



# REMOVAL OF CHROMIUM(VI) FROM WASTEWATER USING CITRIC ACID MODIFIED SUGARCANE BAGASSE

Adel M. Kamal El Dean,<sup>[a]</sup> Elham Y. Hashem,<sup>[a]\*</sup> Mostafa M. Ahmed,<sup>[b]</sup>  
Mohamed A. Mohamed<sup>[c]</sup> and Sawsan M. Hussain<sup>[c]</sup>

**Keywords:** Adsorption; sugarcane bagasse; hexavalent chromium; citric acid.

Toxic metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters. Various methods are available in literature although some of them facing difficulties to be applied. The present study, bagasse from sugarcane industry was used to remove chromium(VI) ions from wastewater. This study presents the adsorption behavior of hexavalent chromium from wastewater using low cost adsorbent modified sugarcane bagasse with citric acid (SCB). The effect of the initial concentration of chromium(VI), biosorbent dosage, temperature, contact time, and pH were studied. It was found that maximum % removal of chromium(VI) is obtained 92.19 % at pH 1.2 and contact time 40 min. The removal is decreased with increase in concentration and also pH. The maximum biosorption capacities  $q_e$  of chromium(VI) ions by SCB was 13.5 mg g<sup>-1</sup>. This work proved that treated bagasse can be used as an efficient adsorbent material for removal of heavy metals from wastewater such as chromium(VI).

\* Corresponding Authors

E-Mail: [elham\\_hashem@yahoo.com](mailto:elham_hashem@yahoo.com)

- [a] Department of Chemistry, Faculty of Science, Assuit University, Assuit, Egypt.  
[b] Department of Chemistry, Faculty of Science, New Valley University, ElKharga, Egypt.  
[c] Sugar Technology Research Institute, Assuit University, Assuit, Egypt.

## INTRODUCTION

The contamination of freshwater and marine environment are discharged by a number of industries, such as metal plating facilities, mining operations and tanneries.<sup>1-3</sup> It is well known that some metals are significantly toxic to human beings and ecological environments.<sup>4</sup> It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures.<sup>5</sup> 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.<sup>6</sup>

It is necessary to eliminate the heavy metals from water and wastewater to protect public health. There are various treatment technologies such as chemical precipitation, ion exchange, membrane separation, and adsorption are known for purification of wastewaters from heavy metals. Among them, 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. Also, olive stones and peach stones were also used for the removal of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup>.<sup>7-16</sup> Sugarcane bagasse was widely used to remove heavy metals.<sup>17-19</sup> Sugarcane bagasse has around 50 % cellulose, 27 % polyoses, and 23% lignin,<sup>20</sup> which have many hydroxyl and/or phenolic functions that can chemically react to produce materials with new properties.<sup>21-22</sup> Only a few among these works investigated the modification of sugarcane bagasse.<sup>23</sup>

Chromium exists in two oxidation states as Cr(III) and Cr(VI). The hexavalent form is 500 times more toxic than the trivalent one.<sup>24</sup> Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage.<sup>25-26</sup> The tanning process is one of the largest polluters of chromium all over the world. The maximum of Cr(VI) levels permitted in wastewater are 5 mg L<sup>-1</sup> for trivalent chromium and 0.05 mg L<sup>-1</sup> for hexavalent chromium.<sup>27</sup> Chromium ions are usually eliminated by precipitation, ion-exchange and adsorption.<sup>28-30</sup> There is no way to predict the best solution of a specific problem without undergoing a series of bench tests to evaluate the available alternatives.<sup>31</sup>

Many traditional methods for chromium removal from wastewater are ineffective at low concentrations. Therefore, researches for making efficient, eco- friendly, and inexpensive adsorbents are intensively developed. Biosorption can be defined as the ability of biological materials to sequester chromium or other heavy metals from even very dilute aqueous solutions by physicochemical processes.<sup>32</sup> The biosorption has some advantages over other techniques,<sup>33</sup> for example, low cost agricultural waste byproducts such as sugarcane bagasse can be used as adsorbent.<sup>34-37</sup> The main objective of this work is to study the Cr(VI) adsorption by a modified sugarcane bagasse adsorbent.

## MATERIALS AND METHODS

UV- visible spectrophotometers (Nicolet Evolution 100) Jenway 3540 pH and Conductivity Meter were used for UV-VIS and conductivity measurements. Stock solutions of 500 ppm of chromium(VI) were prepared from potassium dichromate using double distilled water (0.1 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 100 mL distilled water). Citric acid solution was prepared by dissolution of solid anhydrous citric acid in the appropriate amount of distilled water. The pH values were adjusted by using 0.1 M sodium hydroxide (NaOH) or 0.1 M hydrochloric acid (HCl) solutions.

### Preparation of sugarcane bagasse

Sugarcane bagasse were collected from Assiut city in Egypt. These samples were washed several times using tap and bi-distilled waters to eliminate dust, impurities and other unwanted chemicals and then dried at 105 °C for 48 h. Bagasse was 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. (< or >). Each fraction was stored in a clean polyethylene bottle until needed for the experiments.

### Treatment of sugarcane bagasse by citric acid

Chemical modification of sugarcane bagasse by citric acid was performed by mixing the biomass with 6 or 12 g of citric acid dissolved in 300 ml of water for 30 g sugarcane bagasse. The modified powders were dried at 100 °C overnight. This modification stabilizes the biomass due to insertion and crosslinking of carboxyl groups and increases its cation uptake ability.

### Adsorption measurements

Aqueous stock solutions of 500 ppm of chromium(VI) were prepared from potassium dichromate using double distilled water by carefully weighting out 0.1 g of  $K_2Cr_2O_7$  and dissolved in a 100 mL distilled water. Dilution was made to prepare different initial concentrations.

### Batch biosorption experiments

#### Effect of initial metal ions concentration

Chromium(VI) solutions (20 ml) of different initial concentrations (20, 60, 100, 140, 180 and 200 ppm) was added to 0.2 g of SBS biosorbent made with 2 % citric in at room temperature and the mixture was stirred at 300 rpm for 15 min. Then the absorbance was recorded at wavelength of 365 nm .

