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Effect of the chelating agents on bio-sorption of hexavalent chromium using *Agave sisalana* fibers

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ABSTRACT

The current work is focused on the study of the bio-sorption of hexavalent chromium from aqueous solution using sisal natural fiber (*Agave sisalana*) treated by various chelating agents (ligands) such as urea (UR), thiocarbamide (TC), ethylenediaminetetraacetic acid (EDTA), and diphenyl carbazide (DCZ). The fiber treatments were investigated using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning electron microscope (SEM). The kinetics of chromium bio-sorption was studied in batch presses under the effect of some physicochemical factors such as the nature of chelating agent (F@UR, F@TC, F@DCZ, and F@EDTA), adsorbent dose (2–10 $g \cdot L^{-1}$), chromium initial concentration (100–500 $mg \cdot L^{-1}$), solution pH (1–6), and batch temperature (20 °C–50 °C). This study resulted in an optimum adsorption at a chromium initial concentration of 100 $mg \cdot L^{-1}$, at pH 2, and at 20 °C. The obtained results showed clearly that the treatment with chelating agent boosts the adsorptive capacity of *A. sisalana* fibers Cr(VI) 10.9 $mg \cdot g^{-1}$ to 58.6 $mg \cdot g^{-1}$. The modeling study showed that the adsorption kinetics obey the pseudo-second-order model, with an R^2 in the range of 0.991 and 0.999. The bio-sorption isotherms followed the Langmuir model; the maximum uptake capacity of (F@N, F@UR, F@TC, F@DCZ, and F@EDTA) was found to be respectively, 12.3 $mg \cdot g^{-1}$, 25.33 $mg \cdot g^{-1}$, 28.73 $mg \cdot g^{-1}$, 42.54 $mg \cdot g^{-1}$, and 61.45 $mg \cdot g^{-1}$. The determined adsorption thermodynamics parameters such as enthalpy, free energy, and entropy showed that the adsorption process is exothermic, spontaneous, and has a stable configuration.

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1. Introduction

The elimination of chemical hazards (radioactive elements, textile dyes, heavy metals, and their derivatives) from aquatic environment became an essential environmental process to protect our life. The large diffusion of these pollutants is due essentially to the great development of the main human industrial activities [1–3]. Many industrial processes (manufacture of steel, leather, textiles…) throw liquid and solid wastes contaminated by a lot of heavy metals, such as mercury, chromium, and cadmium [4–5]. These metals became one of the most toxically compounds due to their detrimental effect on the environment and ecosystems, causing damage to the gills of aquatic organisms and disrupting their spawning sites and refuges. The toxicity of these compounds is enhanced through bioaccumulation and they can be transported and released elsewhere, in water sources, sediments, and foods [6–8].

The hexavalent chromium is one of the most toxic metals; people can be exposed to this element by breathing, eating, drinking or by direct contact with chrome compounds [9]. This element is hazardous to health, especially for those working in steel and textile industries. Smokers also have a greater risk of exposure to chromium. It is known that chromium(VI) has various health consequences. In leather factories, it can cause allergic reactions, such as rashes [10] and inhaling it can cause nasal irritation and nosebleeds. Chromium(VI) may have other consequences (rashes, stomach upset and ulcers, respiratory problems, immune system weakness liver and kidney damage, alteration of genetic material, lung cancer, death) [9–10]. Considering the hexavalent chromium carcinogenic nature, the contamination level limit for Cr(VI) in domestic water supplies is 0.05 $mg \cdot L^{-1}$. Its concentration in industrial wastewaters ranges from 0.5 to 270 $mg \cdot L^{-1}$. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 $mg \cdot L^{-1}$ and in potable water is 0.05 $mg \cdot L^{-1}$ [11,12].

Several practical physicochemical techniques have been developed to remove hexavalent chromium from wastewater, including solid phase extraction [13], adsorption [5,14], photocatalyzed reduction [15], chemical precipitation [16], ion exchange [17], reverse osmosis [18], and electrokinetic technique [19]. However, many of these procedures are too costly, especially when used for treating large waste streams. However, the bio-sorption using natural adsorbents such as activated

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carbon, natural clays, marine algae, and plant fibers is among the most practical, green, and economical techniques used for the removal of chromium and their derivatives from aqua mediums [5].

In the past 20 years, natural fibers such as Jute, Hemp, Kapok, and *Agave sisalana* became among the most and low-cost bio-adsorbents, due to their interesting properties, such as surface morphology, good surface area, wide-range porosity, high gas permeability, good diameters, and small inter-fibrous pore size [20]. However, few studies related to the removal of heavy metals using these materials make reference to the bio-sorption of Cr(IV) using *A. sisalana* fibers (Fig. 1.).

