

# FIXED BED COLUMN STUDY ON THE REMOVAL OF CHROMIUM (III) IONS FROM AQUEOUS SOLUTIONS BY USING HEMP FIBERS WITH IMPROVED SORPTION PERFORMANCE

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Cr (III) removal from aqueous solutions by sorption in a fixed bed column filled with alizarin S impregnated hemp fibers has been studied. The effect of the initial metal ion concentration on the Cr (III) sorption process was investigated and the experimental breakthrough curves were obtained. The breakthrough time and saturation time decreased from 110 min to 80 min and from 300 min to 160 min, respectively, with the increase in the initial concentration from 13.00 mg/L to 26.14 mg/L. The increase in the initial concentration from 13.00 to 26.14 mg/L increased the breakthrough sorption capacity from 4.178 to 6.163 mg/g and decreased the percentage of Cr (III) removal from 73.57% to 62.64%. The breakthrough predictions by Thomas model were found to be very satisfactory. The hemp impregnated with alizarin S column removed >90% of Cr (III) from three samples of synthetic wastewaters containing different amounts of other heavy metal ions.

**Keywords:** hemp – alizarin S, Cr (III), sorption, fixed bed column

## INTRODUCTION

In aqueous systems, chromium usually exists in both trivalent and hexavalent oxidation states. Chromium toxicity depends on its oxidation state. Cr (III) is recognized as an essential dietary mineral in low doses, required to potentiate insulin and for the normal glucose metabolism, but it can exert genotoxic effects under prolonged or severe exposure.<sup>1</sup> In contrast, hexavalent chromium is a well-known highly toxic metal, considered a priority pollutant. Cr (III) is up to one hundred times less toxic than Cr (VI).<sup>2</sup> The long term stability of Cr (III) in wastewaters from the textile, leather, tanning, electroplating and metal finishing industries is of great concern. On the other hand, it is possible that Cr (III) is oxidized chemically (by Mn oxides) and microbially (by reducing bacteria) to Cr (VI), thus dangerously increasing its toxicity.

The removal of chromium from wastewaters is principally achieved by methods such as filtration, chemical precipitation, adsorption, ion exchange and electrodeposition.<sup>3</sup> Recently, different low-

cost natural and waste materials have received growing attention among the environmental community as an innovative and economical technology in removing chromium (III) instead of the costly conventional methods (Table 1). Lignocellulosic materials, including both wood residues and agricultural residues, have a chromium sorption capacity comparable to that of other natural or waste sorbents, but they have the advantage of a very low or no cost at all, great availability and simple operational process.<sup>14-15</sup> Hemp fibers belong to this category and mainly consist of cellulose, lignin, some pectin and extractives (fat, waxes, etc.). The strong bonding of heavy metal ions by carboxylic (primarily present in hemicelluloses, pectin and lignin), phenolic (lignin, extractives and pectin) and carbonyl groups (lignin) often involves complexation and ion exchange.<sup>16</sup> In our previous studies, it has been shown that unmodified and modified hemp fibers, a waste material from the textile industry, have important features which

highly recommend their use for the removal of heavy metals from wastewaters.<sup>17-28</sup>

The feasibility of the chromium (III) enrichment capability of natural hemp was ascertained by its impregnation with alizarin S. The effect of the most significant process parameters (pH, contact time, initial concentration of Cr (III) and temperature) on the sorption equilibrium was studied by the batch method.<sup>29</sup> The study of the medium acidity influence revealed that the maximum Cr (III) removal by its sorption on alizarin S pretreated hemp occurred at pH 5.8. On the basis of the obtained results it was assumed that sorption took place by the formation

of a 1:1 chromium (III): alizarin S complex in the impregnated hemp phase. It was shown that the pseudo-second-order model could best describe the sorption kinetics. The Langmuir and Freundlich model isotherms were used to elucidate the observed Cr (III) sorption phenomena. As expected, alizarin S impregnated hemp exhibited higher Cr (III) sorption capacity (6.340 mg/g impregnated hemp) than natural hemp fibers (4.006 mg/g). The obtained values of the isothermal thermodynamic parameters showed that the Cr (III) sorption is an exothermic process of physical nature.<sup>29</sup>

Table 1

A review on some low-cost materials with potential applicability in chrome (III) removal from wastewaters