#### Effect of pH

Biosorption experiments were carried out at different initial pH values (1-12). The initial pH values were controlled using 0.1 M sodium hydroxide ( NaOH ) or 0.1 M hydrochloric acid (HCl). Chromium(VI) (20 ml) solutions of initial concentration of 80 ppm was added to 0.2 g of modified SBS sorbent at room temperature and the mixture was stirred at 300 rpm for 15 min.

#### Effect of biosorbent dosage

In each biosorption experiment, 20 mL of chromium(VI) solutions of initial concentration (100 ppm ) was added to different dosage of modified SBS biosorbent at room temperature and the mixtures were stirred at 300 rpm for 15 min.

### Effect of contact time and kinetics study analysis

Chromium(VI) (20 mL) solutions of initial concentration (100 ppm ) was added to 0.5 g of the modified SBS biosorbent at room temperature and the mixture was stirred on at 300 rpm with a contact times 3, 10, 20, 30, 40, 60, 90 and 120 min.

### Effect of contact time and kinetics study analysis

Chromium(VI) (20 mL) solutions of initial concentration (20, 50 and 80 ppm ) was added to 0.5 g of the biosorbent in a 250 ml flat bottom bottle at room temperature and the mixture was stirred on a shaker at 300 rpm with a contact times 5, 10, 20, 30, 40, 60, 90 and 120 min. The mechanism of the adsorption of chromium(VI) was tested using pseudo first-order and pseudo second-order kinetic models.<sup>38-39</sup> Pseudo first- order and pseudo second-order kinetic models are giving by Eqns. 1 and 2, respectively, in a linear form:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where

$q_t$  is the chromium(VI) solution uptake in  $mg\ g^{-1}$  at time  $t$ ,

$q_e$  is the chromium(VI) solution uptake in  $mg\ g^{-1}$  at equilibrium and

$k_1$  is the pseudo first-order rate constant

$k_2$  is the pseudo second-order rate constant

Values of  $k_1$  and  $q_e$  were obtained from the slope and intercept, respectively of plot of  $\ln(q_e - q_t)$  against  $t$ .  $k_2$  is the rate constant of pseudo second-order reaction. A plot of  $(t/q_t)$  against  $t$  gives  $1/q_e$  as a slope and  $1/(k_2 q_e^2)$  as intercept from which  $k_2$  can be obtained . Both models are tested for suitability using correlation coefficient,  $R^2$ .<sup>40</sup>

### Effect of temperature and thermodynamics studies

Effect of temperature and thermodynamics studies on the biosorption of the chromium(VI) ions were done at different temperature (25, 30, 40 and 60 °C). Chromate(VI) solutions (20 mL) of initial concentration (20, 60 and 80 ppm ) were added to 0.2 g of the modified SBS at room temperature and the mixture was stirred at 300 rpm for 15 min. The mixture was centrifuged after each experiment then the chromium(VI) concentration of the filtrate was determined using UV spectrophotometer .

### Calculation of metal ions uptake

The metal ions uptake at equilibrium was calculated by the following equation :

$$q_e = V \frac{C_0 - C_e}{W} \quad (3)$$

where

$q_e$  in  $\text{mg g}^{-1}$  is metal ions biosorption capacity,

$V$  is the volume of the metal ions solution (L) and

$W$  is the amount of biosorbent (g)

$C_0$  and  $C_e$  are initial and final (equilibrium) metal ion concentrations, respectively ( $\text{mg L}^{-1}$ ).

The removal efficiency of the metal ions was also determined using the following equation:

$$R.E\% = 100 \frac{C_0 - C_e}{C_0} \quad (4)$$

where

R.E % is the percentage of metal ions removed

### Adsorption isotherms

Mathematical model equations such as Langmuir isotherm model and the Freundlich isotherm model described the distribution of metal ion between the liquid and the solid phases.<sup>38-39</sup>

The Langmuir parameters are determined from the following equation.

$$\frac{C_e}{q_e} = \frac{1}{q_m} b + \frac{C_e}{q_m} \quad (5)$$

where

$C_e$  is sorbate concentration at equilibrium in solution  $\text{mg L}^{-1}$

$q_e$  is the amount of chromate(VI) adsorbed at equilibrium ( $\text{mg g}^{-1}$  adsorbent)

$b$  is a constant ( $\text{L mg}^{-1}$ )

$q_m$  is maximum amount of sorbate per unit mass of sorbent when all sites are occupied ( $\text{mg g}^{-1}$ ), where  $b$  and  $q_m$  are the Langmuir constant related to energy and the adsorption capacity, respectively.

$K=b$ =equilibrium adsorption constant related to the affinity of the binding of the sorption.

If a metal removal follows Langmuir isotherm this means that the metal adsorption takes place at specific homogeneous sites and one adsorption layer are on the surface of adsorbent. The essential characteristics of Langmuir isotherm can be expressed into terms of a dimensionless equilibrium parameter ( $R_L$ ), defined by

If a metal removal follows Langmuir isotherm this means that the metal adsorption takes place at specific homogeneous sites and one adsorption layer are on the surface of adsorbent. The essential characteristics of Langmuir isotherm can be expressed into terms of a dimensionless equilibrium parameter ( $R_L$ ), defined by

$$R_L = \frac{1}{1 + kC_0} \quad (6)$$

The value of  $R_L$  indicates the type of isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). The Freundlich parameters are determined from the linear form Freundlich isotherm as following equation

$$q_e = K_f C_e^{1/n} \quad (\text{non-linear}) \quad (7)$$

$$\log q_e = \log K_f + 1/n \log C_e \quad (\text{linear}) \quad (8)$$

If  $1/n$  is lower than 1.0 the adsorbate is favourably adsorbed on the adsorbent ( $0 < 1/n < 1$ ). The type of isotherm can be also irreversible,  $1/n = 0$  or unfavourable,  $1/n > 1$ .  $K_f$ =adsorption capacity at unit concentration ( $\text{L g}^{-1}$ ), related to bonding energy.

## Result and Discussion

### Adsorption of chromium(VI) onto citric acid modified sugarcane bagasse

Adsorption of chromium (VI) from aqueous solution on biosorbents like citric acid modified sugarcane bagasse is a rather complex process affected by several factors like pH, dose, initial concentration, contact time and temperature. The adsorption mechanism varies widely and depends on the type of adsorbent. Most adsorbents interact with chromium(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.

