

ČESKÁ ZEMĚDĚLSKÁ UNIVERZITA V PRAZE

FAKULTA ŽIVOTNÍHO PROSTŘEDÍ

KATEDRA GEOENVIRONMENTÁLNÍCH VĚD



The use of brewer's draff for the biosorption of Cr(VI) from contaminated  
waters

MSc. Thesis

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2013

## Index:

1. Introduction .....	3
2. Literature review .....	4
2.1. Chromium .....	4
2.1.1. Reduction process Cr(VI) to Cr(III) .....	6
2.2. Zlate Hory, Czech Republic .....	10
2.3. Czech Republic, Europe. ....	11
3. Materials and Methods .....	13
3.1. Materials.....	13
3.2. Methods.....	14
3.2.1. Pretreatment .....	14
3.2.2. Column experiment .....	15
3.2.3. Batch experiment.....	16
3.2.4. Adsorption isotherm .....	16
3.2.5. Dissolvent organic carbon.....	18
4. Results and Discussion.....	19
4.1. Column experiments.....	19
4.2. Batch experiment –equilibrium modeling .....	22
4.3. Dissolved organic carbon analyses .....	25
5. Conclusions.....	26
6. References .....	27

## 1. Introduction

During the last decades the industrial production was increasing, resulting in the increasing environmental pollution. The main contaminants are the heavy metal. Chromium, cadmium and lead are the most common. Chromium is a toxic metal that should be removed from the environment because of his mutagenic and carcinogenic properties. Its higher content in the environment is caused by human activity: industries like chrome plating, dye and pigments, tanning, etc...<sup>[1]</sup>

The heavy metals were removed from water by different techniques like precipitation, chelation, ion exchange, reverse osmosis, electrochemical operation, filtration and especially adsorption because of its economical price. Nevertheless, biosorption has become one of the most important purification processes. Nowadays there are a lot of researches to find the most effective low-cost sorbent, like for example dead biomass of algae, fungi, peat moss, grape waste, brewers draffs, etc...<sup>[2]</sup> Moreover, the main requirements for these sorbents are low cost, local availability and minimal pre-treatment.

In Czech Republic, the consumption of beer is the highest, 158.6 L per capita, there are over 120 breweries on an area of 79000 km<sup>2</sup> and the annual production of brewers draff reaches 380 thousands of tons. the average price is 25€ per ton. The aim of this study is to provide information about adsorption process of Cr using batch and packed column experiments. Brewers draff will be compared with another sorbent, waste grape.

In this project, it will be studied the process of adsorption by mainly brewers draff and compared with grape waste. As it is known, brewers draff is a typical by-product of fermentation in beer production. Two different processes will be investigated (bed column and batch experiments) under the influence of operational parametre, pH

In addition, content of dissolved organic carbon (DOC) will be analysed as a determinant of organic matter degradation during the biosorption.

## 2. Literature review

Wastewater discharged by industrial activities is often contaminated by a variety of toxic or otherwise harmful substances which have a negative effect on the water environment. For example, the industry of metal finishing and electroplating units are one of the major sources of heavy metals (Zn, Cu, Cr...) and cyanide pollutants which contribute greatly to the pollution load of the receiving water bodies and therefore increase the environmental risks.

This project is focused especially on chromium removal from the underground waters at the area of Zlate Hory, Czech Republic. Contamination by Cr(VI) originate from a bicycle manufacturing factory.

### 2.1. Chromium

Chromium is a chemical element whose symbol is Cr and atomic number 24. It is a steely-gray, lustrous, hard and brittle metal which takes a high polish, resists tarnishing, and has a high melting point. The discoverer of the element was Louis Nicolas Vauquelin in 1799 although it was used in China like as coat metal weapons over 2000 years ago. <sup>[4]</sup>



Image 1: Chromium as a metal <sup>[5]</sup>

Chromium is naturally found in rocks, plants, soil, volcanic dust and animals. Nevertheless, the excess of this contaminant is added by the chemical and metallurgical industries, basically.

Nowadays, chromium has different applications as: Metallurgy (plating), dye and pigments, synthetic ruby and the first laser, wood preservative, tanning, etc...

### *Metallurgy – Chrome plating* <sup>[6] and [7]</sup>

This is the technique of electroplating a thin layer of chromium onto a metal or plastic object. The chromed layer can be decorative, provide corrosion resistance (our case), ease cleaning procedure or increase surface hardness and sometimes for aesthetic purposes a cheaper imitator of chrome will be used.

### *Dye and pigments* <sup>[7]</sup>

Chrome yellow is a natural yellow pigment made of lead (II) chromate ( $\text{PbCrO}_4$ ). It was used together with cadmium yellow as a pigment. In addition, by mixing chrome yellow with Prussian blue, be chrome green can be obtained.

### *Synthetic ruby and the first laser* <sup>[7]</sup>

Chromium (III) is added into artificial corundum crystals, thus making chromium a requirement for making synthetic rubies. Thanks to synthetic rubies crystals, in 1960 the first laser was produced.

### *Wood preservative* <sup>[7]</sup>

Chromium (VI) salts are used for the preservation of wood. CCA (chromate copper arsenate) is used in timber treatment to protect wood from ageing, fungi or insects, including termites.

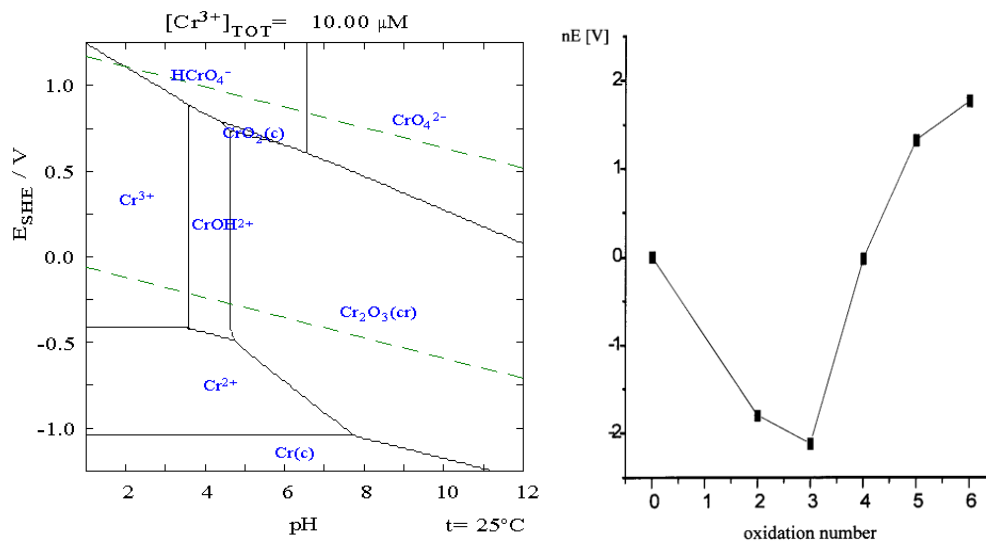
### *Tanning* <sup>[7] and [8]</sup>

Tanning is the process of leather treating to produce nobler material for textile industry. Traditionally, tanning used tannin, an acidic chemical compound, from which the name came. In this process chromium (III) salts take important place. Cr (III) stabilizes the lather by cross linking the collagen fibers.