Low-cost sorbent	Maximum sorption capacity, mg/g	Initial pH	Reference
Banana peel	79.56	4	4
Lignin isolated from black liquor, a waste product from the paper industry	17.97		5
Biological sludge - waste activated sludge	25.64	3	6
Orange waste biomass	29.64-74.88	3-5	7
Rose waste biomass	67.34		8
Agro-waste materials			
• acid-washed sorghum straw	6.96		9
• oat straw	12.97	4	
• agave bagasse	11.44		
Vineyard pruning waste	12.453	4.2	10
Olive stone	5.19	4	11
Wood-rotting fungus viz., <i>Ganoderma lucidus</i>	2.16	4.5	12
Mesorhizobium amorphae strain CCNWGS0123	53.52	4	13

However, practical applications of metal ion removal involve the use of continuous systems (fixed bed columns). In a fixed bed sorption system, the sorbent situated near the influent solution saturates first where maximum sorption takes place initially. This sorption zone moves further as time proceeds and it approaches the end of the bed. When the sorption zone reaches the exit of the bed the effluent concentration becomes equal to the influent concentration.<sup>30</sup> A plot of effluent concentration as a function of time or volume of solution processed is known as breakthrough curve, which underlies the description of the column performance. In addition, continuous systems constitute a suitable approach to industrial applications. In this context, the aim of this study is to evaluate the Cr (III) sorption in a fixed bed column filled with

alizarin S impregnated hemp fibers. The dynamic sorption of Cr (III) ions is interpreted by means of breakthrough curves. The results are described using Thomas and Yoon–Nelson models and reconfirm that the alizarin S pretreated hemp wastes can be a viable alternative in the treatment of wastewaters.

## EXPERIMENTAL

### Sorbent preparation

In these experiments, thick and rigid fibers of hemp with large surface area (28 m<sup>2</sup>/g) and porosity (19Å), high swelling capacity and strong hydrophilic character have been used. These fibers resulted as waste from a textile factory in the North-East region of Romania. The impregnation of hemp fibers with alizarin S was carried out according to the scheme given in Figure 1.

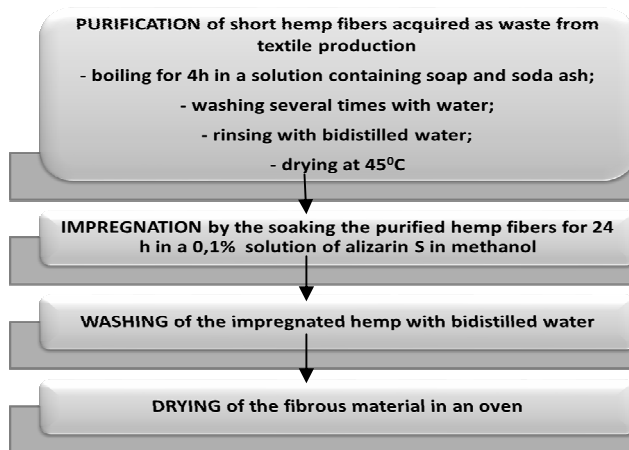


Figure 1: Scheme of hemp impregnation with alizarin S

### Fixed bed column studies

The dynamic sorption studies were carried out in a glass column of 1.5 cm inner diameter and 15 cm in length. A 0.7 g sample of hemp pretreated with alizarin S was packed into the column, achieving a bed height of 7 cm. A layer of wadding glass was fitted at the bottom of column to support the hemp during studies. A stock solution of  $5.10^{-2}$  M was prepared by the dissolution of analytical grade reagent  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in deionised water. Cr (III) solutions with different initial concentrations were fed from the top of the

column. Effluent samples were collected from the bottom of the column at different times. The metal ion concentration in the column effluent samples was determined by atomic absorption spectrometry (210 VGB Buck Scientific atomic absorption spectrometer). The experimental conditions of dynamic sorption of Cr (III) on alizarin S hemp were summarized in Table 2.

The relevant parameters for the hemp impregnated with alizarin S – Cr (III) dynamic sorption system were obtained from the breakthrough curves and calculated as indicated in Table 3.