### Effect of initial chromium(VI) concentration on the biosorption by citric acid modified sugarcane bagasse

The effect of initial metal ions concentration on the biosorption of chromium(VI) by SCB was illustrated in Figure 1. The maximum biosorption capacity ( $q_e$ ) of Cr(VI) ions by SCB modified with 2% or 4% citric acid was proved to be 6.49 and 7.04  $\text{mg g}^{-1}$  at 200 and 180 ppm initial metal ion concentrations, and the maximum removal efficiency was found to be 81.5 and 94.2%, respectively, at 20 ppm initial metal ion concentrations.

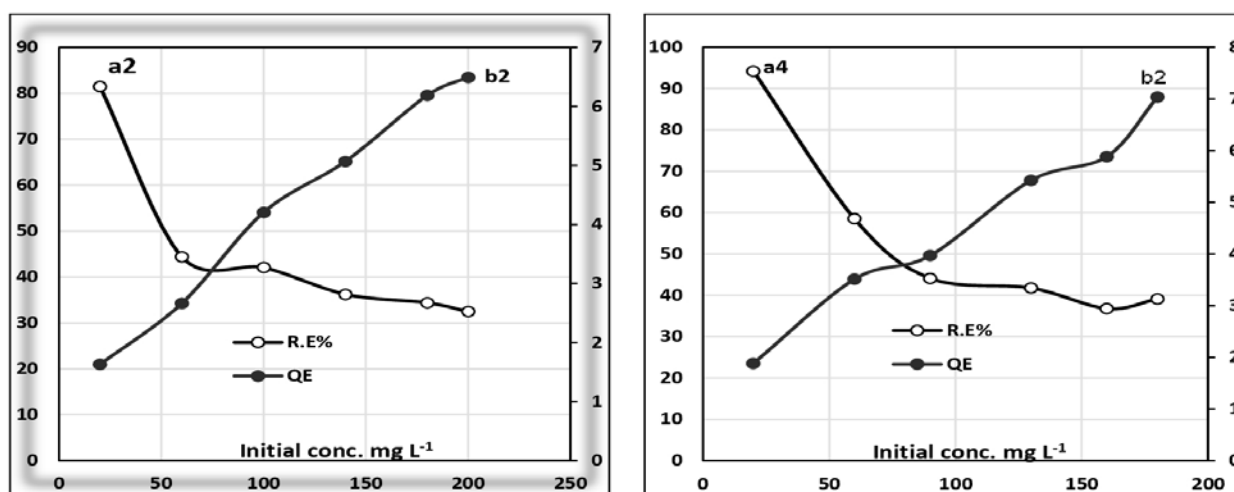
This showed that the amount of metal ions adsorbed ( $q_e$ ) increases as the initial chromium (VI) concentration rises and the removal efficiency decreases as the initial metal ion concentration increases. At low concentrations a greater chance was available for metal ions removal.

### Effect of pH on the biosorption of chromium(VI) by citric acid modified sugarcane bagasse

At different initial pH values (1-12) biosorption experiments were carried out. initial pH values were controlled using 0.1 M sodium hydroxide NaOH or 0.1 M hydrochloric acid HCl. 20 ml of chromium(VI) solution of initial concentration 80 ppm was added to 0.2 g of biosorbent (SCB modified with 2% or 4% citric acid) at room temperature and the mixture was stirred on shaker at 300 rpm

for 15 min. Then the absorbance was recorded at 365 nm. We observed that the lowest absorbance at low pH 1.5 and the biosorption decrease as pH increase.

The amount of chromium(VI) removed by SCB modified with 2 % citric acid at pH 1.5 was 7.21 mg g<sup>-1</sup> and the removal efficiency was 90.1 %.



**Figure 1.** Effect of initial chromium(VI) concentration on the biosorption of the chromium(VI) removal efficiency (a2 and a4) and  $q_e$  (b2 and b4) by 2 or 4 % citric acid modified SCB, respectively.

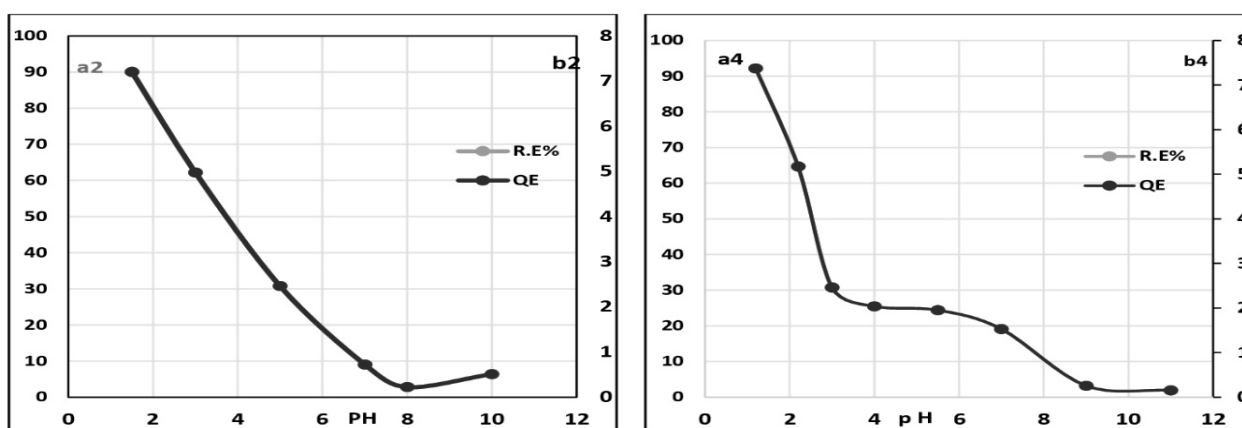
But in the case of SCB modified with 4 % citric acid the amount of chromium(VI) removed at pH 1.2 was 7.4 mg g<sup>-1</sup> and the removal efficiency was 92.2 %. This means that there is strong interaction between the metal ions and the biosorbent in the acidic solution. As shown in Figure 2.

of biosorbent 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0, 1.2 g of modified sugarcane bagasse with Citric acid 2 % or 4 % citric acid at 25 °C and the mixture was stirred on shaker at 300 rpm for 15 min. The increase in the biosorbent dosage make the metal ion removal efficiency increase.