Cr can exist in several chemical forms displaying oxidation numbers from 0 to VI. Only two of them, trivalent and hexavalent Cr, are, however, stable enough to occur in the environment. Cr(IV) and Cr(V) form only unstable

intermediates in reactions of trivalent and hexavalent oxidation states with oxidizing and reducing agents, respectively.

The Cr(III) oxidation state is the most stable (Graphic. 1) and considerable energy would be required to convert it to lower or higher states. The negative standard potential ( $E^{\circ}$ ) of the Cr(III)/Cr(II) metal-ion couple signifies that Cr(II) is readily oxidized to Cr(III), and Cr(II) species are stable only in the absence of any oxidant (anaerobic conditions).



Graphic 1. States of Chromium [9] and [10]

### 2.1.1. Reduction process Cr(VI) to Cr(III)

#### 2.1.1.1. Conventional methods

Conventional heavy metal removal processes are precipitation, ion exchange and reverse osmosis. [20]

#### Precipitation

Equilibration between solid and dissolved forms of Cr is a physical-chemical interaction that is used in treatment processes. Precipitation of Cr(III) occurs as  $Cr(OH)_3(s)$ ,  $FeCr_2O_4(s)$ , or  $Fe_xCr_y(OH)_3(s)$ . The solubility of Cr(III) governs its migration. Precipitation/dissolution is a function of pH, complexation by organic matter, and the presence of other ions. As pH increases,  $OH^{-}$  concentration increases and more Cr precipitate. Organics can complex with dissolved Cr, making removal by precipitation or adsorption difficult. The precipitation of

Cr(III) is useful for increasing Cr(VI) to Cr(III) reaction rates, by Le Chatelier's Principle.

Natural precipitation of Cr(VI) is not a major removal mechanism.  $\text{CaCrO}_4$  was observed to precipitate naturally during summer months at a hazardous waste site. Based on laboratory studies,  $\text{BaCrO}_4$  and Cr/Al coprecipitates were suggested to occur at other sites. Plating tank sludge at the first site contained  $\text{PbCrO}_4$ ,  $\text{PbCrO}_4 \cdot \text{H}_2\text{O}$ , and  $\text{K}_2\text{CrO}_4$ . However, the solids are highly soluble and are not a considerable removal mechanism for Cr(VI).

These three processes (redox reactions, sorption, and precipitation) form the basis of both chemical and biological treatment processes used to influence the balance between Cr(III) and Cr(VI).<sup>[21]</sup>

#### *Ion exchange*

Ion exchange is a frequently used treatment for chromium removal. The technique consists in removing chromium ions from the aqueous phase by replacing them with the anion present in the ion exchange resin. As contaminated water is passed through the resin, contaminant ions are exchanged for other ions such as chloride or hydroxides in the resin.<sup>[22]</sup>

#### *Reverse osmosis*

Reverse osmosis for soluble Cr uses a semipermeable membrane, and the application of pressure to a concentrated solution which causes water, but not suspended or most dissolved solids (soluble Cr), to pass through the membrane. Das et al. demonstrated a chromium removal efficiency of 91-98% using nanofiltration and 98.8-99.7% using reverse osmosis. The benefits are produces high quality water.

### 2.1.1.2. Biosorption

The process of biosorption appeared as a simple and low-cost method, with a great potential of becoming an actual alternative to conventional ones, overcoming the problems of insufficient efficiency and difficult waste handling derived from the precipitation method. [20]

The process of reduction is important because Cr (VI) is generally mobile and toxic, while Cr (III) is insoluble, immobile and relatively nontoxic. There are two main mechanisms of reduction:

- 1) Mechanism I: direct reduction (Fig.1)
- 2) Mechanism II: indirect reduction, with three techniques.
  - a) The adsorption of anionic Cr species (mainly  $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{HCr}_2\text{O}_7^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ) to protonated active sites of the biosorbent (-OH, -COOH, -NH<sub>2</sub>).
  - b) Direct reduction to Cr(III) after contact with electron-donor groups of the biomaterial, while Cr (III) ions remain in the aqueous solution of form complexes on the biomaterial surface
  - c) Cr(VI) binding on the material surface, the reduction of Cr(VI) to Cr(III) by adjacent electron-donor groups and the release of the reduced Cr(III) into the aqueous phase due to repulsion between Cr (III) and positively charged functional groups. [11]

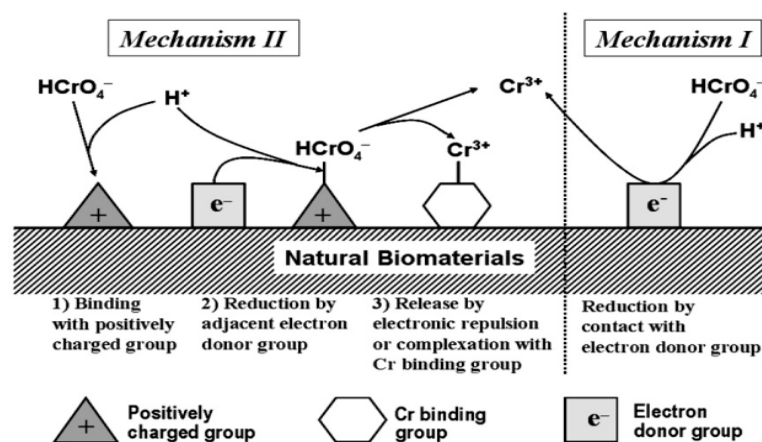


Fig. 1 Mechanism of the Cr(VI) biosorption by natural biomaterial. [11]



