Tartaric Acid Grafted Sugarcane Bagasse for Removal of Chromium(VI) from Aqueous Solutions

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Abstract

Hexavalent chromium is a priority toxic and carcinogenic chemical when present in excess. It is very much required to remove it from effluents before allowing it to enter any water system or on to land. In the present study, the removal of Cr(VI) by adsorptionfrom wastewater using low cost adsorbent modified sugarcane bagasse by tartaric acid (SCB) was studied. The effect of the initial concentration of Cr(VI), bio sorbent dosage, temperature, contact time, and pH were studied. It was noted that the removal decreased with the increase in the initial concentration of Cr(VI) ions and also pH. The adsorption of Cr(VI) from water was favorable at low pH values. The kinetic of the Cr(VI) adsorption on SCB was found to follow pseudo - second order mechanism. The adsorption data can be satisfactorily explained by Freundlich isotherm. This work proved that treated bagasse can be used as an efficient adsorbent material for removal of Cr(VI) from wastewater.

Keywords: Adsorption; Sugarcane bagasse; Hexavalent chromium; Tartaric acid.

1. Introduction

The contamination of water and Environment are discharged by a number of industries, such as metal platingfacilities, mining operations and tanneries.[1] These metals are significantly toxic to

human beings and ecological environments.[2] A serious health hazard result from dissolved heavy metals escaping into the environment which accumulate throughout the food chain in living tissues, multiplying their effects so it is necessary to eliminate them to protect public health[3]. Among various treatment technologies for purification of wastewaters from heavy metals, adsorption was found to be the most commonly used method for eliminating these contaminants, especially at low concentrations.

Different adsorbents have been developed from available natural materials such as activated carbon, pine bark, charcoal, banana peel, tar sands, modified rice husk, zeolites and moss peat.[4-8] Sugarcane bagasse was widely used to remove heavy metals.[9-10] Sugarcane bagasse has around 50 % cellulose, 27 % polyoses, and 23% lignin,[11] which have many hydroxyl and/or phenolic functions that can chemically react to produce materials with new properties.[12] Only a few among these works investigated the modification of sugarcane bagasse.

The maximum of Cr(VI) levels permitted in wastewater are 5 mg L^{-1} for trivalent chromium and 0.05 mg L^{-1} for hexavalent chromium.[13] Chromium ions are usually eliminated by precipitation, ion-exchange and adsorption.[14-16] Many researches for making efficient, eco- friendly, and inexpensive adsorbents are intensivelydeveloped.[17]

The biosorption has some advantages over other techniques,[18] for example, low cost agricultural waste biproducts such as sugarcane bagasse can be used as adsorbent.[19] The main objective of this work is to study the adsorption of hexavalent chromium by low cost adsorbent modified SCB with tartaric acid.

2. Experimental

2.1. Materials and Methods

Aqueous stock solution of 500 ppm of Cr(VI) was prepared from potassium dichromate using double distilled water by carefully weighting out 0.05 g of it and dissolved in a 100 ml distilled water. Tartaric acid solution was prepared by dissolution of solid anhydrous acid in the appropriate amount of distilled water.

The pH values were adjusted by using sodium hydroxide or hydrochloric acid.

2.2. Preparation of sugarcane bagasse

Sugarcane bagasse (SCB) was collected and washed several times using bi-distilled waters to eliminate dust, impurities and other unwanted chemicals. Bagasse was dried at 105 °C for 48 h and powdered in an agate mortar and then sieved through a nylon sieve (hole diameter is 0.710 mm) to obtain the size fractions for samples.