#### Effect of biosorbent dosage on the biosorption of the investigated metal ion

It is an important parameter to determine the capacity of a biosorbent for a given initial concentration. In each biosorption experiment, 20 ml of chromium(VI) solution of initial concentration 100 ppm was added to different dosage

Chromium(VI) removal efficiency was lowest value 14.94 % obtained with 0.1 g and highest value of 83.6 % with 1.2 g of Sugarcane bagasse. This is due to the increase in surface area and availability of biosorption sites. Biosorption capacity  $q_e$  of chromium(VI) onto sugarcane bagasse was highest value 2.99 mg g<sup>-1</sup> with 0.1 g of sugarcane bagasse and lowest value 1.4 mg g<sup>-1</sup> with 1.2 g of sugarcane bagasse with 2 % citric acid.



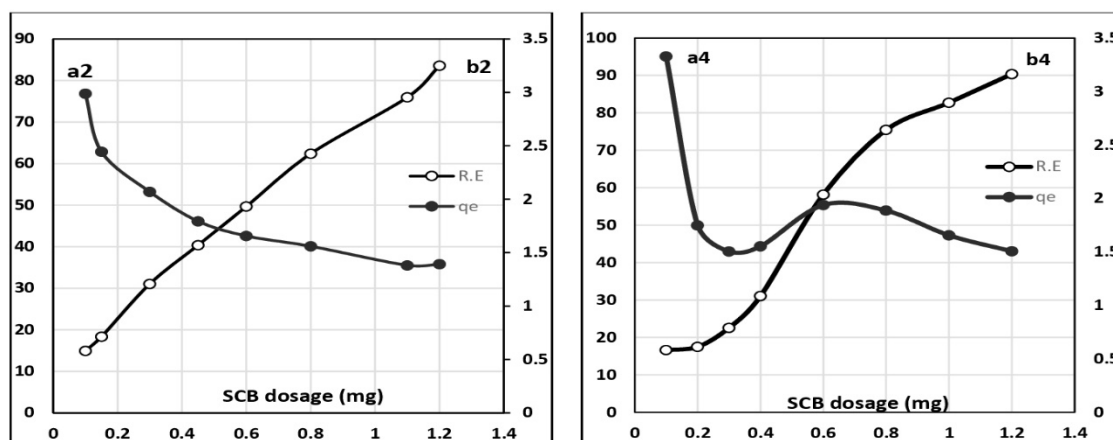
**Figure 2.** Effect of pH on the biosorption of the chromium(VI) removal efficiency (a2 and a4) and  $q_e$  (mg g<sup>-1</sup>, b2 and b4) by 2 % or 4% citric acid modified SCB, respectively.

But in case of SCB with 4 % citric it was noted that the metal ions removal efficiency increase, the lowest value of chromium(VI) removal efficiency was obtained (16.64 % with 0.1 g and highest value (90.36 %) with 1.2 g of sugarcane bagasse. This is due to the increase in surface area

and availability of biosorption sites. Biosorption capacity  $q_e$  of chromium(VI) onto sugarcane bagasse was highest value 3.327 mg g<sup>-1</sup> with 0.1 g of sugarcane bagasse and lowest value 1.51 mg g<sup>-1</sup> the biosorption capacity  $q_e$  of chromium(VI) chromium(VI) onto sugarcane bagasse

decreases as the biosorbent dosage increase due to the splitting effect of the concentration gradient between the metal ions solution and biosorbent. Because of increasing in adsorbent surface area, pores, active sites and number of

unsaturated sites. It was noted that the increasing in the biosorbent dosage bringing a decrease in the amount of metal ions adsorbed per unit weight of biosorbent as showed in Figure 3.



**Figure 3.** Effect of biosorbent dosage on the biosorption of the chromium(VI) ions removal efficiency (a2 and a4) and  $q_e$  ( $\text{mg g}^{-1}$ ) (b2 and b4) by 2 and 4% citric acid modified SCB, respectively.

#### Effect of contact time on the biosorption of the investigated metal ions

The results obtained on the effect of contact time on the biosorption of the chromium(VI) by sugarcane bagasse modified with 2% citric acid or 4% citric acid at 25 °C was shown in Figure 4. It was observed that the increase in the contact time increase the amount of metal ions adsorbed up to 40 minutes. The removal of metal ions was rapid at first and decreased slightly until the equilibrium is reached.

#### Effect of temperature on the biosorption of the investigated metal ion by biosorbent

The result obtained on the effect of temperature and thermodynamics studies on the biosorption of the chromium(VI) was done at different temperature (25, 30, 40 and 60 °C), (20 ml of chromium(VI) solution of initial concentration (20, 60 and 80 ppm) was added to 0.2 g of the biosorbent at room temperature and the mixture was stirred on shaker at 300 rpm for 15 min. The mixture was centrifuged after each experiment then the concentration of the filtrate chromium(VI) was determined using UV spectrophotometer. It was noted that the chromium(VI) removal efficiency and  $q_e$  at different initial concentrations (20, 60, 80 ppm) by modified SCB increases as temperature increases until around 40 °C. 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 due to increase in the movement of the chromium(VI) at higher temperatures.

From the result obtained above, it was noted that the removal efficiency of Cr(VI) and  $q_e$  of chromium(VI) biosorption by SCB at different concentration (80, 60, 20)  $\text{mg L}^{-1}$  increases as temperature increases due to the active sites until around 40 °C, and due to increase in the movement of the metal ion.

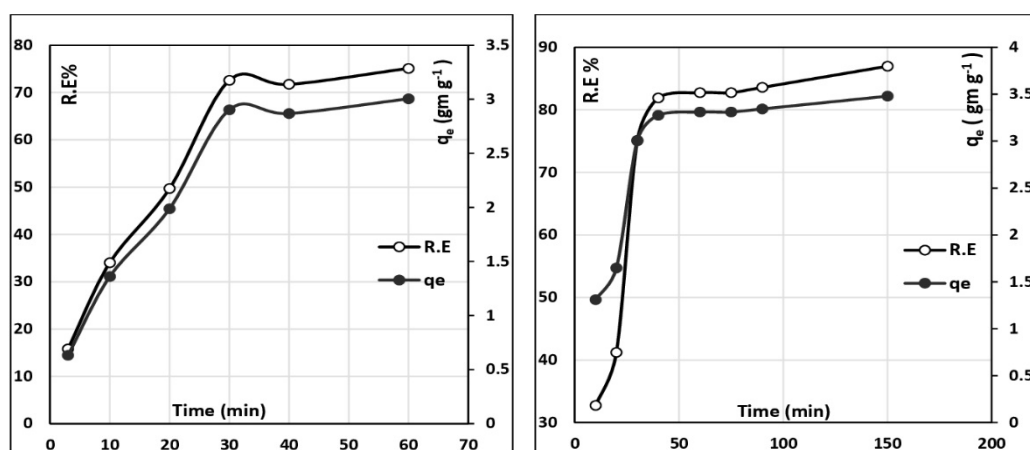
The result was shown in Figure 5.