According to EPA, there are four technologies most promising for application by drinking water system. These technologies include: anion exchange, coagulation and precipitation of reduced Cr(III), adsorption via sulfur modified iron media, and membrane treatment such as nanofiltration and reverse osmosis. <sup>[12]</sup>

In this project we are only interested in +3 and +6 state of Chromium. Cr(VI) usually exists in wastewater as oxyanions such as chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) ions. The latter form is the most toxic. EPA (Environmental Protection Agency) has set the maximum level of total chromium concentration allowed in drinking water at 0.1mg/L

The Chromium (VI) is that causes damages. <sup>[13]</sup>

*Health effects:*

- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Lung cancer
- Death

*Environmental effects:*

- Not biodegradable
- Immobile
- Toxic to organism
- Alteration of genetic materials
- Cancer
- Bad crops
- Damages in the gills of fish that swim near the point of disposal
- In animals:
  - Respiratory problems

- A lower ability to fight disease
- Birth defects
- Infertility
- Tumor formation

Soluble ionic forms of Cr (VI) formed in or added to soils or natural waters will persist indefinitely unless chromate is removed by leaching, adsorption, precipitation, uptake by living cells, or by reduction to trivalent form. Therefore, Cr (III) is an essential human dietary element and is found in many vegetables, fruits, meats, grains and yeast. However, Cr (VI) occurs naturally in the environment from the erosion of natural chromium deposits, and it can also be produced by industrial processes. Basically, Cr (VI) is toxic for the organism. This can modify the genetic material and cause cancer. <sup>[13]</sup>

Once, we saw all drawbacks of Chromium (VI), it's obvious that it should be eliminated from waters or reduced to Chromium (III)

Our studied chromium is basically +6 and we have to remove from water, which comes from Zlate Hory.

## **2.2.Zlate Hory, Czech Republic**

Zlate Hory (Golden hills) is a town located about 260 km from Prague, in the East of Czech Republic. The samples of contaminate water were taken from a area, where a factory of pieces of bicycle. The method used there is electroplating to prevent corrosion. The medium concentration of Cr(VI) at groundwater there is 7 mg/L, but our sample is from a drill hole with higher concentration. This activity is not only one that can pollute the environment because of mining sector, especially gold.

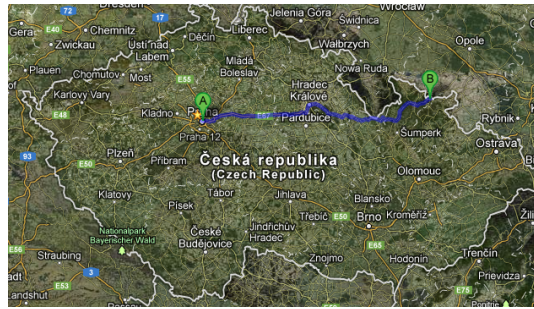
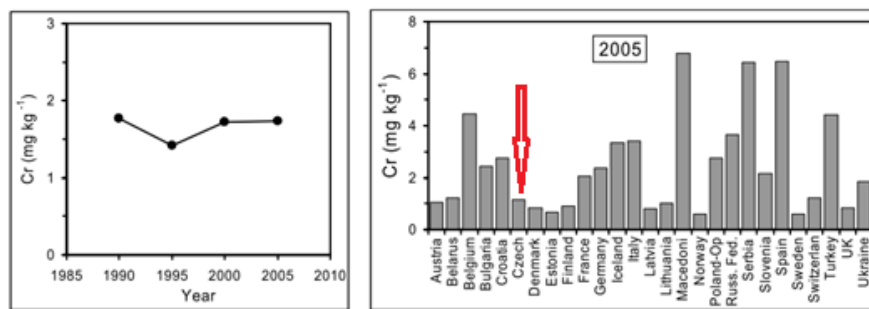


Fig. 2 Map, Czech Republic. [14]

### 2.3. Czech Republic, Europe.

Despite the big activity in the mining sector, Czech Republic does not occupy the highest place of contamination with chromium. In the following graphics, we can see respective levels of Cr concentration between some European countries:



Graphic 2. Comparison between the levels of Cr concentration. [15]

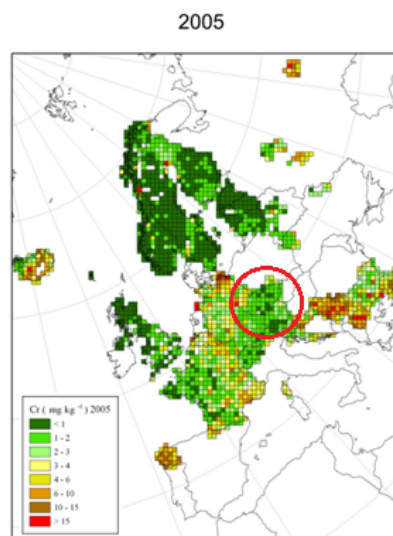


Fig. 3 Czech Republic, Europe. Cr concentration [15]

However, Czech Republic occupies the highest place in consumption of beer, it means, more production of brewers draff.

Beer consumption		
<i>nº</i>	<i>Country</i>	<i>L per capita</i>
1	<b>Czech Republic</b>	<b>158,6</b>
2	Ireland	131,1
3	Germany	110
4	Austria	108,3
5	Australia	104,7
6	United Kingdom	99
7	Poland	95
8	Denmark	89,9
9	Finland	85
10	Luxembourg	84,4

Fig. 4 Consumption of beer.<sup>[16]</sup>

### 3. Materials and Methods

#### 3.1. Materials

The brewers draff was provided by the research and teaching brewery of the Czech University of Life Sciences Prague. The grape waste is supplied by a wine producer from Most, Czech Republic. The contaminate water comes from a drill hole at Zlate Hory, Czech Republic. The medium concentration of Cr (VI) at groundwater there is 7 mg/L, but our sample is from a drill hole with higher concentration (20 mg/L).

Brewers draff was hand-ground with mortar in the pestle and after that it was sieved in such a way that the draffs don't overcome 2 mm of diameter.

During the column sorption experiment, (Fig. 5), the contaminated was pumped from a reservoir (2000 mL) [6] through the glass column [2] (2.5 cm internal diameter, 10 cm and 5 column length; Bio-Rad, USA) using peristaltic pump [1] (BIO-RAD, Econo Pump) with variable speed adjustment. Samples from the glass column were collected at regular intervals using fraction collector (Gilson FC 204) [3], test-tube rack [5] and support test tubes [4].