2.3. Treatment of SCB by tartaric acid

Chemical modification of SCB by tartaric acid was performed by mixing the biomass with 6 or 12 g of tartaric acid dissolved in 300 ml of water for 30 g SCB. The modified powders were dried at 100 °C overnight. This modification stabilizes the biomass due to the formation of ester.[19]

2.4. Calculation of metal ions uptake

The amount of Cr(VI) adsorbed onto SCB at equilibrium q_e mg g^{-1} was calculated by:

$$q_e = V (C_o - C_e) / W \qquad\qquad (1)$$

Where V (L)is the volume of the Cr(VI) solution and W(g) is the dry of SCB, C_o and C_e(mg L^{-1}) are initial and equilibrium metal concentrations, respectively. The removal efficiency of the Cr(VI) was also by the following equation:

$$R.E \% = (C_o - C_e) / C_o * 100 \qquad\qquad (2)$$

2.5. Adsorption isotherms

The distribution of Cr(VI) between the liquid and the solid phases was described by Langmuir and Freundlich isotherm model using the following equations[20-21], respectively.

$$C_e/q_e = 1/ (q_{m*} b) + C_e /q_m \qquad\qquad (3)$$
$$\text{Log } q_e = \log k_f + 1/n \log C_e \quad (\text{ linear }) \qquad\qquad (4)$$

Where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount of metal ion per unit weight of adsorbent and unadsorbed metal ion in solution at equilibrium, respectively, q_m(mg g^{-1}) is maximum amount of sorbate per unit mass of sorbent when all sites are occupied. b (L mg^{-1}) is a constant related to the affinity of the binding sites. The separation factor (R_L)[22], is used to describe the essential characteristics of Langmuir isotherm,it is defined by

$$R_L = 1/ (1+ k\ C_o) \qquad\qquad (5)$$

3. Results and Discussion

3.1. Adsorption of Cr(VI) onto tartaric acid modified SCB

Adsorption of Cr (VI) from aqueous solution on biosorbents like tartaric acid modified SCB is affected by several factors like pH, dose, initial concentration, contact time and temperature. Most adsorbents interact with Cr(VI) through binding of the metal ion on the cellulose / lignin units in the active sites through binding of two hydroxyl groups in the cellulose units.

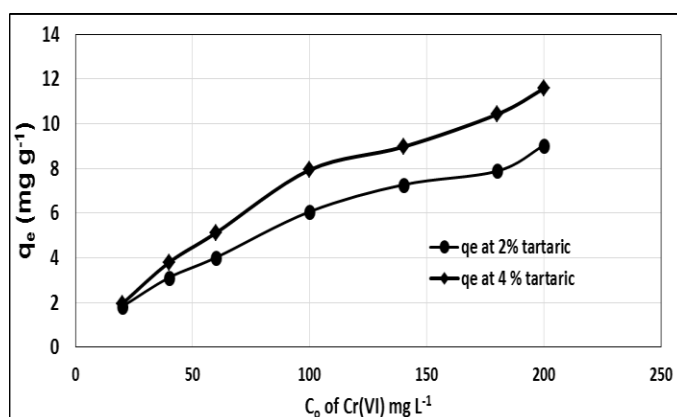### 3.1.1. Effect of initial Cr(VI) concentration on its bio sorption by SCB

The effect of initial metal ions concentration on the bio sorption of Cr (VI) by SCB was studied. 20 ml of different initial concentrations (10, 20, 40, 80, 100, 150 and 200 ppm) of Cr(VI) was added to 0.2 g of SCB modified with 2 % or 4% tartaric acid at 25° C , at pH 1.5 and the mixture was stirred at 300 rpm for 15 min. Then the absorbance was recorded at wavelength of 365 nm. The maximum bio sorption capacity q_e of Cr(VI) ions by SCB modified with 2 % or 4 % tartaric acid was proved to be 9.04 and 11.6 mg g^{-1} at 200 ppm initial metal ion concentrations, as shown in Figure 1 and Tables 1,2. This showed that the amount of metal ions adsorbed (q_e) increases as the initial Cr (VI) concentration rises and the removal efficiency decreases as the initial metal ion concentration increases. Evidently such a behaviour can be attributed to the maintenance of fixed number of binding sites in the fixed adsorbent dosage while increasing the concentration.