**Table 1.** Isotherm constants of chromium(VI) biosorption onto sugarcane bagasse 2% citric

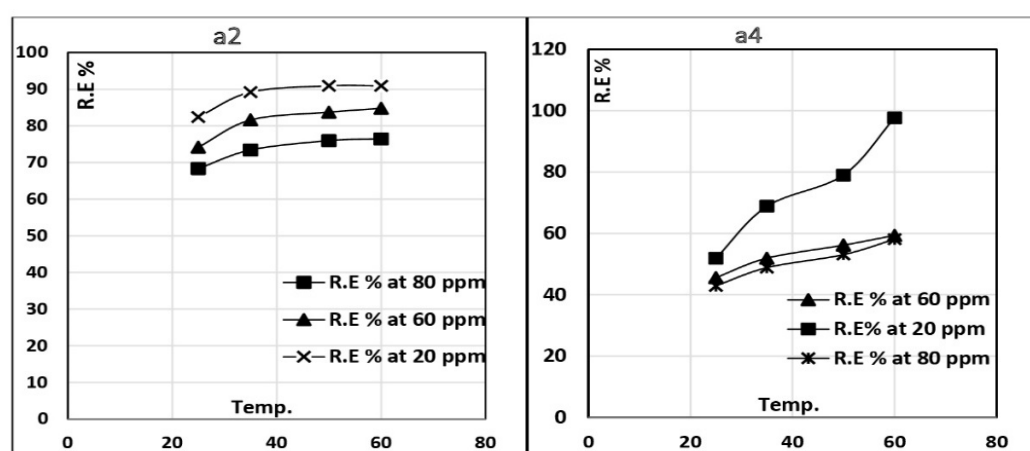
T, K	Langmuir			Freundlich		
	$q_m$ , $\text{mg g}^{-1}$	$b$ , $\text{L mg}^{-1}$	$R^2$	$n$	$K_f$	$R^2$
298	68.027	0.02	0.9338	1.499	2.365	0.9863
308	75.76	0.023	0.8029	1.66	3.76	0.9744
323	88.496	0.025	0.8938	1.56	4.1	0.9834
333	92.59	0.03	0.9393	1.59	4.9	0.9955

**Table 2.** Isotherm constants of chromium(VI) biosorption onto sugarcane bagasse 4% citric

Temp.	Langmuir			Freundlich		
	$q_m$ , $\text{mg g}^{-1}$	$b$ , $\text{L mg}^{-1}$	$R^2$	$n$	$K_f$	$R^2$
298	98.04	0.013	0.9096	1.36	2.23	0.9958
308	63.69	0.052	0.9488	2.1	7.36	0.9945
323	77.52	0.042	0.9762	1.73	5.89	0.9825
333	86.21	0.04	0.8865	1.74	6.42	0.9857



**Figure 4.** Effect of contact time on chromium(VI) removal efficiency (a2 and a4) and  $q_e$  ( $\text{mg g}^{-1}$ , b2 and b4) by 2 and 4 % citric acid modified SCB, respectively.



**Figure 5.** Effect of temperature on chromium(VI) removal efficiency (a2 and a4) at different concentrations (20, 60 and 80 ppm) by 2 and 4 % citric acid modified SCB, respectively.

#### Adsorption isotherm of the investigated metal ions onto biosorbents

Mathematical model equations such as Langmuir isotherm model and the Freundlich isotherm model describe the equilibrium between metal ions adsorbed onto adsorbent and metal ions in solution. Metal ion adsorption isotherms onto biosorbents are presented as a function of the equilibrium concentration of metal ions in the aqueous solution Langmuir and Freundlich isotherms and its parameters of chromium(VI) biosorption onto modified SCB were shown in Tables (1, 2). It was observed that the amount of metal ion adsorbed per unit mass of biosorbents increased with the initial concentration of metal ions.

The essential characteristics of Langmuir isotherm can be expressed into terms of dimensionless equilibrium parameter ( $R_L$ ), defined by

$$R_L = 1 / (1 + k C_0)$$

$R_L$  a dimensionless constant separator factor, the value of  $R_L$  indicates the type of isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). From the experiment onto 2 % citric SCB  $R_L$  values

various from 0.25 to 0.71 for different chromium(VI) concentrations (20, 60, 80) ppm at different temperature (Table 3). From the experiment with 4 % citric SCB  $R_L$  values various from 0.16 to 0.79 for different chromium(VI) concentrations (20, 60, 80 ppm) at different temperatures (Table 4). The results show that the values of  $R_L$  ranged between 0 and 1, thus indicating a favorable metal ions biosorption onto modified sugarcane bagasse

**Table 3.** A dimensionless constants separator factor  $R_L$  chromium(VI) biosorption onto sugarcane bagasse 2 % citric for Langmuir type

$C_0$ , $\text{mg L}^{-1}$	$R_L$			
	25 °C	35 °C	50 °C	60 °C
20	0.714286	0.684932	0.666667	0.625
60	0.454545	0.420168	0.4	0.357143
80	0.333333	0.30303	0.285714	0.25

It was observed that the value of Freundlich exponent  $n$  indicates better biosorption mechanism and formation of relatively stronger bond between adsorbate and biosorbent as  $n$  values wear greater than 1 as shown in Tables 1, 2 and  $1/n$  values of chromium(VI) biosorption onto sugarcane bagasse with 2 % citric were found in the range of 0.6-0.67 and 0.48-

0.74 with 4 % citric at temperature from 298 to 333 K, the  $1/n$  values were between 0 and 1 which means that the chromium(VI) biosorption onto modified sugarcane bagasse are favorable under the studied conditions.

