

# Batch Adsorption of Cr(VI) Ions on Zeolite and Agroindustrial Waste



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Several adsorbents, such as natural zeolite clinoptilolite, modified zeolite, grape and olive wastes have been investigated for removal of chromium (VI) ions from aqueous solutions by performing batch kinetic sorption experiments. Natural zeolite, modified zeolite, grape and olive wastes have removed 5 %, 13 %, 73 % and 62 %, respectively, of Cr(VI) ions from aqueous solution. Equilibrium experimental results were fitted to Langmuir and Freundlich isotherms to obtain the characteristic parameters of each model. According to an evaluation using Langmuir equation, the maximum Cr(VI) adsorption capacity of grape waste was 108.12 mg g<sup>-1</sup> and of olive waste 100.47 mg g<sup>-1</sup> at pH 2. The equilibrium kinetic data were analyzed using pseudo-first-order and pseudo-second-order models, and parameters were estimated by using non-linear regression analysis. Langmuir model and pseudo-second-order model describes better the obtained results than Freundlich model and the pseudo-first-order model. The adsorption of Cr(VI) ions increased with temperature and the negative values of  $\Delta G^\circ$  for investigated adsorbents confirmed the feasibility and spontaneous nature of the adsorption process.

## Keywords:

grape and olive wastes, zeolite, adsorption, hexavalent chromium, kinetic analysis

## Introduction

Pollution by heavy metals has received widespread attention in the recent years, due to its harmful effects on human health as well as fauna and flora of receiving water bodies<sup>1</sup>. The levels of toxic metals in surface waters have been increasing due to pollution caused by industrial wastewater discharges<sup>2</sup>.

Chromium (Cr) is widely used in electroplating, leather tanning, metal finishing, and chromate preparation. Chromium can exist under six oxidation states like most transition metals, but in the Eh-pH (potential-pH diagram) range of natural waters, the only important ones are trivalent Cr(III) and hexavalent Cr(VI). Cr(VI) (chromium trioxide, chromic acid, and bichromate) is the most toxic form, being carcinogenic and mutagenic to living organisms<sup>3-5</sup>. Trivalent Cr(III) (chromium oxide and chromium sulfate) is about 300 times less toxic than Cr(VI), and therefore, has limited hydroxide solu-

bility, it is less mobile, less bioavailable, and a trace amount is essential for healthy growth<sup>3,5</sup>.

Because of its toxicity, Cr(VI) must be largely removed from the wastewater before being discharged into the aquatic system. In the last decades, a lot of studies on chromium adsorption on zeolite<sup>3</sup> and biosorption by various biomaterials, such as bacteria<sup>6</sup>, algae<sup>7</sup>, fungi<sup>8</sup>, industrial wastes, agricultural wastes<sup>1,5,9</sup> and compost<sup>10</sup>, have been undertaken in order to find an alternative to the costly additional effluents treatments, like ion exchange, membrane separation, chemical oxidation and reduction, filtration, electrochemical treatment and adsorption on activated carbons<sup>11</sup>. These high-technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent of energy requirements or generation of toxic sludge or other waste products that require disposal<sup>1,12</sup>.

Natural zeolites are crystalline microporous aluminosilicates with very well-defined structures

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that consist of a framework formed by tetrahedral of  $\text{SiO}_4$  and  $\text{AlO}_4$ . The isomorphous substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral results in a negative charge on the zeolite framework that can be balanced by exchangeable cations. Chromium (VI) in water solution is present as an anion,  $\text{HCrO}_4^-$  or  $\text{CrO}_4^{2-}$ , and natural zeolites need to be engineered to reverse their surface charges to positive in order to enhance Cr(VI) sorbents interactions<sup>3</sup>. Modification of natural zeolite with Fe could enhance chromium removal. Impregnation with Fe(II) increased the carbon surface area, introduced more acidic functional groups.

During production of wine and olive oil, a huge amount of solid waste (fruit skin, pulp, seed fragments) are generated. Throughout history, creative minds have tried to use grape and olive wastes, because disposal of these wastes is a huge environmental problem. Grape and olive wastes have proved to be good adsorbents for the removal of both tri- and hexavalent chromium from water. In addition, some agricultural wastes have the capacity to reduce Cr(VI) to Cr(III), and it has been confirmed that Cr(VI) removal by these biomaterials is due to an “adsorption-coupled reduction” mechanism<sup>11</sup>. The advantages of these materials are: very low or no cost sorbents, great availability, simple operational process, and the fact that through their use as biosorbents, added value is provided to products that otherwise would be considered as a waste<sup>5,13</sup>. Furthermore, these materials can be disposed of without expensive regeneration after adsorption of metals<sup>1</sup>.

The aim of this study was to investigate the adsorption potential of zeolite and agroindustrial wastes, grape and olive wastes, for the removal of Cr(VI) from aqueous solution. During the adsorption of Cr(VI) on grape waste, the reduction of Cr(VI) ions to Cr(III) ions was investigated, and speciation of chromium at different pH was evaluated in MINTEQA (computer program for geochemical equilibrium speciation model for dilute aqueous systems). Langmuir and Freundlich adsorption isotherm models and pseudo-first-order and pseudo-second-order models were used to evaluate the obtained experimental data, and the parameters ( $K_L$ ,  $q_{\text{max}}$ ,  $K_F$ ,  $q_{\text{e,calc}}$ ,  $k_p$ ,  $k_s$ ) were estimated using non-linear regression.