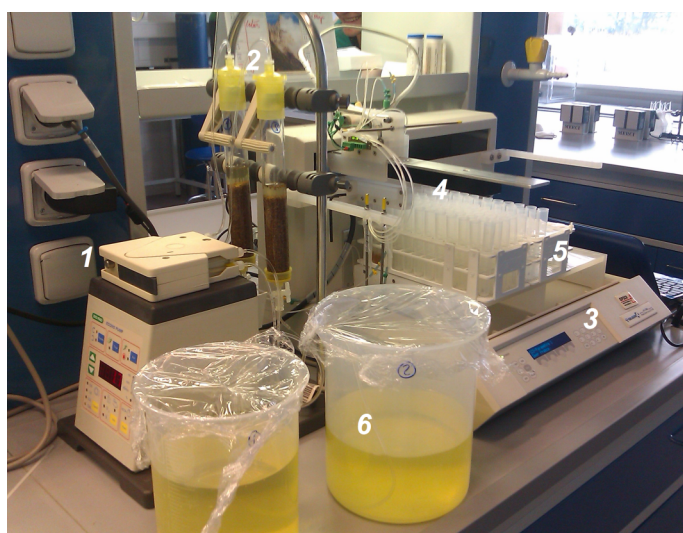


Fig. 5. equipment of adsorption

It is very important, working with known pH for this reason we use pH-meter (WTW, pH 3310 SET 2, Germany). To homogenize the

contaminated water during acidification we need an agitator (Heidolph, MR Hei Standard). Cr concentration was determined by ICP-OES spectrophotometer (Inductively coupled plasma optical emission spectrometry) (Agilent Technologies, 700 Series ICP-OES, USA).

Dissolved organic carbon concentration was determined by Carbon analyzer (Shimadzu TOC/TN Analyzer, Japan).

For the batch experiment the samples were stirred on automatic stirrer(GFL, 3006, Germany). After shaking during 24 hours, the samples were introduced in the centrifuge (Hettich Universal 320, UK)

Furthermore, during all process we used more beakers of different sizes, volumetric flasks, spatulas and pipettes (Eppendorf Research).

## 3.2.Methods

### 3.2.1. Pretreatment

First of all, dry brewery draff and grape waste was prepared. It consists of drying, grinding and sieving the material (< 2 mm).

To reduce the pH of contaminated water to 7, 4.5 and 3, we use the 0.1M HNO<sub>3</sub> (Eq. 1):

$$\frac{65 \text{ g HNO}_3}{100 \text{ g sol}} \cdot \frac{1 \text{ mol}}{(1+14+16 \cdot 3) \text{ gHNO}_3} \cdot \frac{6.84 \text{ g sol}}{5.5 \text{ ml sol}} \cdot \frac{1000 \text{ ml}}{1 \text{ L}} = 12.83 \text{ M HNO}_3 \text{ initial concentration (Eq. 1)}$$

The amount of 0.1M HNO<sub>3</sub> is different depends on the pH:

pH	mL HNO <sub>3</sub> added
7	7
4,5	35
3	46

Table 1. The amount of mL added of

0.1M HNO<sub>3</sub> ro approach the expectative pH

### 3.2.2. Column experiment

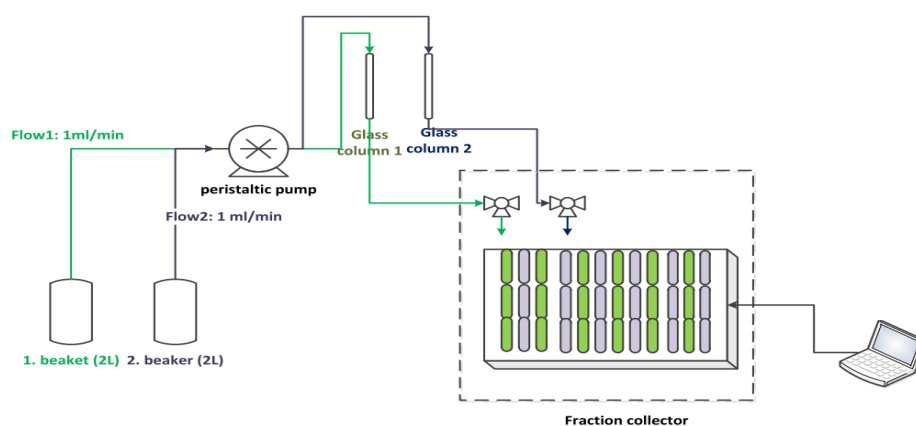


Fig. 6 Scheme of equipments of adsorption.

The scheme of the column experiment is shown in the Fig. 6.

The peristaltic pump operates at a speed of 1 mL/min. The acidified water is fed to the top of the column with the sorbent (brewers draff previously dry, grape waste previously wet). All the experiments were performed in duplicates and average value was calculated. Finally, the samples, which were picked up in periodic interval (Table 2), were diluted (1/10) and analyzed by ICP –OES.

period of time (h)	time (min)	period of time (h)	time (min)	period of time (h)	time (min)
1	0	6 (Total hours =10)	270	14 (Total hours =24)	660
	10		300		720
	20		330		780
	30		360		840
	40		390		900
	50		420		960
	60		450		1020
3 (Total hours =4)	80		480		1080
	100		510		1140
	120		540		1200
	140		570		1260
	160		600		1320
	180				1380
	200				1440
	220				
240					

Table 2. periodic intervals to pick up the samples.

The typical curve (breakthrough curve) obtained from sorption column experiment is shown at Fig. 7.