Table 1. Effect of initial Cr(VI) concentration on the Cr(VI) removal efficiency and q_e (mg g^{-1}) by modified SCB with 2% tartaric acid.

Conc. (ppm)	C_e	R.E%	q_e
20	1.75	91.23	1.83
40	8.79	78.03	3.12
60	19.81	66.99	4.02
100	39.30	60.70	6.07
140	67.26	51.96	7.27
180	101.16	43.80	7.88
200	109.64	45.18	9.04

Table 2. Effect of initial Cr(VI) concentration on the Cr(VI) removal efficiency and q_e(mg g^{-1}) by modified SCB with 4 % tartaric acid.

Conc. (ppm)	C_e	R.E%	q_e
20	0.48	97.58	1.95
40	2.01	94.98	3.80
60	8.79	85.35	5.12
100	20.65	79.35	7.95
140	50.31	64.06	8.97
180	75.74	57.92	10.43
200	84.21	57.89	11.58

Figure 1. Effect of initial Cr(VI) concentration on q_e(mg g^{-1}) by modified SCB with 2% or 4 % tartaric acid.

3.1.2. Effect of pH on the bio sorption of Cr(VI) by SCB

The pH value is an important factor for controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorb ate. Bio sorption experiments were carried out at different initial pH values (1-11). 20 ml of Cr(VI) solutions of initial concentration of 80 ppm was added to 0.2 g of modified SCB at 25 ^{o} C and the mixture was stirred at 300 rpm for 15 min. We observed the highest absorbance at low pH 1.5 and it decreases as pH increases. The amount of Cr(VI) removed by SCB modified by 2 % tartaric acid was (7.2mg g^{-1})and removal efficiency 90.1 % , (7.6 mg g^{-1} and 95.2 % in the case of SCB modified by 4 % tartaric acid). This means that there is strong interaction between the metal ions and the biosorbent in the acidic solution,as shown in Figure 2. The principal driving force for metal ion adsorption is the electrostatic interaction, i.e. attraction between adsorbent and adsorbate. The greater the interaction, the higher the adsorption of heavy metal was found.
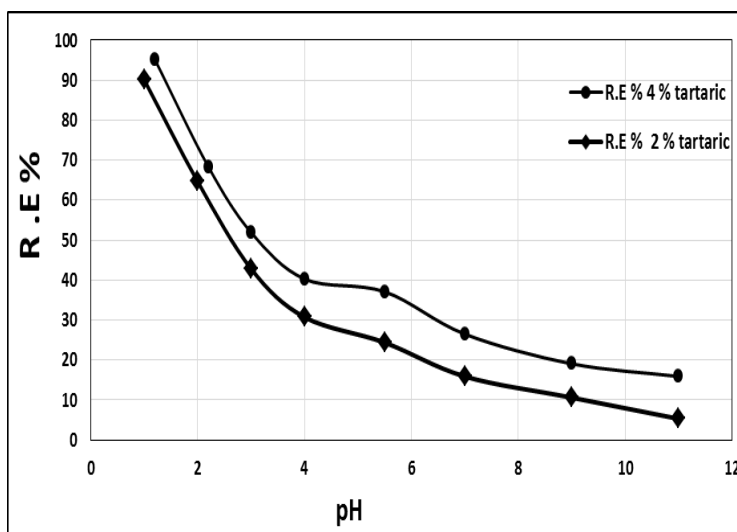

Figure 2. Effect of pH on the Cr(VI) removal efficiency at initial concentration of Cr(VI) (80 ppm) by modified SCB with2 % or 4 % tartaric acid.