## Material and methods

### Materials

The standard solution used in this study was potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) from Merck (USA). The Fe(II) used for zeolite modification was  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  from Merck (USA). The inorganic

Table 1 – Physical characteristics of adsorbents

	Zeolite	Modified zeolite	Grape waste	Olive waste
pH value	6.70	6.45	5.53	6.80
Moisture/%	2.89	2.89	60.00	65.00
Particle size/mm	1–2	1–2	0.2–0.5	0.2–0.5

material used in the experiments was natural zeolite clinoptilolite from the Krapina region, Croatia. Zeolite was washed with demineralized water to remove the particles adhered to its surface and dried at 105 °C for two hours. The dried zeolite was crushed with laboratory jaw crusher (Matest, AO092 TE, Italy) and granulometric analysis was conducted on rotary sieve shaker (Sieve-Shaker Model RA-86-1, WS Tyler, USA). The agroindustrial materials used in the experiments were grape waste and olive waste. Grape waste was generated in the course of wine production of the hills of Pleševica in the western part of Croatia. The waste pomace from the olive oil mill is an oil cake produced by continuous olive oil extraction using two-phase system. The oil cake or pomace was obtained from a local olive oil manufacturer (Agrolaguna Poreč, Croatia). Grape waste and olive waste contained husks and barks. Physical characteristics of selected adsorbents are presented in Table 1.

### Modification of natural zeolite

In a 100-cm<sup>3</sup> Erlenmeyer flask, 10 g of natural zeolite and 30 cm<sup>3</sup> of 20 mmol dm<sup>-3</sup> Fe(II) solution were combined. The mixture was shaken at room temperature for 24 h at 150 rpm, allowed to settle, and the supernatant was removed, followed by washing the zeolite with a few portions of deionized water, and then drying at 105 °C for two hours.

### Adsorption of Cr(VI) ions on natural zeolite, modified zeolite, grape and olive waste

Adsorption experiments were carried out by adding 0.5 g of different adsorbents, natural zeolite, modified zeolite, grape and olive wastes into 100-cm<sup>3</sup> Erlenmeyer flasks containing 50 cm<sup>3</sup> of 1 mg dm<sup>-3</sup> of dichromate solutions at pH value 4,  $T = 20$  °C, and 150 rpm for four hours. The concentrations of chromium (VI) ions in aqueous solution were determined spectrophotometrically at  $\lambda = 540$  nm, using 1,5-diphenylcarbazide method<sup>14</sup>. The method is based on the reaction of 1,5-diphenylcarbazide and Cr(VI), which forms a red-violet colored complex. The total Cr concentration was also determined spectrophotometrically<sup>14</sup>. The concentration of Cr(III) was calculated from the difference be-

tween the total Cr and the Cr(VI) concentration. The pH-value was adjusted by adding a few drops of 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

### Batch adsorption experiments of Cr(VI) on grape and olive waste

Adsorption experiments were carried out by adding 0.05 g of grape and olive waste into 200-cm<sup>3</sup> Erlenmeyer flasks containing 100 cm<sup>3</sup> of different initial concentrations (20 – 120 mg dm<sup>-3</sup>) of dichromate solutions at pH value 2 and at  $T = 20$  °C. All flasks were shaken at 150 rpm for four hours. The concentrations of Cr(VI) were detected spectrophotometrically<sup>14</sup>. The amount of Cr(VI) ion adsorbed  $q_e$  (mg g<sup>-1</sup>) was determined using the following Eq. (1):

$$q_e = \frac{(\gamma_0 - \gamma_e) \cdot V}{m} \quad (1)$$

where  $\gamma_0$  and  $\gamma_e$  represent the initial and equilibrium concentration of Cr(VI) ion (mg dm<sup>-3</sup>),  $V$  is the sample volume (dm<sup>3</sup>), and  $m$  is the mass of dry adsorbent (g). The Cr(VI) removal percentage can be calculated as follows, Eq. (2):

$$\% \text{ removal} = \frac{\gamma_0 - \gamma_e}{\gamma_0} \cdot 100 \quad (2)$$

### Batch kinetics studies

Kinetic experiments were identical to those of equilibrium tests. The aqueous samples were taken at present time intervals, and the concentrations of Cr(VI) ions were determined spectrophotometrically<sup>14</sup>. The amount of Cr(VI) ion adsorbed at time  $t$ ,  $q_t$  (mg g<sup>-1</sup>), was calculated by expression, Eq. (3):

$$q_t = \frac{(\gamma_0 - \gamma_t) \cdot V}{m} \quad (3)$$

where  $\gamma_t$  (mg dm<sup>-3</sup>) is the liquid phase concentrations of Cr(VI) ions at different times.

### Effect of pH value on chromium adsorption and speciation

The effect of pH solution (pH = 2 – 9) on sorption of Cr(VI) ions on grape and olive waste was determined by agitating 0.5 g of different adsorbents and 100 cm<sup>3</sup> of dichromate solution ( $\gamma_0 = 10$  mg dm<sup>-3</sup>). Agitation was provided for 4-h contact time, which was sufficient to reach equilibrium with a constant agitation speed of 150 rpm and at  $T = 20$  °C. The pH value was adjusted by adding a few drops of 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 1 mol dm<sup>-3</sup> NaOH.