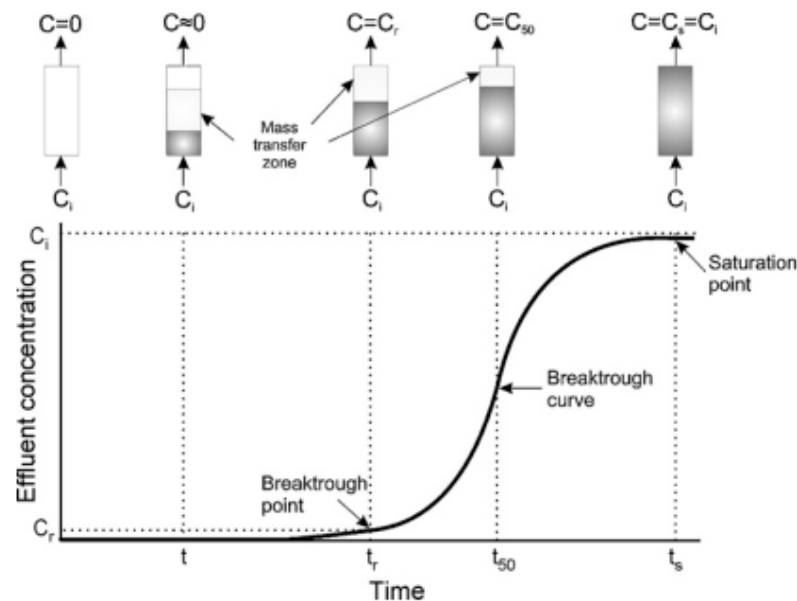


Fig. 7. Representation of a typical breakthrough curve.

The mass transfer zone varies from 0% of inlet concentration to 100% of the inlet concentration. The saturation time,  $t_s$ , is established when the concentration in the effluent is higher than 90-95% on the inlet concentration.

The service or breakthrough time,  $t_r$ , is established when the metal concentration in the effluent reaches a determined value, generally related to the permitted disposal limit for this metal

### 3.2.3. Batch experiment

Samples of 0.4g of each sorbent were prepared in duplicate for different concentration (20, 15, 10, 5 and 2 mg/L) and were shaken during 24h (250rpm) with 40 mL of Cr solution. The concentration of adsorbed Cr was calculated as the difference between Cr concentration in the initial solution and in the solution after sorption. The samples are diluted 1/10 to be analyzed in ICP-OES.

### 3.2.4. Adsorption isotherm

To calculate the maximum sorption capacity, Langmuir sorption model was introduced. The Langmuir isotherm takes an assumption that the



adsorption occurs at specific homogeneous sites within the adsorbent. The generalized Langmuir isotherm can be written in the form:

$$Q_{eq} = \frac{Q_{max}bC_{eq}}{1 + bC_{eq}}$$

Where:

$C_{eq}$  : the equilibrium metal ion concentration (mg/L)

$Q_{eq}$  : the amount of metal ion adsorbed on a sorbent at equilibrium (mg/g)

$Q_{max}$  : the maximum sorption capacity.

$b$  : a Langmuir constant related to energy of adsorption.

Parameters  $Q_{max}$  and  $b$  are higher for the sorption isotherm of the pre-treated material.

Moreover, the Freundlich isotherm model, which demonstrates a multilayer sorption process, exhibited a poorer fit. The Freundlich equation can be expressed as:

$$Q_{eq} = K_F C_{eq}^{\frac{1}{b}}$$

Where;

$Q_{eq}$  : Amount of Cr adsorbed per unit of biomaterial (mg/g)

$C_{eq}$  : equilibrium concentration of Cr (mg/L)

$K_F$  : a constant indicative of the relative adsorption capacity of the adsorbent (mg/g)

$\frac{1}{b}$  : a constant of intensity of the adsorption. [3]

### **3.2.5. Dissolvent organic carbon**

DOC analyses were performed during the column experiments in order to illustrate the concentration of dissolved organic carbon inside the treated contaminated water during time.

## 4. Results and Discussion

### 4.1. Column experiments.

According to the study of Cr(III) biosorption (M. Calero) the contact time must be prolonged to achieve saturation, for this reason our speed is 1ml/min. Depth of sorbent is another important factor. The length of glass column for experiment with brewers draff was 10cm and the depth of this sorbent was approximately 5cm (10g).<sup>[17]</sup>

The curves of this experiment were not successful because the sorbent (brewers draffs) was not conditioned by pH before starting the process. However, grape waste was conditioned.

experiment	sorbent	pH	C <sub>i</sub>
1	bd	7	22,54
2	bd	4,5	18,05
3	bd	3	11,30
4	gw	7	21,24
			18,28

Fig. 8. Table of initial concentration of contaminated water.

#### a) Brewers draff

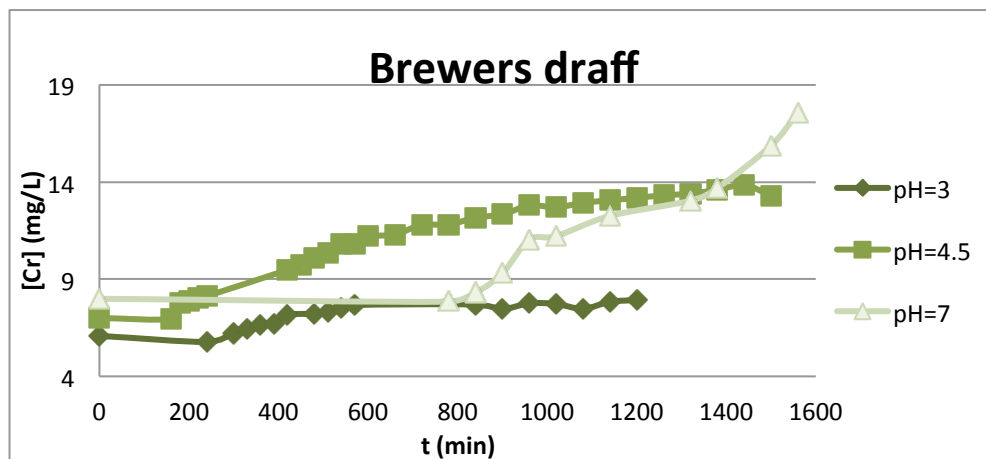


Fig. 9. Absolute values of Cr concentration after adsorption.

