

Biosorption of Chromium (VI) From Single Ion Solutions on Cotton Stalks and Rice Straw Wastes

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Abstract: Industrial activities discharge their effluents containing heavy metals without treatment. The removal of hexavalent chromium (Cr VI) from wastewater is necessary as it is a carcinogen. The aim of this work is to study the removal of (Cr VI) from single ion solution using adsorption technique. Some plant based biomass wastes were tested as biosorbents for Cr (VI) from aqueous solutions. These wastes are cotton stalk wastes (CSW), and rice straw wastes (RSW). Batch scale experiments using Cr (VI) individual single ion solutions were carried out to test the main biosorption parameters such as pH, adsorbent concentration, initial adsorbate concentration, adsorbent particle size and the kinetics of biosorption. The process was pH dependant with an optimal at pH 2 for the tested biosorbents. The capacity of the studied biosorbents to bind chromium (VI) from individual solution was 17.13 and 7.47 mg g⁻¹ for CSW and RSW respectively at 5.0 g l⁻¹ adsorbent concentration and 300 mg l⁻¹ adsorbate initial concentration. Experimental equilibrium data were fitted to Langmuir and Freundlich adsorption isotherms. r² for the relation was 0.9677 and 0.9220 for CSW and RSW respectively in regards to Langmuir isotherm.

Key words: Cotton stalks; Rice straw; Heavy metals; Hexavalent chromium; Adsorption isotherm

I. Introduction

Chromium and its compounds are ubiquitous and persistent environmental contaminants released into natural environment from a variety of anthropogenic sources, including the electroplating, leather tanning processes, chromite ore processing, wood preservation, alloys making, corrosion control, pigment and dyes, and metal finishing industries [1]. Though the removal of Cr from wastewater is obligatory before discharging into aquatic environment, the rest in the effluent will still cause serious environmental impact. Trivalent chromium is essentially non-toxic in contrast to hazardous hexavalent chromium. Therefore, the discharge of Cr into aquatic ecosystems has become a matter of concern over the last few decades [2]. Cr (VI) concentration in industrial wastewater ranges from 0.5 to 270,000 mg/l [3]. The maximum levels permitted in wastewater are 5 mg/l for Cr (III) and 0.05 mg/l for Cr (VI) [4]. With this limit, it is essential for industries to treat their effluent to reduce Cr (VI) levels to the acceptable levels.

Many conventional techniques, including chemical precipitation, membrane separation, ion exchange, reverse osmosis and solvent extraction have been employed for the treatment of metal bearing industrial effluents [5]. However, the disadvantages of these methods such as secondary pollution, high chemical or energy requirements, or high cost have recently shifted a large amount of studies to develop more efficient removal processes for heavy metal control.

Adsorption of metals on activated carbon derived from different sources has been studied [6]; lignite and anthracite [7]; carbonaceous materials derived from agricultural wastes [8] and activated carbon fibers [9] have also been reported without concern about energy spent for charring or carbonization.

Biosorption is an emerging and innovative technology using biomasses to remove pollutants from wastewater, especially those that are not easily biodegradable such as heavy metals and dyes [10]. A variety of biomaterials such as bacteria [11], fungi [12], yeast [13], and algae [14] were tested as Cr VI adsorbents.

Bio-wastes (plant based biomass) are generated as a by-product of industry and agriculture [15-17]. Some of these were selected to bind these pollutants. Some authors reported the biosorption of Cr VI adsorption on plant shells [18-19], on sugarcane bagasse [20], Agaricus bisporus [21], and on coconut coir pith [2], on fermentation waste [22], on pistachio hull waste [23], and on biodiesel waste residue [24]. The adsorption process is a one stage process that can apply the rule of treating wastes using other wastes as fascinating option in contemporary environmental management.

Cotton and rice are from the major economy crops in Egypt. Many of the agricultural by-product streams in Egypt are not economically used, i.e. 3 million tons of rice straw [25] is burned in the field, creating serious environmental problems (air pollution; smog formation). The well-known "Black Cloud" is a yearly health problem covering all over Cairo. Cotton stalk waste constitutes a voluminous material and produced in large quantities annually (1.6 million tons) as reported by [26].

The present work aimed at determining the potential of powdered cotton stalk wastes (CSW), and rice straw wastes (RSW) as chromium (VI) biosorbents from synthetic aqueous solutions.

II. Materials and methods

The wastes under investigation were thoroughly washed with running tap water, then distilled water and dried at 100^o C. The obtained dried CSW and RSW were crushed into small pieces, then were powdered in an electric grinder, after that they were sieved to a mesh size of 0.09, 0.125, 0.25 and 0.5 mm. The obtained powder was used without further modification.