Speciation of Cr was done in working pH and concentration using the software of MINTEQ 3.0. MINTEQ is a chemical equilibrium modeling sys-

tem for water chemistry calculations, chemical speciation, titration curves, pH calculations, ion adsorption, etc. The initial chromium concentration was set at 60 mg dm<sup>-3</sup>.

### Effect of adsorbent dosage

The effect of adsorbent mass ( $m = 0.05, 0.1,$  and 0.5 g) on sorption of Cr(VI) ions on grape and olive waste was determined by agitating different masses of adsorbents and 100 cm<sup>3</sup> of dichromate solution ( $\gamma_0 = 100$  mg dm<sup>-3</sup>) at pH value 2,  $T = 20$  °C, and 150 rpm.

### Effect of temperature

The effect of temperature ( $T = 20, 30,$  and 50 °C) on sorption of Cr(VI) ions on grape and olive wastes was determined by agitating 0.05 g of different adsorbents and 100 cm<sup>3</sup> of dichromate solution ( $\gamma_0 = 50$  mg dm<sup>-3</sup>) at pH value 2 and 150 rpm.

## Results and discussion

### Adsorption of Cr(VI) ions on natural zeolite, modified zeolite, grape and olive waste

The removal of Cr(VI) from aqueous solution using different sorbents is presented in Fig. 1. It may be seen that the natural zeolite and modified zeolite removed less than 15 % of Cr(VI), while grape and olive wastes removed about 70 % percent of Cr(VI) ions during 30 minutes. After three hours, the modified zeolite removed 50 % of Cr(VI) ions from aqueous solutions, which indicated that the rate of adsorption of Cr(VI) ions on natural and modified zeolite was slower than on agricultural waste. Natural zeolite had not efficiently removed Cr(VI) ions above the concentrations of 5 mg dm<sup>-3</sup>, while modified zeolite removed 75 % of Cr(VI) ions at initial concentration of 10 mg dm<sup>-3</sup> during 180 min. The framework structure of natural zeolite contains interconnected voids that are filled with cations that can be exchanged with other cations. Due to the negative charges of Cr(VI) oxyanions, the natural zeolite cannot efficiently remove Cr(VI) from aqueous solution, because it has no affinity to anions<sup>15,16</sup>. Agroindustrial wastes removed all Cr(VI) ions during 180 minutes, because agroindustrial waste contains carbohydrate polymers, cellulose, and hemicelluloses bound to the lignin in lignocellulosic residues by hydrogen bond and covalent bonds, and metal binding takes place mainly through chemical functional groups such as carboxyl and hydroxyl<sup>5</sup>.

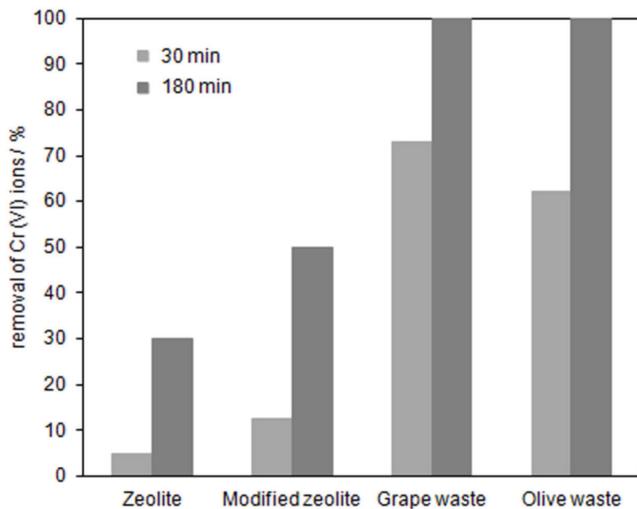


Fig. 1 – Percentage of removal of Cr(VI) ions by natural zeolite, modified zeolite, grape and olive wastes ( $\gamma_0 = 1 \text{ mg dm}^{-3}$ ,  $V_0 = 50 \text{ cm}^3$ ,  $m = 0.5 \text{ g}$ ,  $\text{pH} = 4$  and  $T = 20 \text{ }^\circ\text{C}$ )