Table 2  
Experimental conditions of Cr (III) dynamic sorption on alizarin S pretreated hemp wastes

$C_0$ (mg Cr/L)	Volume of solution passed through column (mL)	Flow rate (mL/min)	Collecting /time (mL/min)
13.00	500	2.1	2.5
26.14	900	2.0	2.5

Table 3  
Description of relevant parameters in breakthrough analysis

Parameter	Definition	Equation applied for parameter computing
Breakthrough time ( $t_b$ , min)	Time required to reach the breakthrough point. It is considered on the basis of the effluent discharge limit for Cr (III). So, the breakthrough time has been obtained for an effluent Cr (III) concentration of 5 mg/L <sup>31</sup>	
Saturation time ( $t_s$ , min)	Time required to reach the saturation point. It is usually considered when the effluent concentration remains close to influent concentration for a long period	
Length of mass transfer zone (MTZ, cm) in the bed <sup>32</sup>	Time interval between $t_b$ and $t_s$ MTZ shows the efficiency in the overall use of the hemp impregnated with alizarin S	$\text{MTZ} = H \left( 1 - \frac{t_b}{t_{sat}} \right)$ where: H is length of sorbent bed (cm); $t_b$ is

Breakthrough capacity, $q_b$ , mg/g	Amount of Cr (III) retained per unit of dry weight of sorbent at breakthrough point	breakthrough time (min); $t_s$ is saturation time (min)
Saturation capacity, $q_s$ , mg/g	Amount of Cr (III) retained per unit of dry weight of sorbent at saturation point	$q_b = \frac{(C_0 - C_b) \cdot V_b}{m}$ $q_s = \frac{(C_0 - C_s) \cdot V_s}{m}$ where: $C_0$ is initial Cr (III) concentration; $C_b$ and $V_b$ are concentration and volume of effluent, respectively, at the breakthrough point; $C_s$ and $V_s$ are concentration and volume of effluent, respectively, at the saturation point; $m$ is sorbent mass (g)
Cr (III) sorption yield (R%)	Removal percent	$R\% = \frac{(C_0 - C_b)}{C_b} \cdot 100$ $C_0$ is initial concentration; $C_b$ is concentration of effluent at breakthrough point

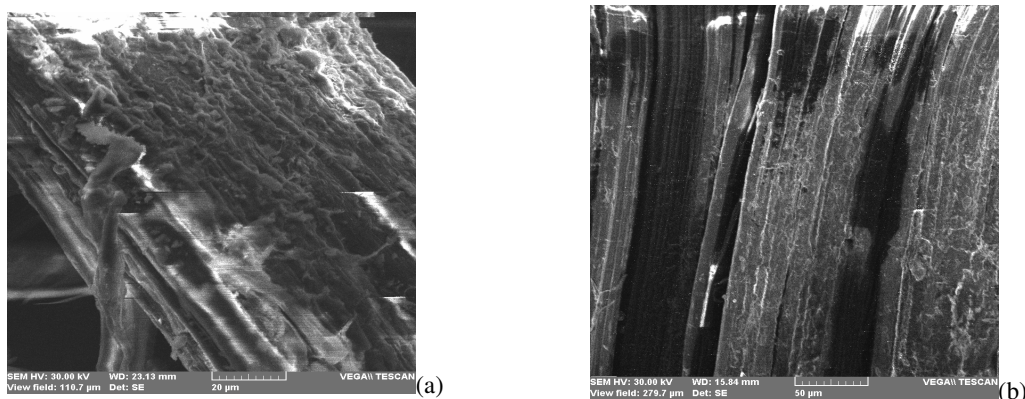


Figure 2: Electron micrographs of a) natural hemp fibers; b) hemp fibers impregnated with alizarin S

The rate of exhaustion (AER, g/L) is defined as mass of sorbent deactivated per unit volume of water treated at the breakthrough point and was calculated by the following equation:<sup>35</sup>

$$AER = \frac{\text{mass of sorbent (g) in column}}{\text{volume of water treated (L)}}$$

## RESULTS AND DISCUSSION

### Characterization of hemp impregnated with alizarin S

The choice of alizarin S as modifier agent for hemp fibers is based on the major role of the chelating reagent in the selective retention of trace pollutants on natural polymeric substrates. The morphological structure of natural hemp and alizarin S – hemp fibers was studied by electron microscopy (Bruker AXS-Microanalyse GmbH microscope). Figure 2 shows the images of hemp fiber (a) and hemp loaded with alizarin S (b). The images clearly show the morphological changes occurring on the surface of the hemp fiber after the treatment with a solution containing alizarin S.

The reagent leaching out from the hemp strongly suggests physical adsorption achieved probably by intermolecular forces of van der Waals type and hydrogen bonds between the hydroxyl groups of the cellulosic substrate and those of the alizarin on hemp or in solution.