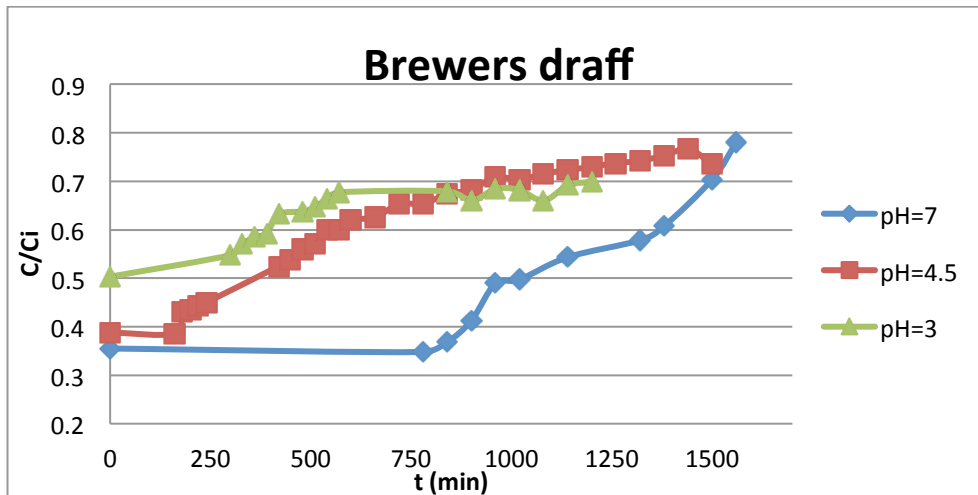


Fig. 10 Relative values of Cr concentration after adsorption

C	concentration after adsorption
C <sub>i</sub>	initial concentration

It was obtained to kind of curves. First one is with absolute values and the second one with relative values.

In the first one, we can observe the real number of concentration on Cr in each experiment of brewers draff with different pH. In conditions with lowest pH the process of adsorption works better but the second graphic seems different. The reason of this difference comes from the different analyzed initial concentrations of Cr by ICP-OES.

However, some studies confirm that the in condition of acid pH, sorbent adsorbs potentially. <sup>[18]</sup> So, the absorption is more efficient with decreasing the pH.

Hence, the best option is working with acid pH, in our case pH=3, the service time is longer for the lowest concentration, especially observe in the first graphic.

b) Grape waste.

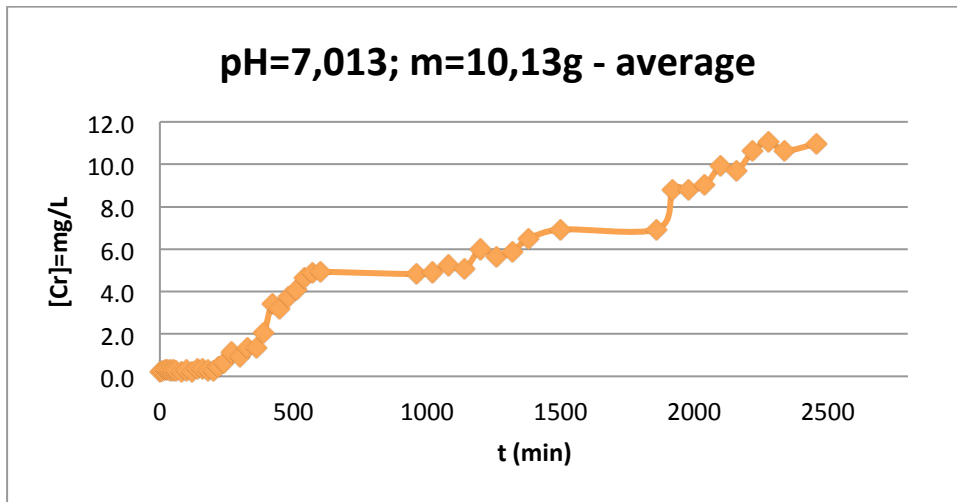


Fig. 11. Breakthrough curve of adsorption with grape waste. pH=7

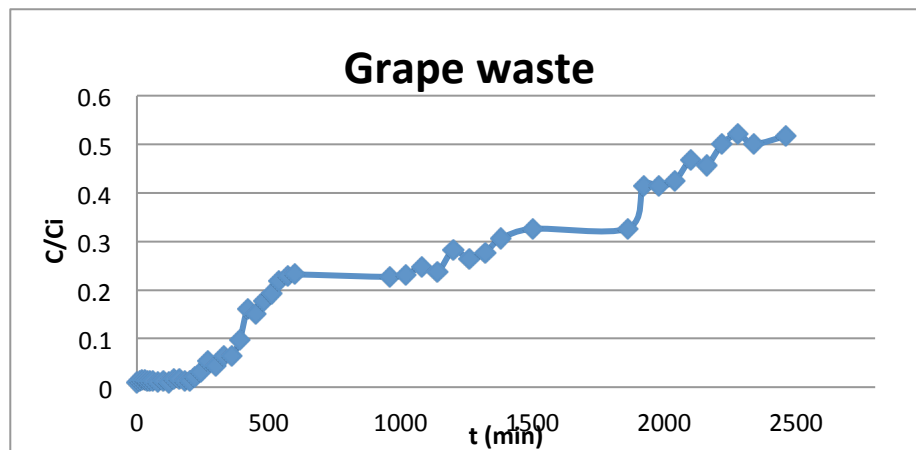


Fig. 12 Breakthrough curve (relative values) of adsorption with grape waste.

Once seen the graphics of adsorption with grape waste, the best results were obtained obviously in this experiment. The concentration of Cr approaches to 0 during approximately 250 min.

In the second graphic, the curve does not even approach 60% of initial concentration after 20 hours.

c) Comparison between brewery draff and grape waste at pH=7.