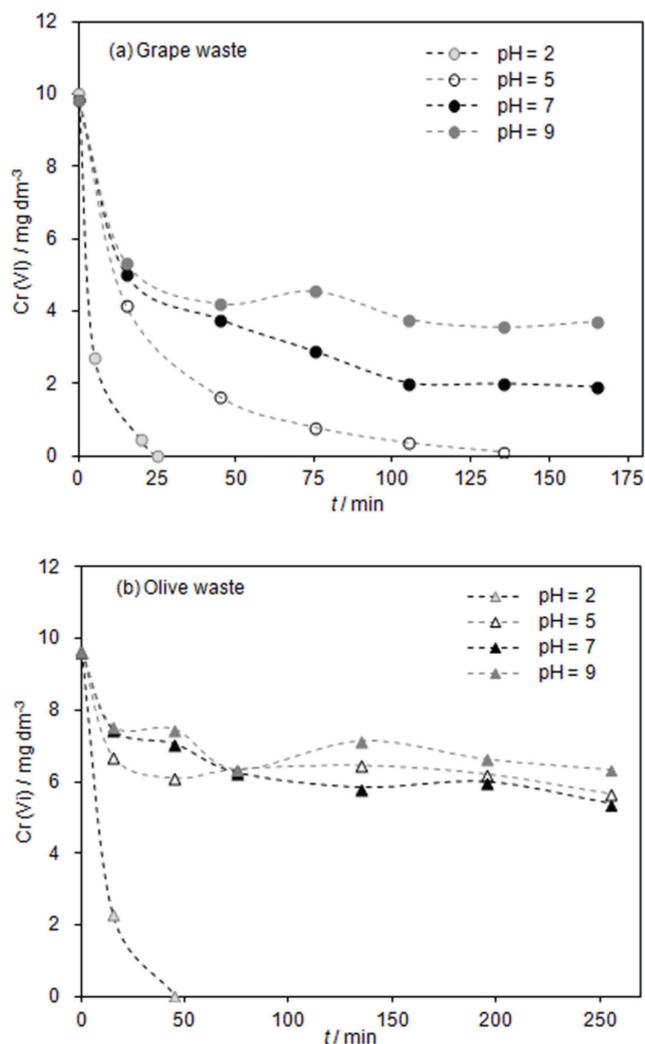
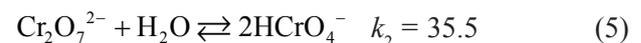


Fig. 2 – Effect of pH value on the adsorption of Cr(VI) on grape waste (a) and olive waste (b) ( $\gamma_0 = 10 \text{ mg dm}^{-3}$ ,  $V_0 = 100 \text{ cm}^3$ ,  $m = 0.5 \text{ g}$  and  $T = 20 \text{ }^\circ\text{C}$ )

### Effect of pH value on chromium adsorption and speciation

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process, and thus, the role of hydrogen ion concentration was examined from solutions at different pH from 2 to 9. The pH of the aqueous solution influences Cr speciation and the dissociation of active functional groups ( $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$ ).

The maximum uptake levels of Cr(VI) were observed at pH 2.0. As shown in Fig. 2(a) and (b), the uptake of Cr(VI) increased with a decrease in the solution pH. At lower pH, the surface of grape and olive waste was positively charged, and electrostatic force of attraction occurred with  $\text{HCrO}_4^-$ , i.e. the functional groups (amino and carboxyl) in the surface of the grape and olive waste were protonated and restricted the approach of cationic species as the result of repulsive forces<sup>5,17</sup>. However, at higher pH values, the surface of grape and olive waste was negatively charged resulting in a repulsive force between grape and olive waste and  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , i.e. the degree of protonation decreased, and the functional groups became negatively charged ( $\text{pH} > \text{pK}_a$ )<sup>5,17,18</sup>. Aqueous Cr(VI) exists as five main species:  $\text{H}_2\text{CrO}_4$ ;  $\text{HCrO}_4^-$ ;  $\text{CrO}_4^{2-}$ ;  $\text{HCr}_2\text{O}_7^{2-}$ ;  $\text{Cr}_2\text{O}_7^{2-}$  (Fig. 3), the distribution of which depends on pH and total Cr concentration<sup>5</sup>. At solution pH values between 2 and 6, Cr(VI) ions are probably in solutions as  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  species, at lower pH ( $\text{pH} < 2$ ) the principal species are  $\text{Cr}_4\text{O}_{13}^{2-}$  and  $\text{Cr}_3\text{O}_{10}^{2-}$ <sup>5</sup>. The following equilibrium may be written for the Cr(VI) anions present in aqueous solution<sup>5,19</sup>,  $k$  – constant of dissociation:



When comparing the results presented in both figures, emphasis must be made to the faster kinetics of Cr(VI) sorption on grape waste compared to that of Cr(VI) sorption on olive waste, especially at pH 2. Further, at pH 5, grape waste removed all Cr(VI) ions, while olive waste did not. At pH values higher than 6, there is no significant adsorption of Cr(VI) due to competition of the anions  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{OH}^-$  for the adsorption sites (Fig. 3)<sup>5</sup>, Equations 4–6. Aqueous phase pH governs the speciation of metals as well as the dissociation of active functional sites on the sorbent<sup>4</sup>. Grape and olive wastes are lignocellulosic materials, but there are many different types of lignin in different types of lignocellulosic materials<sup>5</sup>. Based on the results<sup>9</sup> obtained by FTIR-ATR analysis, the oxygenated functions of lignin structure (guaiacyl, syringyl) were