### FTIR spectral analysis

FTIR spectroscopy was applied to identify the functional groups of hemp and alizarin S impregnated hemp fibers responsible for metal adsorption. To reveal systematic changes in the spectral features upon reaction with metal ions, FTIR spectra were obtained for the sample before and after reacting with Cr (III) ions (FT-IR spectrometer Bruker Vertex 70) (Fig. 3).

A comparison among these spectra shows that these changes may be explained by metal ions being associated with carboxylate and hydroxylate anions, which reveals that carboxyl and hydroxyl groups are dominant in the process of metal ion uptake (Table 4).

### Breakthrough analysis

The design of a fixed bed sorption system depends on the effects of various operational parameters, such as initial sorbate concentration, bed depth and flow rate. Due to its priority

influence on the general position of the breakthrough curves, the effect of the initial metal ion concentration on the dynamic Cr (III) removal using hemp pretreated with alizarin S was investigated.

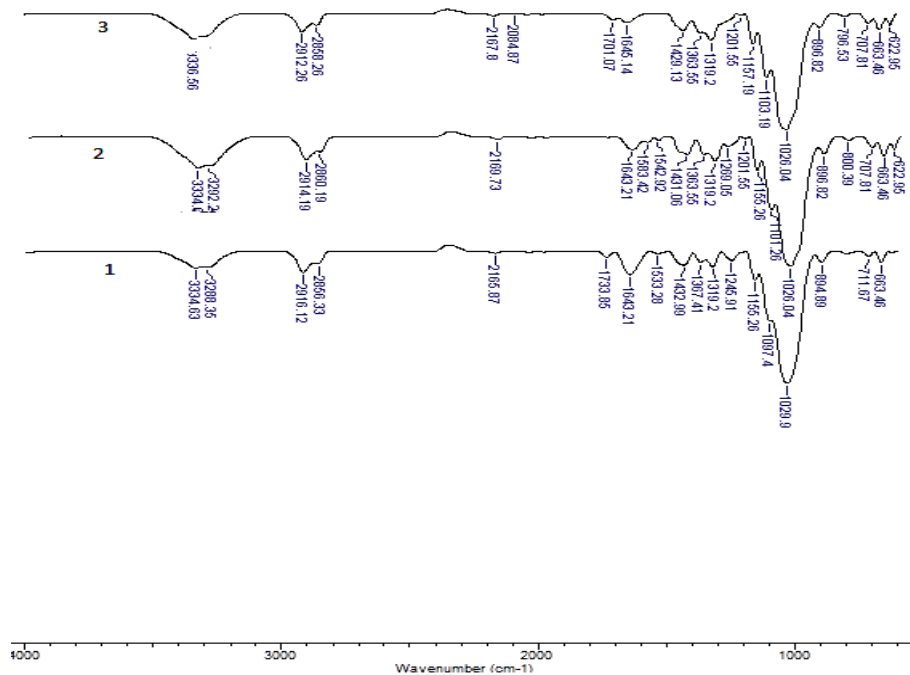


Figure 3: IR spectra for (1) hemp fibers, (2) alizarin S impregnated hemp fibers and (3) alizarin S impregnated hemp fibers – Cr (III) systems

Table 4  
Main FTIR spectral characteristics of hemp before and after sorption of Cr (III)

Transmission band (cm <sup>-1</sup> )			Assignment
Untreated hemp (1)	Hemp treated with alizarin (2)	After Cr (III) adsorption (3)	
3288.35	3292.2	3294.13	The stretching of O–H bonds results in vibrations within a range of frequencies/wavenumbers, which indicate the presence of O–H bonds of carboxylic acids and/or free hydroxyl groups
2916.12	2914.19	2912.26	Indicates symmetric or asymmetric C–H stretching vibration of aliphatic acids
1733.85	-	1701.07	Represents the stretching vibration of C=O bonds, which originates from non-ionic carboxyl groups
1643.21	1643.21	1645.14	Suggests the involvement of the C–O group in metal binding
1533.28	1542.92	-	Double bands of carboxylic group
1432.99	1431.06	1429.13	Relates the C-H deformations and aromatic groups ring vibration
1097.4	1101.26	1103.19	Existence of stretching vibrations of C–O of alcohol groups and carboxylic acids
1029.9	1026.04	1026.04	Indicative of ring breathing with C-O stretching

The experimental breakthrough curves at two different Cr (III) initial concentrations are presented in Figure 4. The obtained values for the experimental breakthrough parameters are tabulated in Table 5.