3.1.3. Effect of bio sorbent dosage on the bio sorption of the Cr (VI)

The effect of adsorbent mass on the mass adsorption ofCr(VI) was investigated at intial metal ion concentration 80 ppm. In each bio sorption experiment, 20 mL of Cr(VI) solution of initial concentration (80 ppm) was added to different dosage of modified SCB biosorbent with 2% or 4% tartaric acid at 25 ^{o} C , at pH 1.5 and the mixtures were stirred at 300 rpm for 15 min.It was observed that the increase in the biosorbent dosage makes the Cr(VI) removal efficiency increases as shown in Figure 3.This is due to the increase in surface area and availability of biosorption sites, but the amount adsorbed by unit mass, decreases. This is due to unsaturation of adsorption sites and particle interaction which will decrease the total surface area.
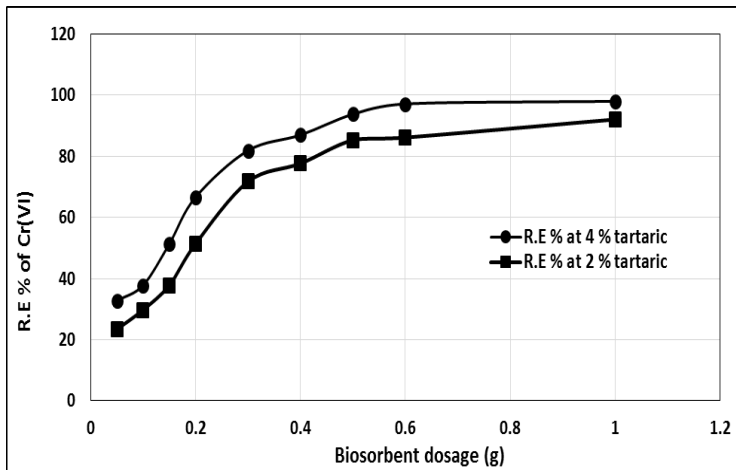

Figure 3. Effect of bio sorbent dosage on the Cr(VI) removal efficiency at initial concentration of Cr(VI) (80 ppm) by modified SCB with 2 % or 4 % tartaric acid.

3.1.4. Effect of contact time on the biosorption of Cr(VI)

The results obtained of the effect of contact time on the bio sorption of the Cr(VI) by SCB modified with 2 % or 4 % tartaric acid at 25^{0}C were shown in Figure 4.Chromium(VI) solution (20 mL)of initial concentrations (20, 50 and 80 ppm)at pH 1.5 were added to 0.2 g of the biosorbent in a 250 ml-flat bottom bottle at

$25^{o}C$ and the mixture was stirred on a shaker at 300 rpm with different contact times. The mechanism of the adsorption of Cr(VI) was tested using pseudo first-order and pseudo second-order kinetic models.[23-24] It was observed that the increase in the contact time increase the amount of metal ions adsorbed up to 40 minutes. The rapid removal at the initial contact time may be attributed to long time of contact and availability of active sites, after the equilibrium is reached at 40 minutes. The adsorption dynamics was affected by initial metal ion concentration.
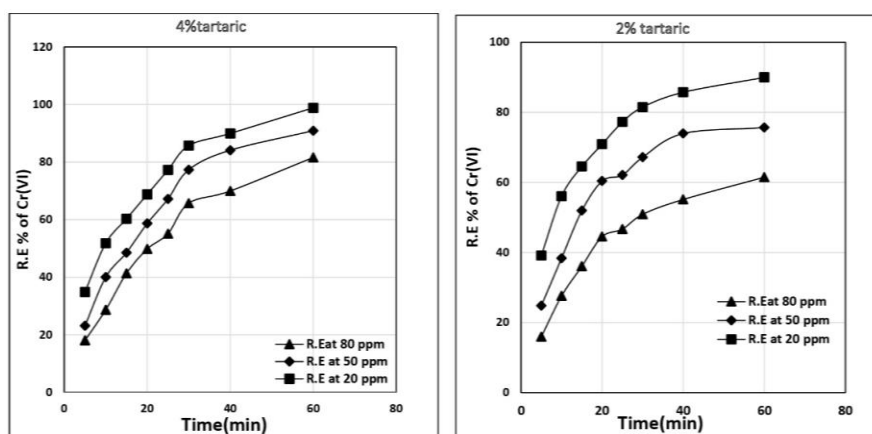

Figure 4. Effect of contact time on Cr(VI) removal efficiency at different initial concentrations (20, 50 and 80 ppm) by modified SCB with 2% or 4 % tartaric acid.