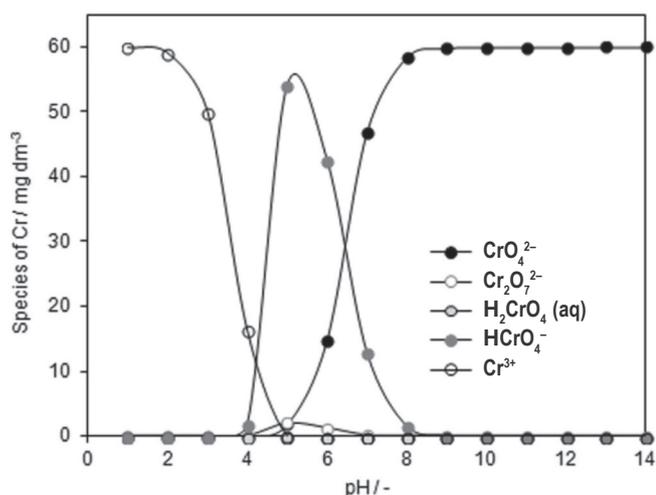
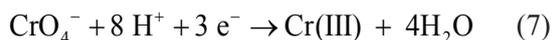


Fig. 3 – Concentration of Cr species depends on pH ( $\gamma_0 = 60 \text{ mg dm}^{-3}$ ) using MINTEQ software

involved in the protonation and the adsorption of Cr(VI) on grape waste. FTIR analysis given by Malkoc *et al.*<sup>1</sup> indicated that –OH groups and/or –NH stretching and carboxyl groups had played a major role in Cr(VI) sorption on olive waste.

Many earlier studies have claimed that Cr(VI) was removed from the aqueous phase through an adsorption mechanism, whereby anionic Cr(VI) ion species bind to positively charged groups of biomaterials<sup>1,4</sup>. Nowadays, the “adsorption-coupled reduction” reaction is widely accepted as the true mechanism of Cr(VI) adsorption by natural biomaterials under acidic conditions due to its high redox potential value (above +1.3 V at standard condition)<sup>1,4,5,17,18</sup>. From Fig. 4, it may be seen that, as the concentration of Cr(VI) ions decreased, the concentration of Cr(III) ion, which was not initially present, was found to increase. These results suggest that Cr(VI) ions had adsorbed on the adsorbent in the form of anionic species  $\text{HCrO}_4^-$  by the esterification reaction (Fig. 3) and then reduced to Cr(III) through electron donation from the electronic rich polyphenolic aromatic ring according to the following reaction:



It is important to point out that protons and electrons (supplied by the electron-donor groups in the biomaterial) are required for the reduction of Cr(VI) to Cr(III). Cr(VI) remains bound to the biomaterial surface if there is a small number of electron-donor groups in the biomaterial or protons in the aqueous phase. Thiol, phenolic and carboxylic functional groups have been reported as electron-donor groups in biomaterials<sup>5,20</sup>. At pH values from 2 to 4, the chromium is in the form of trivalent chromium, Figs. 3 and 5, Eqs. (8) and (9)<sup>5</sup>:

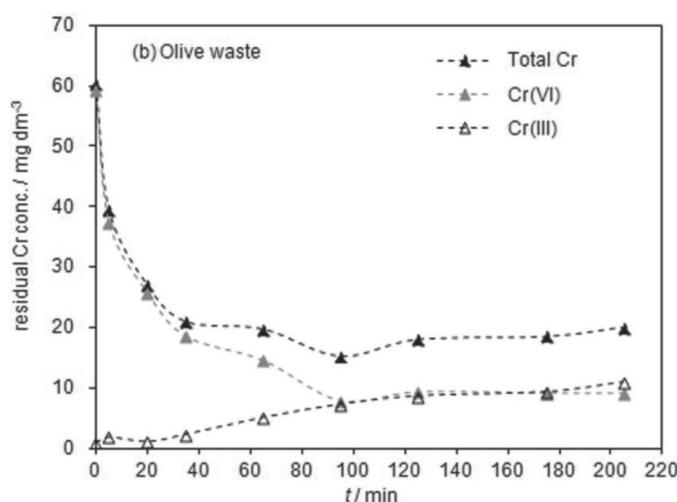
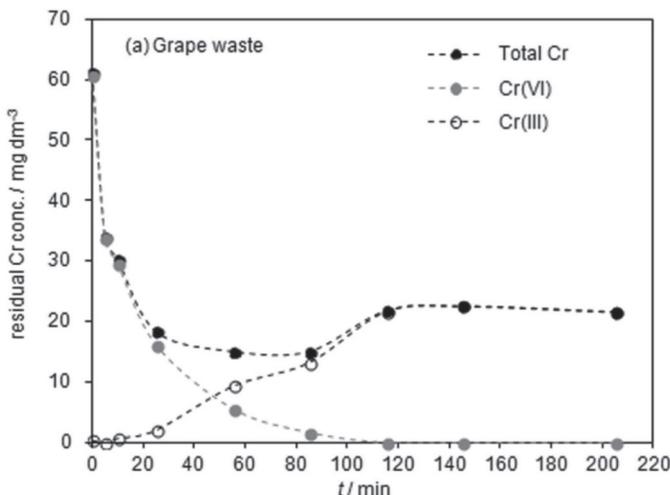
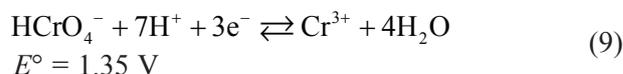
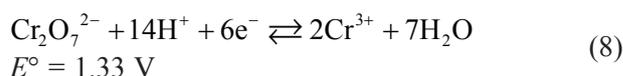