Figure 4 shows that as Cr (III) initial concentration increases, the breakthrough curve becomes steeper and shifts toward the origin. This behavior may be explained by the fact that the binding sites became saturated more quickly in the system at higher initial concentrations.<sup>33</sup> This statement is confirmed in terms of breakthrough time in Table 5. Thus, the experimental values of the breakthrough time (the position at  $C_t/C_0 = 0.25$ ) in Table 5 decrease with an increase in Cr (III) initial concentration from 13.00 to 26.14 mg/L. Therefore, the volumes of solution treated at the breakthrough point are found to decrease from 300 to 220 mL with this increase in the initial concentration. Similarly, the saturation time (the position at  $C_t/C_0 = 0.99$ ) and the volume of solution processed at the saturation point decreased with the increase in Cr(III) initial concentration, as shown in Table 5. According to the obtained results, the Cr (III) sorption capacity of hemp impregnated with alizarin S at breakthrough and saturation is greater at higher Cr (III) initial concentrations (Table 5). This increasing trend is due to the fact at higher initial concentration of the tested metal ion the increased concentration gradient between the surface of the sorbent and the solution results in an improvement of the driving force for mass transfer. These results agree with those of other published studies concerning the fixed bed column sorption of different heavy metal ions on marine green alga *Ulva reticulata*, *Pinus sylvestris* sawdust or *Sargassum wightii* biomass.<sup>34-36</sup> On the other hand, Cr (III) sorption yield decreases as the initial Cr (III) concentration increases. This behavior can be explained by the fact that when

the column gets to the to saturation, the amount of Cr (III) sorbed is very low in comparison with the Cr (III) amount passing through the column.<sup>33</sup> A similar trend was observed for the Cr (III) sorption by olive stone.<sup>37</sup>

The mass transfer zone (MTZ) is the active surface of the sorbent (hemp loaded with alizarin S) in which Cr (III) sorption occurs. As the influent concentration was doubled, the MTZ length decreased from 3.37 cm to 2.75 cm for 13.00 mg/L and 26.14 mg/L, respectively (Table 5). At low concentration, meaning low concentration gradient, the driving force is not sufficient to enhance mass transfer (limitations due to the resistance to film diffusion and intraparticle diffusion) and the mass transfer zone is enlarged.<sup>34</sup> Higher concentration of Cr (III) ions in the initial solution provides a stronger driving force for metal ion sorption and, consequently, the sorption sites are saturated faster, which leads to a shorter mass transfer zone.

During continuous flow operation, the sorbent is gradually exhausted. The rate of hemp – alizarin S exhaustion is found to be 1.40 and 0.736 g/L for the initial concentration of 13.00 and 26.14 mg/L, respectively, as presented in Table 5. These data are in good agreement with those recently reported in the literature for chromium (VI) sorption on a fixed bed column of polypyrrolle/Fe<sub>3</sub>O<sub>4</sub> nanocomposite.<sup>33</sup>

#### Modelling of breakthrough curves

In order to model the breakthrough behavior of Cr (III) sorption by hemp fibers loaded with alizarin S, Thomas and Yoon-Nelson models were used to match the experimental data.

Table 5  
Different experimental parameters of the breakthrough curves for Cr (III) sorption by hemp fibers pretreated with alizarin S

$C_0$ (mg/L)	$t_b$ (min)	$V_b$ (mL)	$q_b$ (mg/g)	$t_s$ (min)	$V_s$ (mL)	$q_s$ (mg/g)	MTZ (cm)	Cr (III) sorption yield (%)	Sorbent exhaustion rate (g/L)
13.00	110	300	4.178	300	750	6.894	3.37	73.57	1.400
26.14	80	220	6.163	160	425	10.781	2.75	62.64	0.736

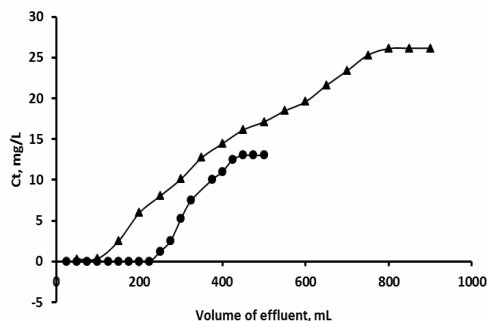


Figure 4: Breakthrough curves for fixed bed column sorption of Cr (III) by hemp impregnated with alizarin S ( $C_0 = \bullet$  13 mg/L;  $\blacktriangle$  26.14 mg/L)