All chemicals used were of analytical grade. Single ion stock chromium (VI) solution (1000 mg l⁻¹) was prepared in distilled water using potassium dichromate for individual solution. All the working solutions were prepared by diluting the stock solution with distilled water. The investigated wastes were obtained from nearby farms (CSW and RSW).

2.1 The chemical composition of wastes

Cotton stalks contain 30% cellulose and 13% hemicelluloses and about 31% lignin [27]. Rice straw was reported to contain, cellulose (37.4%), hemicellulose (44.9%), lignin (4.9%) and silicon ash (13.1%) [28]. Also, Wartelle and Marshall [29], reported that rice straw has a composition of cellulose, hemicelluloses, lignin and silica ash of 43.3, 25.1, 5.4 and 13.1% respectively.

2.2 Experimental methods

All biosorption studies were carried out at ambient temperature (25 ± 5^o C). A 50 ml aliquot of the solution containing the desired quantity of chromium (VI) was treated with 1.0 g of powdered cotton stalk wastes (CSW) or powdered rice straw wastes (RSW) for 24 h. The adsorbate/adsorbent mixture was filtered on qualitative filter paper and the filtrate was analyzed for the remaining chromium (VI) concentration using the standard 1,5 diphenylcarbazide method [30]. Percentage chromium removal (Re %) was calculated using the formula:

$$\text{Re \%} = (1 - C/C_0) * 100$$

Where C and C₀ are the final and initial concentrations of chromium (VI) in the test solution, respectively.

2.2.1 pH

The effect of pH on the adsorption of chromium (VI) onto CSW and RSW was also studied using 50 ml aliquot of solution containing 300 mg l⁻¹ chromium (VI). One gram of each of CSW and RSW was added separately to 50 ml chromium (VI) solution (300 mg l⁻¹) to cover pH range of 2 to 10. The pH was adjusted by adding either dilute H₂SO₄ or NaOH and the sorbent / adsorbate mixture was left for 24 h, then the amount of remained chromium (VI) was measured spectrophotometrically as mentioned before.

2.2.2 Adsorbate concentration

Adsorbate / adsorbent behavior was tested with Cr (VI) concentration range from 100 – 500 mg l⁻¹ and adsorbent concentration of 20 g l⁻¹.

2.2.3 Particle size

The effect of adsorbent particle size was investigated by using 1g of each biosorbent with particle size of 90, 125, 250 and 500 μm to 50 ml chromium (VI) solution (300 mg l⁻¹) at pH 2 for 24 hours then the filtrate was measured for residual Cr (VI).

2.2.4 Adsorbent dose

Sorbent dose optimization experiment was done by adding different weights of CSW and RSW with a range of 0.25 – 2.0 g to 50 ml chromium (VI) solution (300mg l⁻¹) at the optimum pH and left for 24 h. The amount of residual chromium (VI) was then calculated as mentioned above.

2.2.5 Kinetics (Contact time)

Kinetics of biosorption was also studied for CSW and RSW over time period of 24 hours with initial adsorbate concentration of 300 mg l⁻¹ at the optimum pH for the wastes under investigation. The residual quantity of Cr (VI) over the different time intervals was measured spectrophotometrically as previously mentioned.

III. Results and discussion

3.1 Effect of pH on Cr(VI) adsorption capacity

It has been reported that the solution pH is an important parameter affecting biosorption of heavy metal ions [1, 6]. The obtained results for the different biosorbents have revealed that decreasing pH leads to an increase in both adsorption efficiency and adsorption capacity for chromium (VI). A pH of 2 was chosen as optimum value to carry out the experiments, at which the maximum adsorption efficiency and capacity were recorded for CSW and RSW for individual Cr (VI), (Figure 1). This behavior could be explained on the basis of change in the surface charge of the biosorbent, whereas at low pH of 2, the H⁺ ions concentration in the aqueous system increased and the surface of biosorbent acquires positive charge by absorbing H⁺ ions, so the positively charged surface sites on biosorbent favor the biosorption of anionic chromate ions due to the electrostatic attraction leading to maximum biosorption [31]. These results are in agreement with that reported by [22,32-33].

3.2 Effect of particle size on Cr (VI) biosorption

Investigation showed that particles size of 90, 125, 250 and 500 μm have removal percentage of 99.51, 98.89, 89.82 and 96.06 % for CSW and 71.02, 55.32, 53.23 and 23.48 % for RSW in the same sequence (Figure 3). The results obtained showed that that the highest removal percentage was noticed for the smallest particle size. This could be due to the increase in surface area with the decrease in particle size. This is clearly noticed for RSW while it is not that clear for CSW.