Fig. 4 – Concentration of total chromium, hexavalent and trivalent chromium in solution as a function of time after contact with grape waste (a) and olive waste (b) ( $\gamma_0 = 60 \text{ mg dm}^{-3}$ ,  $V_0 = 100 \text{ cm}^3$ ,  $m = 0.5 \text{ g}$ ,  $\text{pH} = 2$  and  $T = 20 \text{ }^\circ\text{C}$ )



From Fig. 4a, it may be seen that, in equilibrium stage at pH 2, the Cr(VI) ions were completely removed, one part was adsorbed on grape waste, and the other was reduced to trivalent chromium, while at pH 5 the concentration of Cr(III) was in trace, which was also reported by Chand *et al.*<sup>21</sup> Values obtained in program MINTEQ were higher, because in this program, the concentrations of chromium species were determined in pure aquatic solution without an adsorbent, Fig. 5. At pH 2, the concentration of Cr(III) obtained in MINTEQ was  $40 \text{ mg dm}^{-3}$  higher than that obtained in the experiment, because in the experiment a part ( $40 \text{ mg dm}^{-3}$ ) of Cr(VI) was adsorbed on grape waste.

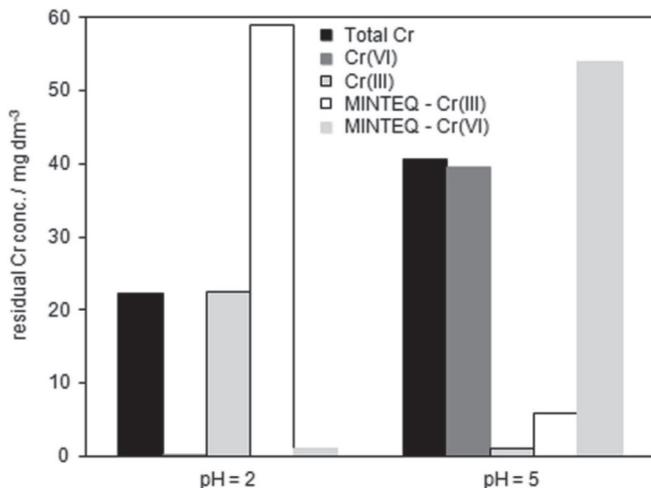


Fig. 5 – Concentration of chromium species at different pH values determined in experiment and modeled in MINTEQ software ( $\gamma_0$  (Cr(VI)) = 60 mg dm<sup>-3</sup>,  $V_0$  = 100 cm<sup>3</sup>,  $m$  (grape waste) = 0.5 g and  $T$  = 20 °C)

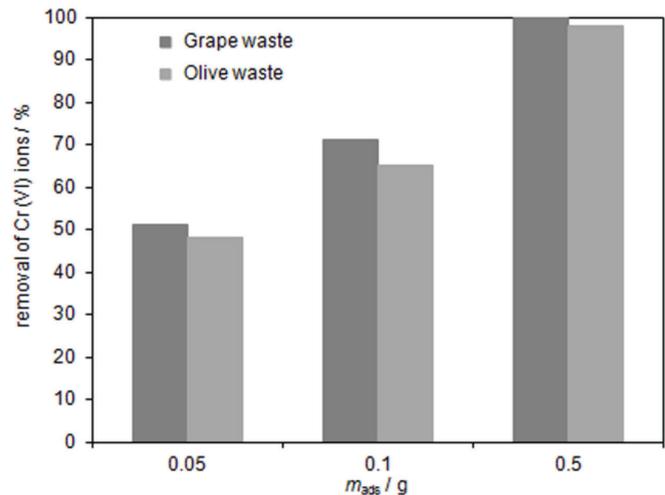


Fig. 6 – Effect of adsorbent concentration on removal of Cr(VI) by grape and olive waste during 240 min ( $\gamma_0$  = 100 mg dm<sup>-3</sup>,  $V_0$  = 100 cm<sup>3</sup>, pH = 2 and  $T$  = 20 °C)

### Effect of adsorbent dosage

The effect of grape and olive waste dosage on adsorption of chromium (VI) is presented in Fig. 6. The results show that the percentage of removal of Cr(VI) increases rapidly with increase in the dose of grape and olive waste, due to the greater availability of the adsorbent<sup>4,22</sup>. The uptake of Cr(VI) showed a reverse trend in the removal percentage adsorptions. With increasing adsorbent dosage from 0.05 to 0.5 g, the adsorption of Cr(VI) ion per unit weight of adsorbent decreased for grape and olive waste from 98 to 19 % and from 95 to 18 %, respectively. Such behavior was obvious, because with an increase in adsorbent dosage, the number of active sites available in the adsorbent for the removal Cr(VI) ions will be high, and low for lower adsorbent dosages, due to the progressive saturation of active sites. Similar results have been reported in other literatures<sup>4,17</sup> for the biosorption of Cr(VI) using tea factory waste and *Caryota urens*.

Fig. 7 shows the influence of adsorbent dosage on adsorption of Cr(VI) ions and on reduction of Cr(VI) to Cr(III). It is evident that, as the mass of adsorbent increases, the concentration of Cr(VI) ions and Cr(III) ions in solution decreases. The concentration of Cr(III) ions decreases because as the mass of adsorbent increases the adsorption of Cr(VI) ions are faster and less Cr(VI) ions are reduced to Cr(III).