3.1.5. Effect of temperature on the bio sorption of Cr(VI) by modified SCB

Effect of temperature on the bio sorption of the Cr(VI) ions was done at different temperatures (25, 35, 40, 50 and 60 °C). 20 mL of Cr(VI) solution of initial concentrations (50, 80and 100 ppm) at pH 1.5 were added to 0.2 g of the modified SCB at 25 ° C and the mixture was stirred at 300 rpm for 15 min. The mixture was centrifuged after each experiment then the Cr(VI) concentration of the filtrate was determined using UV spectrophotometer. It is confirmed that adsorption of chromium (VI) increases with increasing of temperature for all concentrations. Further, low initial concentrations of the solution showed improved percentage of

adsorption in comparison with higher concentration solutions. It was noted that the Cr(VI) removal efficiency and q_e at different initial concentrations (50, 80, 100 ppm) by modified SCB increases as temperature increases until around 40 °C, as shown in Figure 5. Because of the presence of the active site as the temperature increases the adsorption capacity will increase. This means that the rising of the temperature encourages the biosorption. Increase in binding could be due to increase in surface activity and increased kinetic energy of the chromium (VI) metal ions.
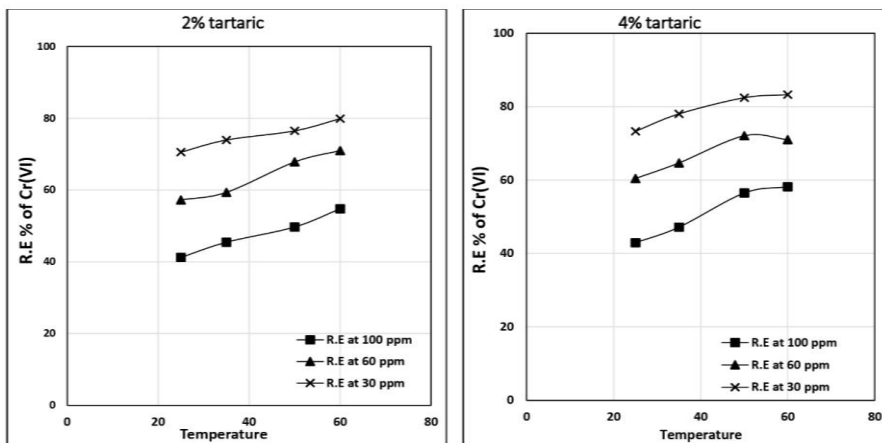

Figure 5. Effect of temperature on Cr(VI) removal efficiency at different initial concentrations (50, 80 and 100 ppm) by modified SCB with 2% or 4 % tartaric acid.

3.1.6. Adsorption isotherm of Cr(VI) onto bio sorbents

The distribution of Cr(VI) between the liquid and the solid phases was described by Langmuir and Freundlich isotherm model. The parameters obtained from the different isotherms provide important information about the adsorption mechanisms and surface properties[25]. Langmuir and Freundlich isotherms and its parameters of Cr(VI) bio sorption onto modified SCB were shown in Figure 6. and Tables (3&4). The value of Freundlich exponent *n* indicates better bio sorption mechanism and formation of relatively stronger bond between adsorb ate and bio sorbent as *n* values wear greater than 1.0 and 1/*n* values were between 0.0 and 1 which means that the Cr(VI) bio sorption onto modified SCB are favourable under the