3.3 Kinetics of Cr (VI) biosorption

Results have revealed that Cr VI adsorption increased gradually over time from 15 minutes to 24 h with initial chromium (VI) concentration of 300 mg l⁻¹, onto CSW, and RSW whether for individual Cr(VI) (Figure 3). It could be noticed that that rapid biosorption occurred within first 15 min and then swing until reach equilibrium after 24 hours, this could be explained on the ground that when exterior surface of the biosorbent reaches saturation, the chromate ions enter into the pores of the biosorbent particles and were adsorbed by interior surface of the solid particles. This process takes relatively longer time [31].

3.4 Effect of initial Cr (VI) concentration on biosorption

Adsorption capacity of Cr(VI) with initial concentrations ranged from 100 to 500 mg l⁻¹ onto CSW and RSW respectively was depicted in Figure 4. Adsorption capacity, at 500 mg l⁻¹ Cr (VI) individual solutions, has values of 15.79 and 9.75 mg g⁻¹ for CSW and RSW respectively (Figure 4).

3.5 Effect of biosorbent dosage

Effect of CSW and RSW dosage on adsorption capacity profiles was studied. Figure 5 showed that the highest adsorption capacity achieved was 17.13 and 7.47 mg l⁻¹, in Cr(VI) single ion solutions for CSW and RSW respectively, at a dosage of 10.0 and 20 g l⁻¹ for CSW and RSW respectively.

3.6 Sorption isotherm

Adsorption data is usually described by adsorption isotherm such as linear, Langmuir and Freundlich isotherms. These isotherms relate the metal uptake per unit mass of adsorbent q_e to the equilibrium adsorbate concentration in the bulk phase C_e . According to Kumar and Ahmad [31], Langmuir model assumes that the biosorption sites are homogenous and the monolayer coverage of the adsorbate is at the outer surface of the biosorbent, while the Freundlich model is employed to describe the heterogeneous system, which is characterized by the heterogeneity factor $1/n$, that gives an indication of the favorability of biosorption, whereas the value of $1/n < 1.0$ represent favorable biosorption conditions. The linear equation of Langmuir and Freundlich models respectively are:

$$1/q_e = (1/Q^0 + (1/bQ^0C_e))$$

$$\text{Log } q_e = \text{log } k_F + 1/n \text{ log } c_e$$

Where q_e is the amount of adsorbate at equilibrium (mg/g), Q^0 and b are constants related to adsorption capacity and the energy of adsorption respectively. The Freundlich constant k_F and $1/n$ are related to the biosorption capacity and heterogeneity factors related to binding strength respectively. Both Langmuir and Freundlich parameters were obtained from the intercept and slope of the plot between $1/q_e$ versus $1/c_e$ and $\text{log } q_e$ vs. $\text{log } c_e$, respectively.

The data obtained fit both the Langmuir and Freundlich isotherm for the studied biosorbents. The correlation coefficients and adsorption parameters for Langmuir and Freundlich isotherms were summarized in table 1.

Table (1): Langmuir and Freundlich isotherm parameters for Cr (VI) biosorption onto CSW and RSW

Biosorbents	Langmuir			Freundlich		
	Q ^o	b	(r ²)	k _F	1/n	(r ²)
CSW	15.1997	0.5801	0.9677	0.7509	0.2344	0.8947
RSW	8.3558	0.1133	0.9220	0.4656	0.1982	0.9566

3.7 Structure and adsorption mechanism

Biosorption of Cr (VI) at acidic pH2 may be attributed to the electrostatic attraction of dominant negatively charged chromate ions (HCrO₄)⁻. Commonly, the electrostatic interaction, surface complexation, and ion-exchange mechanisms may be identified as the major adsorption mechanisms that work individually or in combinations for the adsorption of metal ions on the adsorbents [34]. Charged sites on the biosorbents are those formed by the protonation, that means addition of proton (H)⁺ to an atom, molecule or ion, of polysaccharides found in cotton stalk and rice straw [35-37].

Sorption kinetics can be controlled by several independent processes that could act in series or in parallel, such as the following: (i) bulk diffusion, (ii) external mass transfer (film diffusion), (iii) chemical reaction (chemisorption), and (iv) intraparticle diffusion. Also, it is quite common that more than one process can contribute to the system performance at the same time [38]. In this regards, it is worthy to mention that it was also reported that Cr (VI) removal is a two stage process, where Cr (VI) is firstly adsorbed then a reduction step on adsorbent surface took place [32].