### Adsorption isotherms

Adsorption isotherms describe how pollutants interact with adsorbent materials, and so they are critical to optimize the use of adsorbents. In order to optimize the design of an adsorption system for

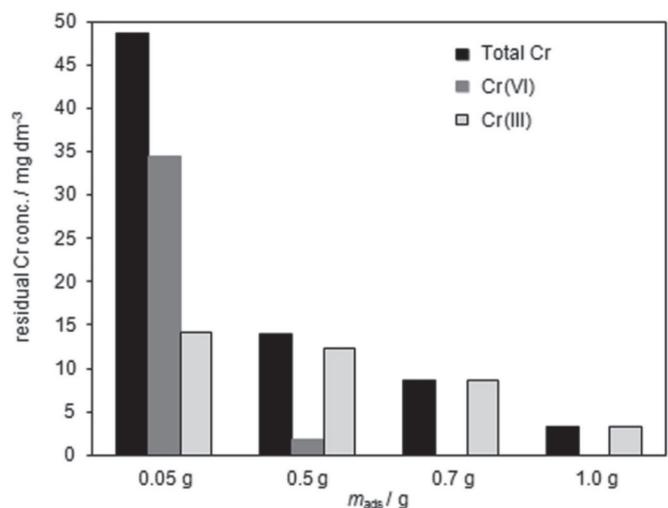


Fig. 7 – Influence of adsorbent concentration on concentration of Cr(VI) ions and Cr(III) ions in aqueous solution ( $\gamma_0$  = 60 mg dm<sup>-3</sup>,  $V_0$  = 100 cm<sup>3</sup>, pH = 2 and  $T$  = 20 °C)

removal of Cr(VI) ions from aqueous solutions, it is important to establish the most appropriate correlation for equilibrium curve (Fig. 8). From Fig. 8, it may be seen that Cr(VI) adsorption capacity of grape and olive waste increased with increase of initial chromium concentration in aqueous solutions, indicating that plenty of readily accessible sites are available at the start of adsorption. After equilibration, when the adsorbent becomes saturated, a plateau is reached, indicating that no more sites are available for further adsorption.

Several isotherm equations have been used for the equilibrium modeling of adsorption system. The Langmuir isotherm is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on adsor-

bate surface, the energy of adsorption is constant, and there is no migration of adsorbate molecules in the surface plane<sup>23</sup>. Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance<sup>24</sup>. The Langmuir isotherm model is defined by Eq. (10):

$$q_e = \frac{q_{\max} \cdot K_L}{(1 + K_L \cdot \gamma_e)} \quad (10)$$

where  $q_e$  is equilibrium concentration of chromium (VI) on the adsorbent ( $\text{mg g}^{-1}$ ),  $\gamma_e$  is the equilibrium concentration of Cr(VI) in the solution ( $\text{mg dm}^{-3}$ ),  $q_{\max}$  is the maximum monolayer adsorption capacity of the adsorbent for Cr(VI) ( $\text{mg g}^{-1}$ ), and  $K_L$  is the Langmuir adsorption constant relating to the free energy of adsorption ( $\text{dm}^3 \text{mg}^{-1}$ ). Table 2 presents the values of Langmuir constants, which were estimated by non-linear regression analysis using Least Squares method implemented in Scientist software. Based on other literature, it may be seen that grape and olive waste have higher adsorption capacity for Cr(VI) ions than other sorbents like modified zeolite<sup>15,16</sup>, compost<sup>10</sup>, biomass<sup>25,26</sup>, gelatin biosorbent<sup>27</sup>. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor  $R_L$  that is given by:

$$R_L = \frac{1}{(1 + K_L \cdot \gamma_0)} \quad (11)$$

where  $\gamma_0$  ( $\text{mg dm}^{-3}$ ) is the highest initial concentration of adsorbate, and  $R_L$  values between 0 and 1 imply favorable adsorption<sup>23</sup>. The values of  $R_L$  for grape and olive waste in this study have been found to be 0.1798 and 0.0927, respectively, indicating that adsorption of Cr(VI) ions on grape and olive waste is favorable.

Freundlich isotherm describes non-ideal and reversible adsorption, not restricted to formation of monolayer<sup>23</sup>. The Freundlich equation is an empirical relationship whereby it is assumed that the adsorption energy of a metal binding to a site of an adsorbent depends on whether or not the adjacent sites are already occupied<sup>25</sup>. The form of Freundlich model is:

