from the *Leucaena leucocephala* tree which are fiber, treated fiber, and charcoal. The results show that the biosorbents could be used as Cr$^{3+}$ ions captures from aqueous solution. The removal percentage ($\% R$) was dependent on the specific surface area ($A$). $A$ and
% R were increased after treatment from about 82 to 87 m²g⁻¹ and 89% to 92%, respectively. Moreover, the obtained charcoal showed the highest A and % R (about 423 m²g⁻¹ and 97%, respectively) due to the possible porous structure of its surface. It is suggested that to carry out further studies (such as applying other isotherm models and surface characterisation) to investigate the nature of interfacial adhesion onto the surface of biosorbents from *Leucaena leucocephala* tree.

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