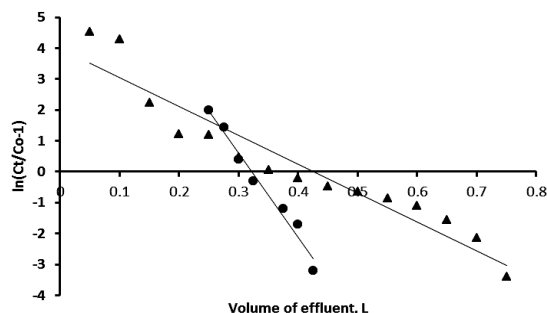


Figure 5: Linear Thomas plots for column sorption of Cr (III) on hemp impregnated with alizarin S at 2 initial concentrations ( $\bullet$  13 mg/L;  $\blacktriangle$  26.14 mg/L)

Table 6

Characterization of fixed bed sorption of Cr (III) onto hemp – alizarin S by means of Thomas and Yoon–Nelson model parameters

Initial Cr (III) concentration (mg/L)	Thomas model			Yoon–Nelson model			
	$K_T$ (L/min·mg)	$q_{0(T)}$ (mg/g)	$R^2$	$K_{YN}$ (min <sup>-1</sup> )	$\tau$ (min)	$q_{0(YN)}$ (mg/g)	$R^2$
13.00	$4.41 \cdot 10^{-3}$	8.987	0.974	0.044	114.47	4.46	0.902
26.14	$7.88 \cdot 10^{-4}$	15.897	0.912	0.052	95.75	7.86	0.954

### Thomas model

Due to its simplicity and reasonable accuracy in breakthrough under various conditions, the Thomas solution is one of the most general and widely used models in column performance theory. This model is based on the assumption of Langmuir's kinetics of adsorption–desorption, without axial dispersion. Its main hypothesis is that the rate driving force obeys second-order reversible reaction kinetics.<sup>38</sup>

The following linearized form of Thomas equation has been used in this study:<sup>39</sup>

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_T \cdot q_{0(T)} \cdot m}{F} - \frac{K_T \cdot C_0}{F} \cdot V$$

where  $C_0$  is initial Cr (III) concentration (mg/L);  $C_t$  is equilibrium concentration (mg/L) at time  $t$  (min);  $k_T$  is Thomas constant (L/min·mg);  $F$  is volumetric flow rate (L/min);  $q_{0(T)}$  is maximum column capacity (mg/g), determined by the Thomas model;  $m$  is mass of sorbent (g) and  $V$  is volume (L).

From the slope and the intercept of the straight line obtained by plotting  $\ln(C_0/C_t - 1)$  versus  $V$ , the values of the Thomas parameters ( $k_T$  and  $q_{0(T)}$ ) can be determined.

The applicability of the Thomas model to the experimental data provided by the dynamic sorption of Cr (III) ions from aqueous solutions

with different initial concentrations on hemp impregnated with alizarin S is shown in Figure 5.

The characteristic parameters derived from the linear Thomas plots for the sorption of Cr (III) by hemp loaded with alizarin S packed column are listed in Table 6.

It is obvious from Table 6 that the values of Thomas rate constant,  $k_T$ , decreases as the initial Cr (III) concentration increases. At the same time, the hemp – alizarin S maximum sorption capacity of Cr (III), determined by the Thomas model,  $q_{0(T)}$  increases as the initial metal concentration increases. These trends are in good agreement with recent literature data reporting on the sorption of Cr (III) ions from aqueous solution by olive stone in a fixed bed column.<sup>37</sup> They can be justified by taking into account the fact that the gradient concentration is the driving force of the sorption process. Thus, a higher driving force due to an increased concentration of Cr (III) results in an improved performance of the column packed with hemp loaded with alizarin S.

It is well known that a direct comparison between the sorbents is difficult due to the use of different experimental conditions. However, the maximum Cr (III) sorption capacity of the hemp loaded with alizarin S, determined by the Thomas model, is compared in Figure 6 with other low-cost sorbents that were used for the column

removal of Cr (III). It can be seen from Figure 6 that the Cr (III) sorption capacity of hemp impregnated with alizarin S is significant and comparable, so that the lignocellulosic substrate

with improved sorption performance can be considered as a valuable alternative in the treatment of industrial effluents.