**Table.4.** A dimensionless constants separator factor  $R_L$  for chromium(VI) biosorption onto sugarcane bagasse treated with 4 % citric

$C_0, \text{mg L}^{-1}$	$R_L$			
	25 °C	35 °C	50 °C	60 °C
20	0.793651	0.490196	0.543478	0.555556
60	0.561798	0.242718	0.284091	0.294118
80	0.434783	0.16129	0.192308	0.2

Freundlich model has a better fitting model according to linearity coefficient  $R^2 = 0.9955$  than Langmuir model  $R^2 = 0.9393$  for chromium(VI) biosorption onto modified sugarcane bagasse with 2 % citric and Freundlich model has a better fitting model according to linearity coefficient  $R^2 = 0.9958$  than Langmuir model  $R^2 = 0.9762$  for chromium(VI) biosorption onto modified sugarcane bagasse with 4 % citric. Thus, biosorption of chromium(VI) onto modified sugarcane bagasse follows Freundlich isotherms model describing the adsorption in aqueous system.

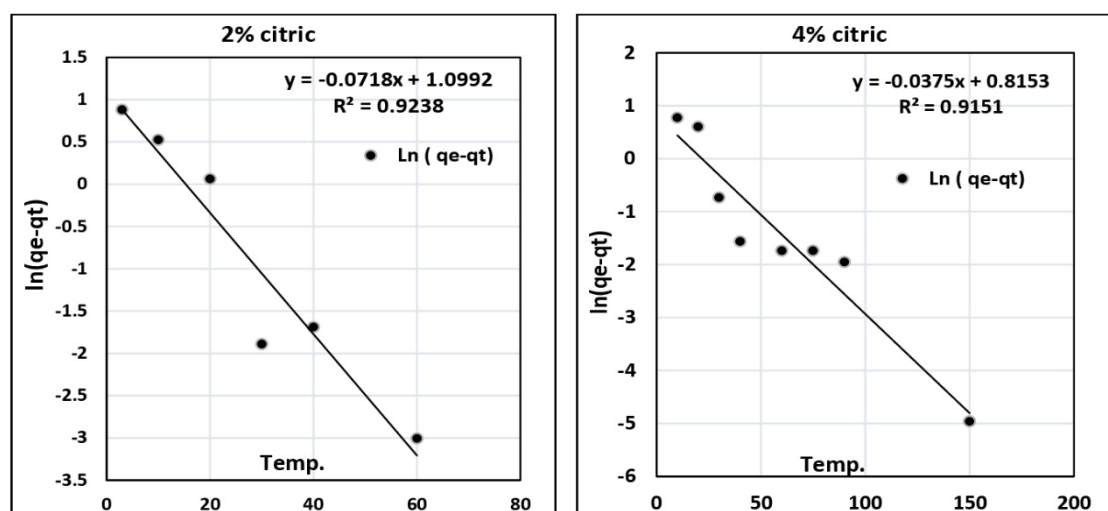
#### Kinetic studies on the biosorption of the investigated metal ions on biosorbent .

The mechanism of the adsorption of chromium(VI) was tested using pseudo- first- order and pseudo- second- order kinetic models. From experimental data obtained of sorption time investigation the adsorption kinetic of the removed chromium(VI) from aqueous solution was studied. The pseudo- second- order model is the best fitting model according to linearity coefficients  $R^2 = 0.9995$  but pseudo- first- order has linearity coefficients  $R^2 = 0.9233$ . The experimental  $q_e = 2.1$  close to the calculated  $q_e = 2.3$  determined from the plot of the pseudo- second- order model when the sugar cane bagasse treated with 2 % citric acid.

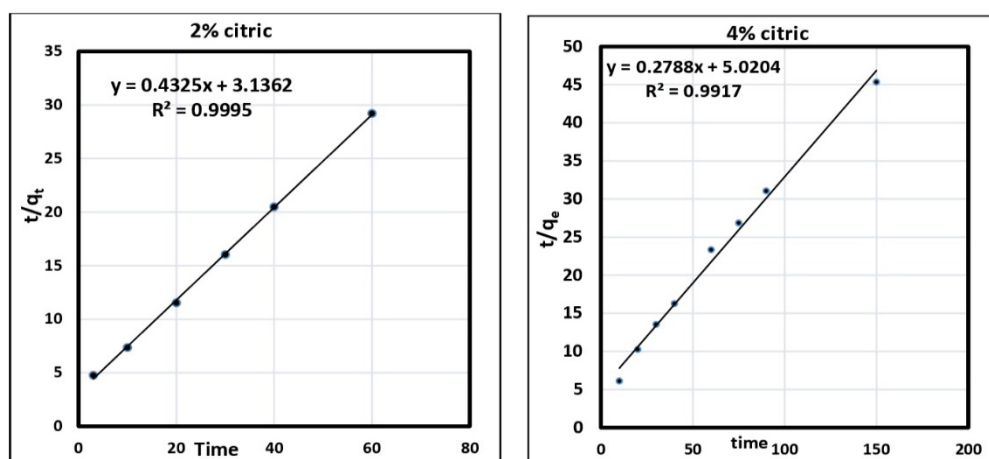
In the same time when the sugarcane bagasse treated with 4 % citric acid the pseudo- second- order model is the best fitting model according to linearity coefficients  $R^2 = 0.9917$  but pseudo- first- order has linearity coefficients  $R^2 = 0.9151$ . The experimental  $q_e = 3.3$  close to the calculated  $q_e = 3.6$  determined from the plot of the pseudo- second- order model as shown in Table 5, Figures 6 and 7.