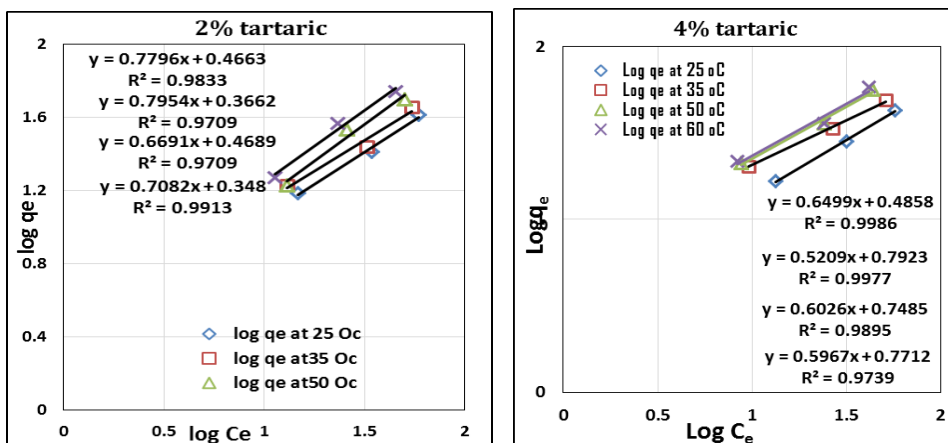studied conditions. Freundlich model has a better fitting model according to linearity coefficient R^2.

Figure 6. Linearized bio sorption isotherms of Freundlich

Table 3. Isotherm constants of Cr(VI) bio sorption onto SCB 2 % tartaric acid.

Temp.°K	Freundlich		
	n	*K*$_f$	*R²*
298	1.28	2.93	0.9833
308	1.26	2.32	0.9709
323	1.49	2.94	0.9709
333	1.41	2.23	0.9913

Table 3. Isotherm constants of Cr(VI) bio sorption onto SCB 4 % tartaric acid

Temp. °K	Freundlich		
	n	*K*$_f$	*R²*
298	1.54	3.06	0.9986
308	1.92	6.2	0.9977
323	1.66	5.6	0.9895
333	68	5.9	0.9739

The results show that the values of R_L ranged between 0 and 1, thus indicating a favourable metal ions bio sorption onto modified SCB.

3.1.2. Kinetic studies on the bio sorption of the Cr(VI) ions on SCB .

The mechanism of the adsorption of Cr(VI) was tested using pseudo first order and pseudo second order kinetic models (equations 6 and 7)

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad\qquad\qquad (6)$$

$$(t / q_t) = 1 / (k_2 q_e^2) + (t / q_e) \qquad\qquad (7)$$

Where, k_1 is the rate constant of pseudo first-order, q_t is the Cr(VI) ions solution uptake in mg/g at time t and q_e is the Cr(VI) ions solution uptake in mg/g at equilibrium. A plot of $\ln (q_e-q_t)$ against t was made and q_e and k_1 values were obtained from the slope and intercept, respectively. k_2 is the rate constant of pseudo-second order . Plot of (t/q_t) against t gives $(1/ k_2 q_e^2)$ as intercept from which k_2 can be obtained and $(1/q_e)$ as slope. Both models are tested for suitability using correlation coefficient, R^2.It was found, the pseudo- second order model is the best fitting model according to linearity coefficients R^2 and the experimental q_e was closed to the calculated q_e for 2 % or 4% tartaric acid respectively, as shown in Figure7. and Table 6.
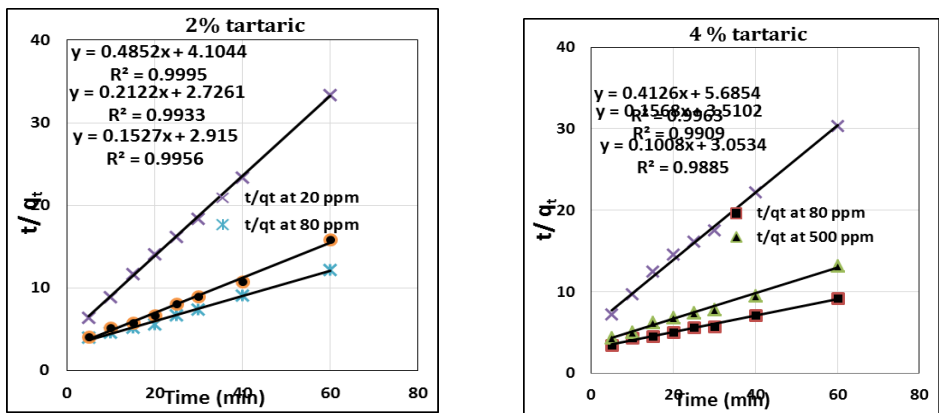