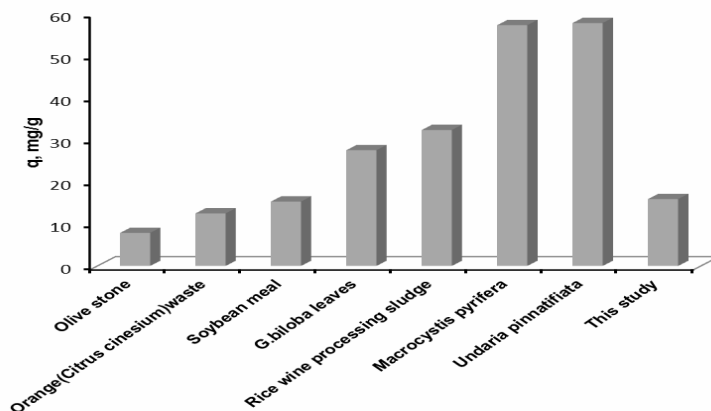


Figure 6: Comparison of Thomas sorption capacity of different sorbents with that of hemp impregnated with alizarin S (olive stone,<sup>37</sup> orange (*Citrus cinesium*) waste,<sup>31</sup> soybean meal,<sup>41</sup> *G. biloba* leaves,<sup>42</sup> rice wine processing sludge,<sup>43</sup> *Macrocystis pyrifera*,<sup>44</sup> *Undaria pinnatifata*,<sup>44</sup> this study)

The values of the linear regression coefficients ( $R^2$ ) for 13.00 mg/L and 26.14 mg/L were 0.974 and 0.912, respectively (Table 6). This fact shows that Thomas model fits very well with the experimental breakthrough data. Thomas model predicts monolayer sorption, which is also confirmed by our earlier batch sorption studies where the experimental data fitted very well with Langmuir isotherm.<sup>29</sup> Furthermore, the Thomas Cr (III) sorption capacity (8.897 mg/g) of the hemp impregnated with alizarin S is higher than its corresponding Langmuir sorption capacity (6.34 mg/g). This discrepancy between sorption capacities in batch and column experimental systems is in good agreement with the findings from other studies.<sup>30</sup> It may be due to the reason that the hemp impregnated with alizarin S favors improved solid state diffusion in fixed bed column mode, compared to the batch operation.

#### Yoon–Nelson model

Yoon and Nelson proposed a less complicated model based on the assumption that the rate of decrease in the probability of sorption for each sorbate molecule is proportional to the probability of sorbate breakthrough on the sorbent.<sup>45</sup> The linear form of the Yoon–Nelson model used in this study is represented as follows:<sup>46</sup>

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN} \cdot t - \tau \cdot k_{YN}$$

where  $C_t$  is effluent concentration at time  $t$  (mg/L);  $C_0$  is metal ion initial concentration (mg/L);  $k_{YN}$  is Yoon–Nelson rate constant ( $\text{min}^{-1}$ );  $\tau$  is time required for 50% sorbate breakthrough;  $t$  is sampling time (min). A plot of  $\ln\left(\frac{C_t}{C_0 - C_t}\right)$  versus

$t$  gives a straight line with a slope of  $k_{YN}$  and intercept of  $-\tau \cdot k_{YN}$ .

According to the Yoon–Nelson model, the amount of metal ion sorbed in a fixed bed is half of the total metal ion entering the adsorption bed within  $2\tau$  period.<sup>47</sup> In this context, for a given bed, the column sorption capacity in the Yoon–Nelson model,  $q_{0(YN)}$  can be computed with the following equation:

$$q_{0YN} = \frac{q_{(total)}}{m} = \frac{\frac{1}{2}C_0[(r/1000) \times 2\tau]}{m} = \frac{C_0 \cdot r \cdot \tau}{1000 \cdot m}$$

where  $C_0$  is initial concentration (mg/L);  $r$  is flow rate (mL/min);  $m$  is weight of sorbent (g) and  $\tau$  is time required for 50% sorbate breakthrough.

The characterization of the Cr (III) dynamic sorption on the hemp impregnated with alizarin S by means of the Yoon–Nelson model is illustrated in Figure 7.