**Table 5.** Kinetic parameters of chromium(VI) biosorption onto modified sugarcane bagasse

Citric acid, %	Pseudo- first- order			Pseudo- second- order			Observed, $q_e, \text{mg g}^{-1}$
	$K_1, \text{min}^{-1}$	$q_e, \text{mg g}^{-1}$	$R^2$	$K_2, \text{g mg}^{-1} \text{min}^{-1}$	$q_e, \text{mg g}^{-1}$	$R^2$	
2	0.07	3.001	0.9233	0.05965	2.312	0.9995	2.1
4	0.04	2.26	0.9151	0.0155	3.587	0.9917	3.3



**Figure 6.** Pseudo- first- order functions for biosorption of chromium(VI) by 2 or 4 % citric acid modified SCB



**Figure 7.** Pseudo- second-order functions for biosorption of chromium(VI) by 2 or 4 % citric acid modified SCB

## Conclusion

Removal of poisonous hexavalent form of chromium from solutions was possible using selected adsorbents modified sugarcane bagasse was the most effective for which the removal reached more than 92 % for Cr(VI) at concentration of 200 ppm at pH 1.2. Increase in the dose of adsorbent, initial concentration of Cr(VI) and increase in contact time up to 40 minutes are favorable for all increase the adsorption of Cr(VI). The kinetic of the Cr(VI) adsorption on sugarcane bagasse 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 sugarcane bagasse can be used for the treatment of chromium effluent.

## References

- Low, K. S., Lee, C. S., Sorption of cadmium and lead from aqueous solutions by spent grain, *J. Process Biochem.*, **2000**, *36*, 59–64. DOI: [10.1016/S0032-9592\(00\)00177-1](https://doi.org/10.1016/S0032-9592(00)00177-1)
- Sarma, H., Metal Hyperaccumulation in Plants: A Review Focusing on Phytoremediation Technology, *J. Environ. Sci. Technol.*, **2011**, *4*, 118-138. DOI: [10.3923/jest.2011.118.138](https://doi.org/10.3923/jest.2011.118.138)
- Bailey, S. E., Olin, T. J., Bricka, R. M., Adriana, D. D., A review of potentially low-cost sorbents for heavy metals, *J. Water Research*, **1999**, *33*, 2469–2479. DOI: [10.1016/S00431354\(98\)00475-8](https://doi.org/10.1016/S00431354(98)00475-8)
- Dorris, K. L., Zhang, Y., Shukla, A., Bin, Yu., Shukla, S. S., The removal of heavy metal from aqueous solutions by sawdust adsorption removal of copper, *J. Hazard Mater.*, **2000**, *B80*, 33–42. DOI: [10.1016/S0304-3894\(00\)00278-8](https://doi.org/10.1016/S0304-3894(00)00278-8)
- Inglezakis, V. J., Loizidou, M. D., Grigoropoulou H. P., Ion exchange of Pb<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup> and Cr<sup>3+</sup> on natural clinoptilolite: selectivity determination and influence of acidity on metal uptake, *J. Colloid Interface Sci.*, **2003**, *261*, 49-54. DOI: [10.1016/S0021-9797\(02\)00244-8](https://doi.org/10.1016/S0021-9797(02)00244-8)
- Al-Asheh, S., Banat, F., Al-Omari, R., Duvnjak, Z., Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data, *Chemosphere*, **2000**, *41*, 659- 665. DOI: [10.1016/S0045-6535\(99\)00497-X](https://doi.org/10.1016/S0045-6535(99)00497-X)
- Dakiky, M., Khamis, M., Manassra, A. Mer'eb, M., Selective adsorption of chromium (VI) in industrial wastewater using lowcost abundantly available adsorbents. *Adv. Environ. J.*, **2002**, *6*, 533- 540. DOI: [10.1016/S1093-0191\(01\)00079-X](https://doi.org/10.1016/S1093-0191(01)00079-X)
- Anwar J., Shafique, U., Zaman, W., Salman, M., Dar, A., Anwar, S., Removal of Pb (II) and Cd (II) from water by adsorption on peels of Banana, *Bioresour. Technol.*, **2010**, *101*, 1752-1755. DOI: [10.1016/j.biortech.2009.10.021](https://doi.org/10.1016/j.biortech.2009.10.021)
- Zeatoun L., Younis, N., Rafati, R., Evaluation of activated and non-activated tar sands for the removal of phenol and cadmium from aqueous solutions, *Water Quality Research Journal of Canada*, **2004**, *39*, 252-257. DOI: [10.2166/wqrj.2004.035](https://doi.org/10.2166/wqrj.2004.035)
- Kumar, U., Bandyopadhyay, M., Sorption of cadmium from aqueous solution using pretreated rice husk, *Bioresour. Technol.*, **2006**, *97*, 104-109. DOI: [10.1016/j.biortech.2005.02.027](https://doi.org/10.1016/j.biortech.2005.02.027)
- Erdem, E., Karapinar, N., Donat, R., The removal of heavy metal cations by natural zeolites, *J. Colloid Interface Sci.*, **2004**, *280*, 309-314. DOI: [10.1016/j.jcis.2004.08.028](https://doi.org/10.1016/j.jcis.2004.08.028)
- Lee, B. G., Rowell, R. M., Removal of Heavy Metal Ions from Aqueous Solutions Using Lignocellulosic Fibers, *Journal of Natural Fibers*, Vol. *1(1)*, **2004**, 97-108. DOI: [10.1300/J395v01i1n01\\_07](https://doi.org/10.1300/J395v01i1n01_07)
- Ferro-Garcia, A. M., Rivera-Utrilla, J., Rodriguez-Gordillo, J., Bautista-Toledo, I., Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by products, *Carbon*, **1988**, *26*, 363-373. DOI: [10.1016/0008-6223\(88\)90228-X](https://doi.org/10.1016/0008-6223(88)90228-X)
- Ibrahim, S., Subramaniam, P., Khan, A. N., "Elimination of Heavy Metals from Wastewater Using Agricultural Wastes as Adsorbents" *Malaysian Journal of Science*, **2004**, *23*, 43–51, <https://pdfs.semanticscholar.org/a603/35e0733cbc8898133680f77bf95d...>
- Liu, C., Hao Ngo, H., Guo, W., Equilibrium and kinetic studies of various heavy metals on sugarcane Bagasse, *Journal of Water Sustainability*, **2015**, *5(2)* 59–73, DOI: [10.11912/jws.2015.5.2.59-73](https://doi.org/10.11912/jws.2015.5.2.59-73)
- Lim, P. A., Aris, Z. A., A review on economically adsorbents on heavy metals removal in water and wastewater, *Rev. Environ. Sci Biotechnol.*, **2014** *13*, 163–181 DOI: [10.1007/s11157-013-9330-2](https://doi.org/10.1007/s11157-013-9330-2)
- Joseph, O., Rouez, M., Métivier-Pignon, H., Bayard, R., Emmanuel, E., Gourdon, R., Adsorption of heavy metals on to sugar cane bagasse: Improvement of adsorption capacities due