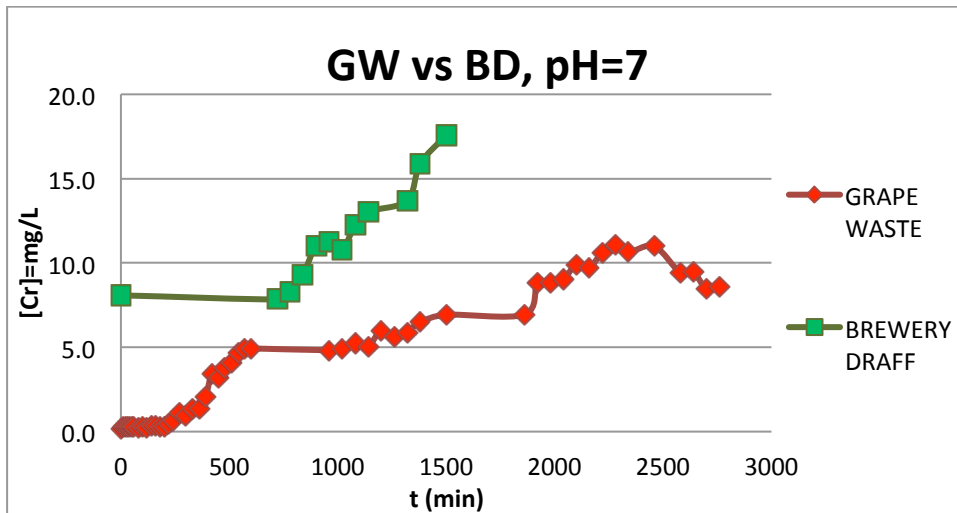


Fig. 13. Comparison between BD and GW with absolute values

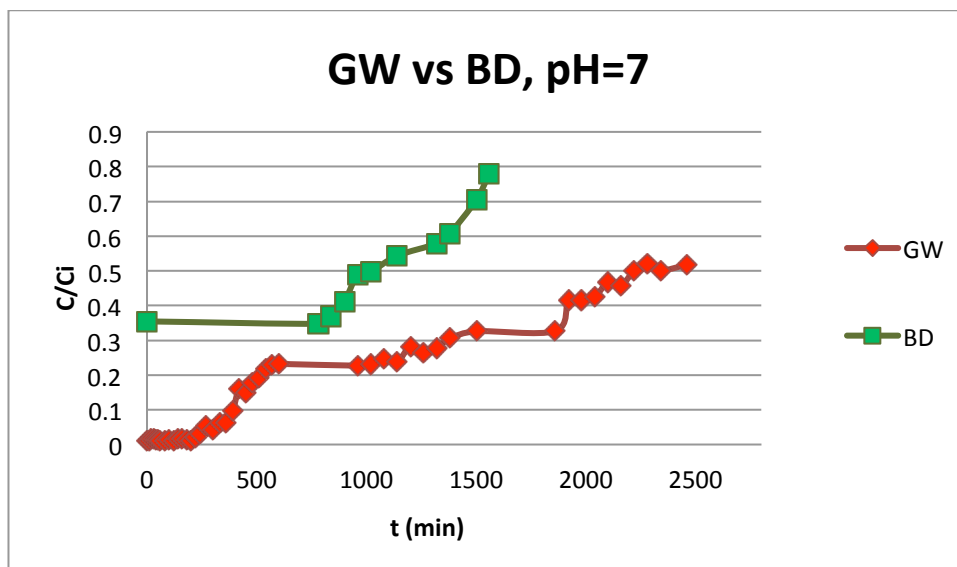


Fig. 14. Comparison between GW and BD with relative values.

It is obvious that Grape Waste is better sorbent than Brewery Draffs. Grape Waste is maintained about 0 mg/L of the concentration of Cr, in any moment it is approached to the curve of Brewery draffs. In fact, until approximately minute 2000 the level of the Cr concentration with grape waste doesn't approach at the minimum concentration in the beginning of brewery draffs.

#### 4.2. Batch experiment –equilibrium modeling

##### a) Brewers draff

The measured data fitted well the Langmuir model. This model supports a monolayer sorption theory. Maximum sorption capacity was calculated to be

45.8 mg/g. Figure X shows the measured data with the curve calculated from the Langmuir model.

Langmuir - brewers  
draff

k	0,07
Qmax	45,8

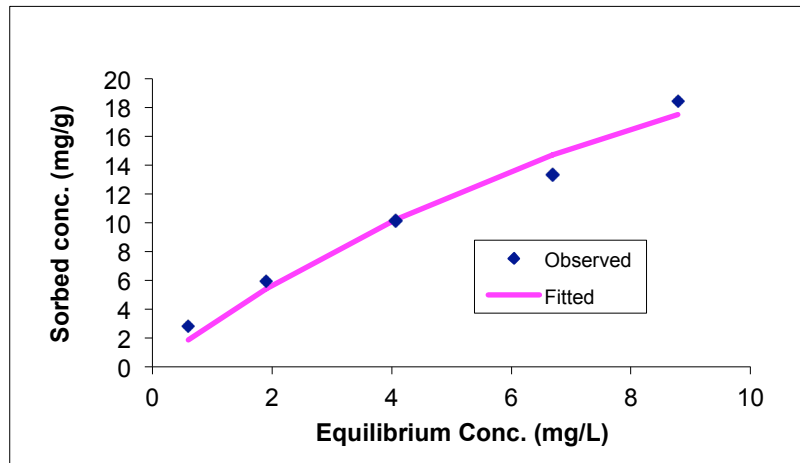


Fig. 15 . Curve of sorbed concntration. Langmuir

Freundlich -  
brewers draff

k	3,6
n	0,733

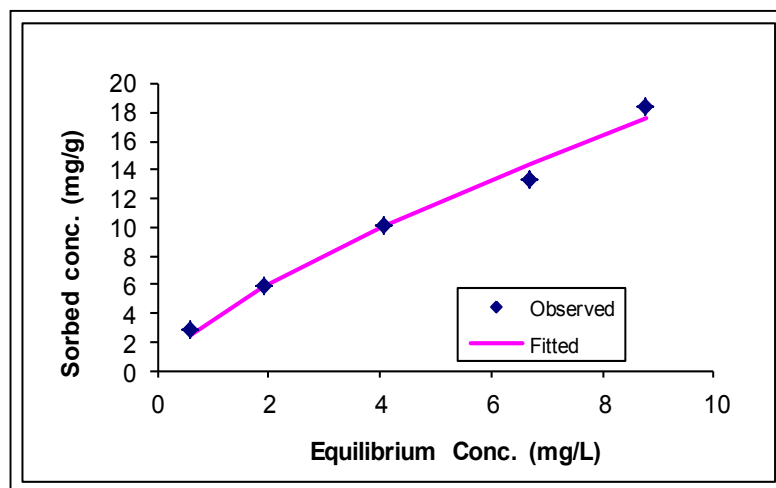


Fig. 166 . Curve of sorbed concntration. Freundlich

b) Grape waste

Experimental data did not fit well the Langmuir model in the case of grape waste. It can be concluded that the sorption mechanism is more complicated and does not follow the monolayer theory. The maximum sorption capacity was calculated to be 137.8 mg/g