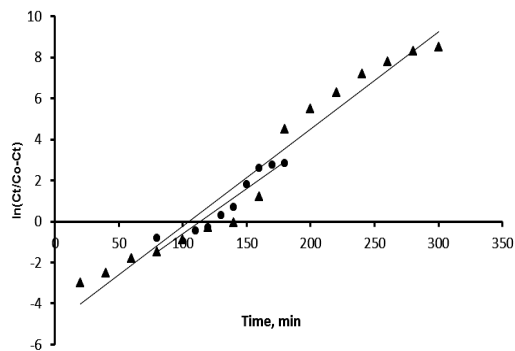


Figure 7: Linear Yoon–Nelson plots for the dynamic sorption of Cr (III) from aqueous solutions with different initial concentration on hemp fibers loaded with alizarin S (● 13 mg/L; ▲ 26.14 mg/L)

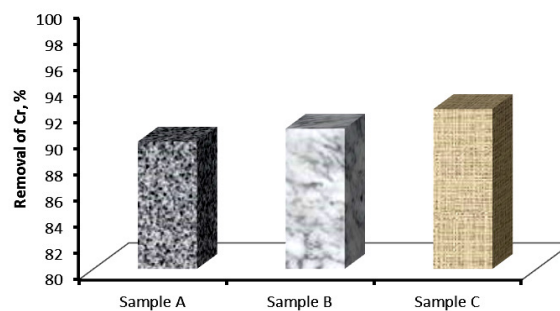


Figure 8: Removal of Cr (III) from samples of synthetic wastewaters

Table 7  
Heavy metal concentrations in the samples of synthetic wastewaters under study

Sample	mg Cr(III)/L	mg Zn(II)/L	mg Cu(II)/L	Volume of wastewaters
A	12	5	4	500
B	21	12	10	500
C	34	20	14	500

It is clear from Table 6 that the values of the Yoon–Nelson rate constant,  $k_{YN}$ , increase as the initial concentration increases. This behavior is similar to that previously reported for the biosorption of Cr (III) on a fixed bed column prepared by olive stone.<sup>37</sup> This may be explained by the fact that the increase in initial concentration of the metal ion increases the competition between the sorbate species for the sorption sites, which ultimately results in a higher rate of retention. It is known that  $k_{YN}$  and  $\tau$  are inversely related, so that, as expected, the time required for 50% breakthrough,  $\tau$ , decreases with increasing the influent concentration of Cr (III). The hemp – alizarin S column sorption capacity, calculated based on the results of the Yoon–Nelson model,  $q_{0(YN)}$ , increases with the increase of the initial concentration of Cr (III).

Smaller values of the linear regression coefficients ( $R^2$ ) for the Yoon–Nelson plots (Table 6) than those for the Thomas plots suggest that the optimal solution for the description of the investigated hemp – alizarin S fixed bed column is provided by using the Thomas model.

#### Performance of hemp – alizarin S column in treating wastewaters

Since the ultimate objective of the metal sorption technology is the removal of metal ions from wastewaters, fixed bed column sorption

experiments were conducted with three samples of synthetic wastewaters containing ions of Cr (III), Zn (II) and Cu (II) in different amounts (Table 7). The performance of the column (bed height = 7 cm; flow rate = 2 mL/min) is given in Figure 8. The results show that the hemp impregnated with alizarin S column removed >90% of Cr (III) and the Cr (III) removal was not influenced by the presence of other metal ions. This is due to the selectivity of hemp fibers loaded with alizarin for Cr (III).

#### CONCLUSION

The removal of Cr (III) from aqueous solutions by sorption in a fixed bed column filled with alizarin S impregnated hemp fibers has been studied. The effect of the initial metal ion concentration on the Cr (III) sorption process was investigated and the experimental breakthrough curves were obtained. The values of the experimental breakthrough parameters were calculated and interpreted. The experimental values of the breakthrough time and saturation time decrease with the increase of Cr (III) initial concentration. The Cr (III) sorption capacity of hemp impregnated with alizarin S at breakthrough and saturation is greater at higher Cr (III) initial concentrations. On the other hand, Cr (III) sorption yield decreases as the initial Cr (III) concentration increases. This behavior can be

explained by the fact that when the column reaches saturation, the amount of Cr (III) sorbed is very low in comparison to the Cr (III) amount passing through the column. As the influent concentration was doubled, the mass transfer zone length decreased from 3.37 cm to 2.75 cm. The rate of hemp – alizarin S exhaustion was computed and found to be 1.40 and 0.736 g/L for the initial concentration of 13.00 and 26.14 mg/L, respectively. Thomas and Yoon–Nelson models were applied to the experimental data and was found that the optimal solution for the description of the investigated hemp – alizarin S fixed bed column is provided by the Thomas model. The hemp impregnated with alizarin S column removed >90% of Cr (III) from three samples of synthetic wastewaters containing various amounts of different heavy metal ions Zn (II), Cu (II)). The sorption bed under study in fixed column provides an alternative solution to ameliorate the quality of wastewater contaminated with Cr (III).

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