- to anaerobic degradation of the biosorbent, *Environ. Technol.*, **2009**, *30*(13), 1371–1379. DOI:10.1080/09593330903139520
- <sup>18</sup>Kumar, A., Sahu, O., Sugar Industry Waste as Removal of Toxic Metals from Waste Water, *World J. Chem. Educ.*, **2013**, *1*(1), 17-20. DOI:10.12691/wjce-1-1-5
- <sup>19</sup>Zodape, G.V., Dhawan, V. L., Wagh, R. R., Sawant, A. S., "Contamination of heavy metals in seafood marketed from Vile Parle and Dadar markets of suburban areas of Mumbai, West Coast of India, *Int. J. Environ. Sci.*, **2011**, *1*(6), 1184-1192, Doi:10.6088/ijes.00106020012
- <sup>20</sup>Caraschi, J. C., Campana, F. S. P., Curvelo, A. A. S., Carboximetilação de polpas de bagaço de cana de açúcar e caracterização dos materiais adsorventes obtidos *Polímeros. Cien. Tecnol.*, **1996**, *3*, 24.
- <sup>21</sup>Xiao, B., Sun, X. F., Sun, R. C., The Chemical Modification of Lignins with Succinic Anhydride in Aqueous Systems, *Polym. Degrad. Stability*, **2001**, *71*, 223-231. doi.org/10.1016/S0141-3910(00)00133-6
- <sup>22</sup>Navarro, R. R., Sumi, K., Fujii, N. and Matsumura, M. Mercury Removal from Wastewater Using Porous Cellulose Carrier Modified with Polyethyleneimine. *Water Res.*, **1996**, *30*, 2488-2494. doi.org/10.1016/0043-1354(96)00143-1
- <sup>23</sup>Krishnan, K.A., Anirudhan, T.S., Removal of mercury(II) from aqueous solutions and chlor-alkali industry effluent by steam activated and sulphurised activated carbons prepared from bagasse pith: kinetics and equilibrium studies. *J. Hazard. Mater.*, **2002**, *92*, 161–183. DOI:10.1016/S0304-3894(02)00014-6
- <sup>24</sup>Karnitz-Jr. O., Alves-Gurgel, L. V., Perin de Melo, J. C., Botaro, V. R., Sacramento Melo, T. M., Pereira de Freitas Gil, R., and Frédéric Gil, L., Adsorption of Heavy Metal Ion from Aqueous Single Metal Solution by Chemically Modified Sugarcane Bagasse, *Bioresour. Technol.*, **2007**, *98*, 1291-1297. doi.org/10.1016/j.biortech.2006.05.013
- <sup>25</sup>Kowalski, Z., Treatment of chromic tannery wastes. *J. Hazard. Mater.*, **1994**, *37*, 137–141. doi.org/10.1016/0304-3894(94)85042-9
- <sup>26</sup>US Department of Health and Human Services, **1991**. Toxicological Profile for Chromium. Public Health Services Agency for Toxic substances and Diseases Registry, Washington, DC.
- <sup>27</sup>Cieslak-Golonka, M., 1995. Toxic and mutagenic effects of chromium(VI). *Polyhedron*, **1996**, *15*(21), 3667–3689. DOI:10.1016/0277-5387(96)00141-6
- <sup>28</sup>Acar, F.N., Malkoc, E., The removal of chromium(VI) from aqueous solutions by *Fagus orientalis* L., *Bioresource Technol.*, **2004**, *94*, 13–15. DOI:10.1016/j.biortech.2003.10.032
- <sup>29</sup>Tiravanti, G., Petruzzelli, D., Passino, R., Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery. *Water Sci. Technol.*, **1997**, *36*, 197–207. DOI:10.1016/S0273-1223(97)00388-0
- <sup>30</sup>Dahbi, S., Azzi, M., de la Guardia, M., Removal of hexavalent chromium from wastewaters by bone charcoal, *Fresenius J. Anal. Chem.*, **1999**, *363*, 404–407. DOI:10.1007/s002160051210
- <sup>31</sup>Orhan, Y., Buyukgangor, H., The removal of heavy metals by using agricultural wastes. *Water Sci. Technol.*, **1993**, *28*, 247–255. DOI:10.2166/wst.1993.0114
- <sup>32</sup>Kemmer, N. F., Precipitation, *Nalco Water Handbook*, Publisher McGraw Hill, **1988**, 10.18–10.20, (Chapter 10).
- <sup>33</sup>Volesky, B., Holan, Z. R., Biosorption of Heavy Metals. *Biotechnol. Prog.*, **(1995)** *11*, 235–250. doi/abs/10.1021/bp00033a001
- <sup>34</sup>Mohan, D., Singh, K. P., Single and multicomponent adsorption of Cd (II) and Zn (II) using activated carbon derived from Bagasse-an agricultural waste, *Water Res.*, **(2002)**, *36*, 2304-2318. DOI:10.1016/S0043-1354(01)00447-X
- <sup>35</sup>Khan, N. A., Ali, S. I., Ayub, S., Effect of pH on the Removal of Chromium (Cr) (VI) by Sugarcane Baggase. *Sci. Tech.*, **2001**, *6*, 13-19. DOI: 10.24200/squjs.
- <sup>36</sup>Corbett, J. F., Pseudo first-order kinetics, *J. Chem. Educ.*, **1972**, *49* (10), p 663, DOI: 10.1021/ed049p663
- <sup>37</sup>Ho, Y. S., McKay, G., Pseudo-second order model for sorption processes, *Process Biochem.*, **1999**, *34*(5), 451-465. doi.org/10.1016/S0032-9592(98)00112-5
- <sup>38</sup>Langmuir, I., The constitution and fundamental properties of solids and liquids I. Solids, *J. Am. Chem. Soc.*, **1916**, *38*(11), 2221–2295 DOI: 10.1021/ja02268a002
- <sup>39</sup>Freundlich, H. M. F., Uber die Adsorption in Losungen, *Z. Phys. Chem.*, **1906**, *57*, 385-470

Received: 12.03.2019.

Accepted: 21.05.2019.