Recently, great efforts have been devoted to improving the adsorptive properties of these fibers by essential physicochemical modifications of their surface. E. Padmini *et al.* [21] treated the sisal using sodium carbonate for the removal of nickel from aqueous solutions; whereas, T. Hajeeth *et al.* [22] modified the surface of sisal fibers using acrylic acid to remove Cr(VI) from aqueous solution. The main objective of the present study is the removal of chromium(IV) from aqueous solution using sisal fibers as a bio-adsorbent. Hence, in order to obtain a suitable removal of this toxic metal, we treated the natural fibers with various chelating agents such as urea (UR), thiocarbamide (TC), diphenyl carbazide (DCZ), and ethylenediaminetetraacetic acid (EDTA); the high chelating properties of these ligands, can improve the adsorptive capacity of the treated sisal fibers for the removal of this toxic element from aqueous medium.

The bio-sorption mechanism was studied under the effects of some physicochemical factors such as the nature of the chelating agents (F@UR, F@TC, F@EDTA, and F@DCZ), fiber amount, contact time, solution pH, Cr(VI) initial concentration, and medium temperature. The bio-sorption thermodynamic parameters such as free energy ($\Delta G^{\ominus}$), enthalpy ($\Delta H^{\ominus}$), and entropy ($\Delta S^{\ominus}$), have been determined at a different temperature.

2. Experimental

The used *A. sisalana* natural fibers were perched from local farms. All solutions were prepared from analytical grade reagent (sodium dichromate, urea, thiocarbamide, ethylenediaminetetraacetic, and diphenyl carbazide). A stock standard solution of chromium(VI) was prepared by dissolving 500 mg of sodium dichromate $Na_2Cr_2O_7$ (Merck) in 1 L of double distilled water. The medium pH was adjusted using hydrochloric acid and sodium hydroxide solution (0.1 $mol \cdot L^{-1}$).

2.1. Preparation of adsorbents

The sisal natural fibers were chopped in small pieces of size approximately 10 mm and sieved using the appropriate mesh sieve. The collected fiber samples were cleaned at room temperature using nitric acid solution (0.1 $mol \cdot L^{-1}$), and with hydrogen peroxide (10%) for 1 h then, oven dried at 80 °C for 24 h. The cleaned sisal fibers were treated using the various chelating agents, under stirring at room temperature for 48 h as shown in Fig. 2. The treated fibers were then washed several times with double distilled water, centrifuged at 3000 $r \cdot min^{-1}$, and oven dried again for 24 h at 80 °C. The treated fibers have been characterized by infrared spectroscopy.

2.2. Batch adsorption studies

The bio-sorption experiments were made in batch method under the effect of some physicochemical factors. All sorption experiments

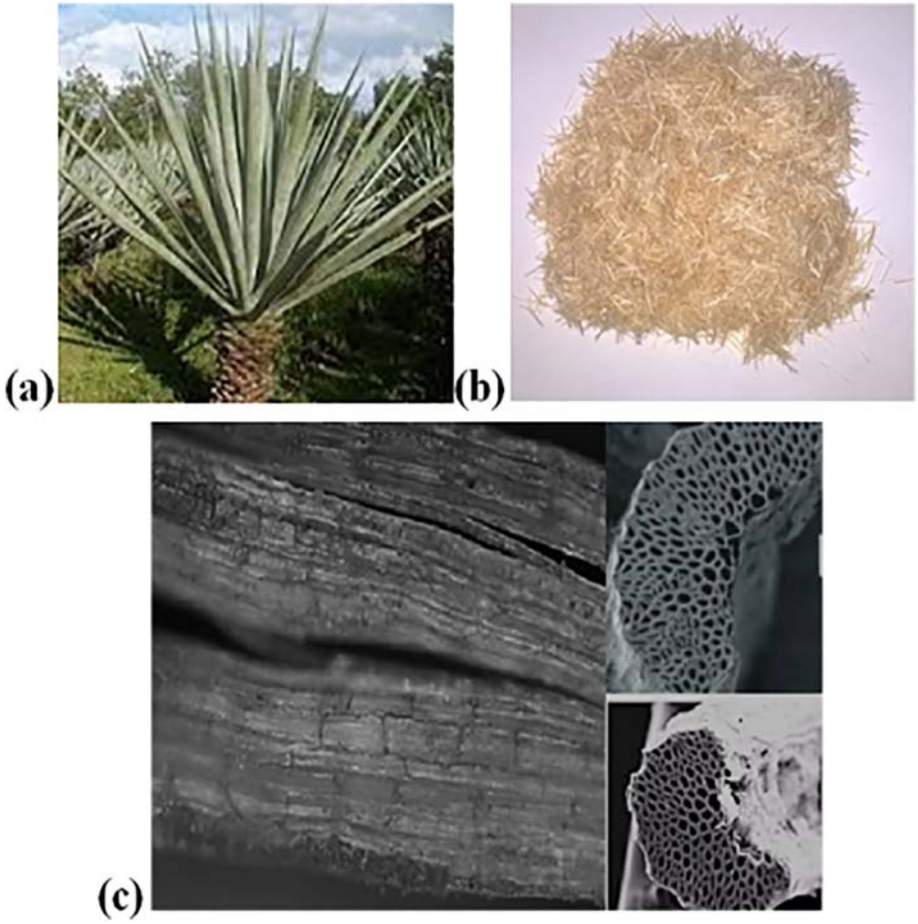

Fig. 1. (a) *Agave sisalana*, (b) chopped sisal fibers, and (c) SEM image of their surface.

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