Langmuir -grape  
waste

k	0,001
Qmax	137,8

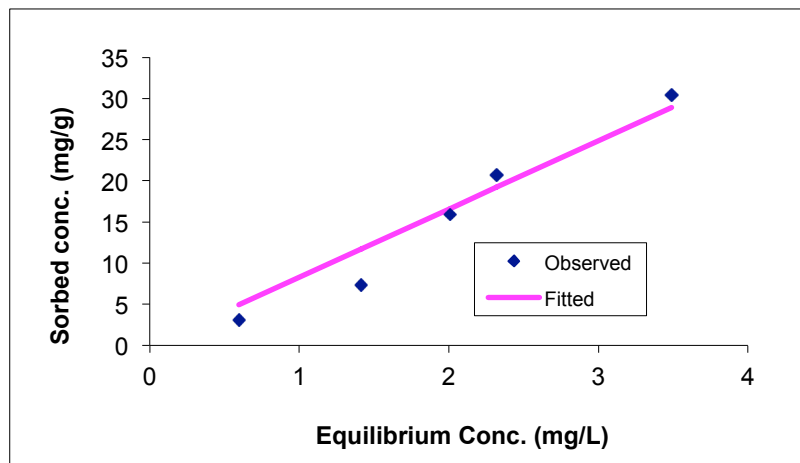


Fig. 17 curve of sorbed concentration. Langmuir

Freundlich - grape  
waste

K	6,24
n	1,291

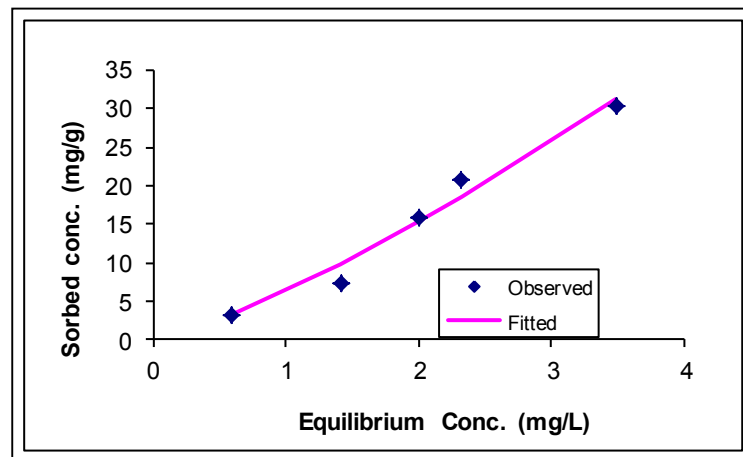


Fig. 188 curve of sorbed concentration. Freundlich



### 4.3. Dissolved organic carbon analyses

In the Toc experiments we analyze the concentration of Dissolved Organic Carbon contained in the samples of contaminated water after the packed bed column.

So in the next graphic we can observe the DOC concentration in front of time, case of different ph with the same sorbent: Brewery draffs.

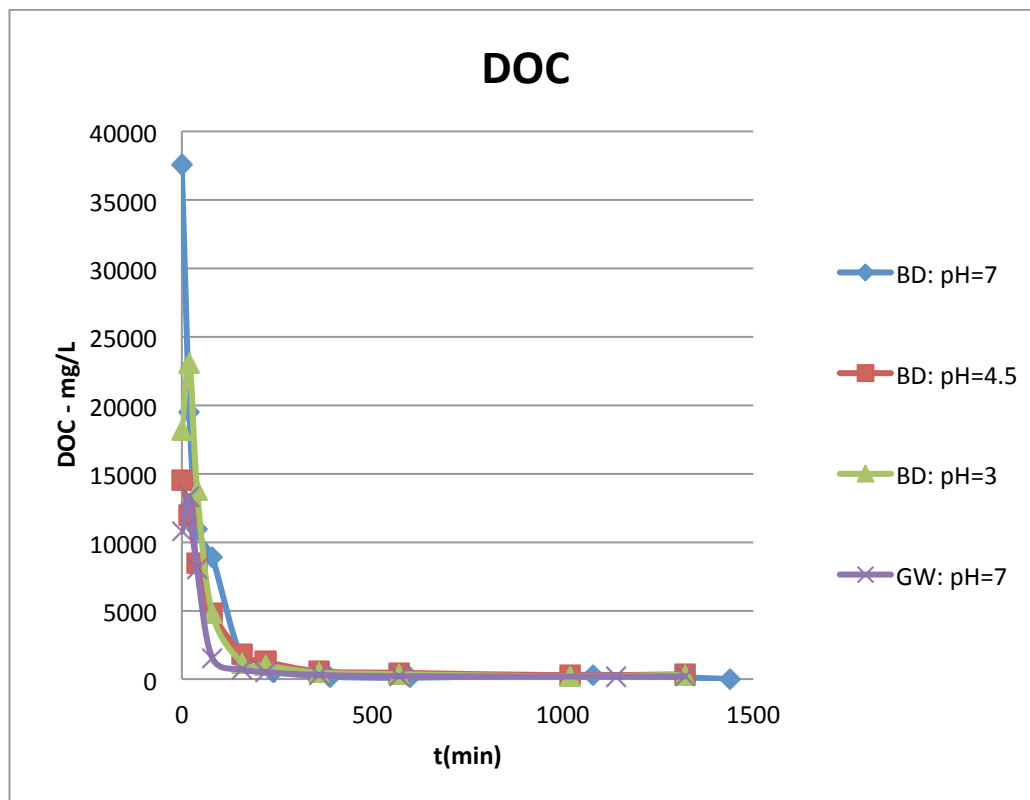


Fig. 19. TOC analysis

We can observe the exponential tendency of the curve, in relation that the less time, the higher DOC concentration. The pH is a factor that does not affect the behavior of DOC concentration nevertheless until approximately 200 min concentration of DOC is different relying on the pH and sorbent even so the final points are in the same level, close to 0 mg/L of DOC.

In addition, with this curves we can see the lowest concentration of our unwanted pollute that every experiment can approach.

## 5. Conclusions

Different methods were studied to determinate the low cost and effective sorbent. The glass column experiment showed that the adsorption is totally dependent on the pH and initial condition. A low pH makes the biomaterial surface more positive. The more positive the surface charge of the biomaterial, the faster the rate of Cr (VI) removal from the aqueous phase. <sup>[19]</sup>

Moreover the batch experiments show that grape waste as better sorbent than brewers draff, the maximum capacity of adsorption is higher.

As a conclusion, brewers draff was found to be an effective sorbent for removal hexavalent chromium from contaminated water. Although grape waste showed better results and proprieties, brewers draff was is more economical and abundant in Czech Republic because of the highest production of beer so its by-product.

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