Figure 7. pseudo- second order for bio sorption of Cr(VI) by 2 % or 4% tartaric acid modified SCB

Table 6. Kinetic parameters of Cr(VI) **biosorption onto modified SCB with 2% or 4% tararic acid.**

Concentration	Pseudo- second order 2% tartaric acid			Pseudo- second order 2%, 4% tararic acid.			Observed q_e mg g^{-1}
	K_2 (g mg^{-1}.min^{-1})	q_e (mg g^{-1})	R^2	K_2 (g mg^{-1}.min^{-1})	q_e (mg g^{-1})	R^2	
At C_o 20 ppm	0.06	2.1	0.9995	0.03	2.4	0.9963	2.15,2.5
At C_o 50 ppm	0.02	4.7	0.9933,	0.01	6.3	0.9909	4.3,6.1
At C_o 80ppm	0.01	6.5	0.9956	0.0033	9.9	0.9885	6.2,9.7

Conclusion

Removal of poisonous Cr(VI) from solutions using selected adsorbents modified SCB was the most effective for the removal reached more than 97 % for Cr(VI) at concentration of 80 ppm at pH 1.5. Increase in the dose of adsorbent, initial concentration of Cr(VI) and increase in contact time up to 40 minutes are favourable for all increase the adsorption of Cr(VI). The kinetic of the Cr(VI) adsorption on SCB was found to follow pseudo - second order mechanism. The adsorption data can be satisfactorily explained by Freundlich isotherm. Higher sorption capacity of this sorbent indicates that SCB can be used for the treatment of chromium effluent.

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الملخص العربي

إزالة الكروم (IV) من المحاليل المائية باستخدام مصاصة قصب السكر المعالج بحمض الطرطريك.

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تقدم هذه الدراسة استخدام بقايا بعض النباتات الطبيعية مثل مصاصة قصب السكر والذي يوجد بوفرة فى مصر كمادة مازة لكثير من الملوثات العضوية وغير العضوية من المحاليل المائية. وتشير نتائج البحث إلى ان النسبة المئوية لإزالة الكروم (IV) من المحاليل المائية تزداد مع زيادة كمية مسحوق مصاصة قصب السكر المعالج بواسطة تركيزات مختلفة من حمض الطرطريك المضافة ونقص التركيز الابتدائي للفلز كان أعلى معدل امتزاز عند قيمة منخفضة للرقم الهيدروجينى تصل الى 1.5 والزمن الأمثل للاهتزاز 40 دقيقة علاوة على ذلك فان كفاءة إزالة المعادن وغيرها من الملوثات تزداد بارتفاع درجة الحرارة . وكانت أعلى نسبة مئوية لإزالة الكروم (IV)على سطح مصاصة القصب تساوى 95 % . واشارت العمليات الحسابية ان قيم معامل التصحيح تتراوح بين الصفر والواحد الصحيح مما يشير أن عملية الامتزاز عملية مفضلة. كما وجد أن الامتزاز يتبع معادلة الرتبة الثانية الظاهرية اكثر من الرتبة الأولى. وكذلك قيم أس فروينداش اكبرمن الواحد الصحيح مما يدل على ان الامتزاز يتبع فروينداش ايزوثيرم واكثر ملاءمة مقارنة بلانجمير ايزوثيرم و ان عملية الامتزاز هى أفضل ميكانيكية لتفسير ما يحدث بين الفلز وسطح مصاصة قصب السكر كبقايا نباتية متاحة ورخيصة وصديقة للبيئة.