Also, it can be noticed that a similar trend in regards to the behavior of both adsorbents upon investigating the effect of pH, contact time and adsorbent concentration with a large difference (ca. 50%) in adsorption capacity between CSW and RSW, this may be attributed to the difference in lignin content (reported in 2.1), as it was 31% in CSW compared to 4.9-5.4% in RSW. Such adsorption behavior of lignin was reported by [39, 40] because lignin is highly functionalized polymer containing ether linkages, aliphatic and aromatic hydroxyl groups that render lignin the character of a model sorbent.

IV. Conclusion

In this work, the performance of CSW and RSW as Cr (VI) adsorbents was investigated. Also, the binding mechanism of both adsorbents in regards to their chemical composition was discussed. Langmuir and Freundlich adsorption isotherms were used to explain the adsorption process with r² more than 0.9. In conclusion, the study would be helpful in the field of using agro based wastes in Cr (VI) biosorption.

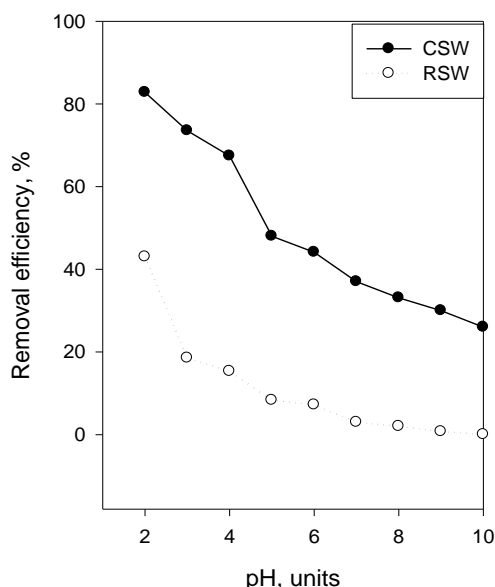


Fig. 1. Effect of pH on adsorption process

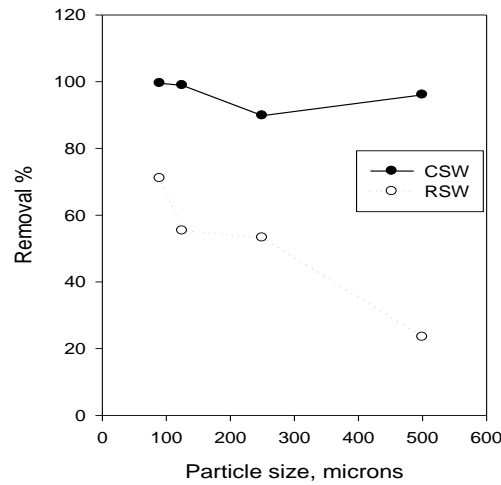


Fig. 2. Effect of adsorbent particle size on adsorption process

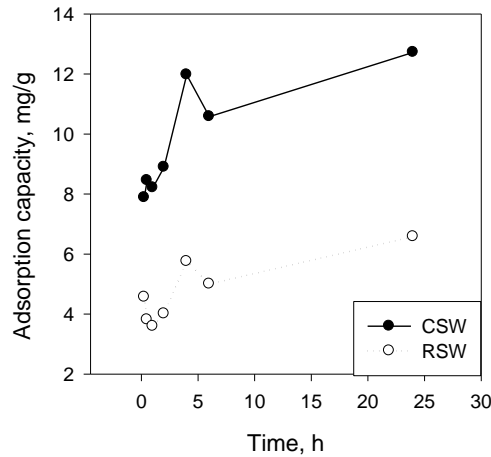


Fig. 3. Effect of time on adsorption process

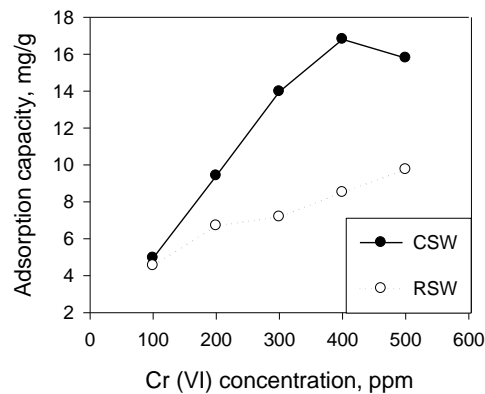


Fig. 4. Effect of adsorbent initial concentration on adsorption process

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