$$q_e = K_f \cdot \gamma_e^{1/n} \quad (12)$$

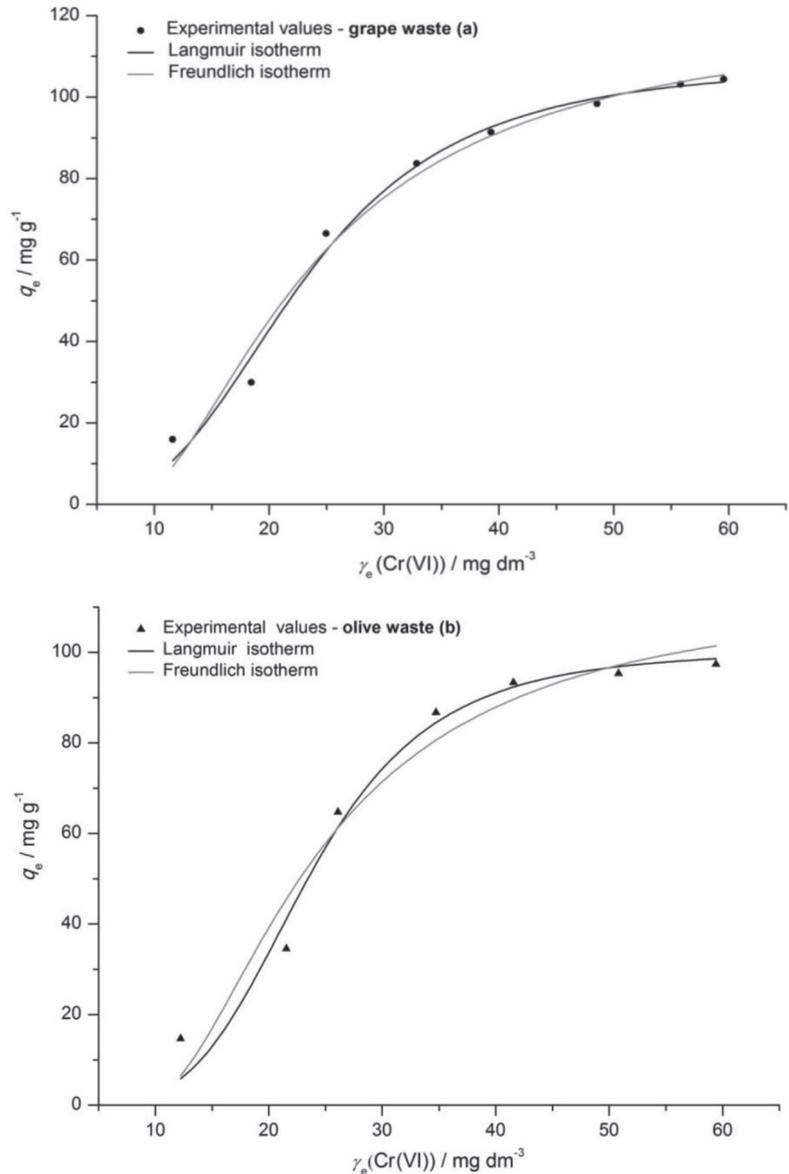


Fig. 8 – Adsorption isotherms of Cr(VI) adsorption on grape waste (a) and olive waste (b) ( $m = 0.05 \text{ g}$ ,  $V_0 = 100 \text{ cm}^3$ ,  $\text{pH} = 2$  and  $T = 20 \text{ }^\circ\text{C}$ )

where  $K_f$  is the Freundlich adsorption capacity constant and whose units vary with  $1/n$ , and  $1/n$  (dimensionless) represents the adsorption intensity of surface heterogeneity and ranges between 0 and 1, becoming more heterogeneous as its value comes closer to zero. Whereas, a value below unit implies chemisorptions process, where  $1/n$  above one is an indication of cooperative adsorption<sup>23</sup>. The Freundlich isotherm parameters were estimated by non-linear regression analysis using Least Squares method implemented in Scientist software.

Based on regression coefficient, it may be seen that Langmuir model better describes experimental values than Freundlich model, suggesting that the surface of the sorbent is homogeneous. The maximum adsorption capacity of grape and olive waste was the same.

Table 2 – Parameters and correlation coefficient ( $R^2$ ) of equilibrium isotherm models for the adsorption of Cr(VI) on grape and olive waste

Isotherm	Adsorbent		
	Parameters	Grape waste	Olive waste
Langmuir	$K_L/\text{dm}^3 \text{ mg}^{-1}$	0.0380	0.0816
	$q_{\text{max}}/\text{mg g}^{-1}$	108.12	100.47
	$R^2$	0.9847	0.9676
Freundlich	$K_F$	23.23	43.033
	$n$	2.70	4.95
	$R^2$	0.9743	0.9386

### Kinetic modeling of Cr(VI) adsorption on grape and olive waste

Cr(VI) removal as a function of initial metal ion concentration and contact time is given in Fig. 9(a) and (b). The initial Cr(VI) ion concentration was varied from 20 to 120 mg dm<sup>-3</sup>, while time was varied from 90 to 300 min. The maximum Cr(VI) removal was attained within 2 hours, after which further removal was negligible possibly due to the quick exhaustion of adsorption sites thereafter. These results are consistent with the results reported in the sorption of Cr(VI) using sunflower waste biomass and carbonaceous adsorbents prepared from waste biomass<sup>25,28,29</sup>. Further, it may be observed that the Cr(VI) removal rate was high in the first 30 minutes, and with time, it gradually slowed down. The initial rapid phase may involve adsorption or ion exchange at the cell surface. In contrast, the

subsequent slower phase may involve other mechanisms, such as complexation, saturation of binding sites leading to intraparticle diffusion, or other slow chemical reactions<sup>18,23,27</sup>. A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases, thus increases the uptake<sup>4,23,30,31</sup>.

In order to predict the mechanism involved in the present sorption process and potential rate controlling such as chemical reaction processes, two kinetics models were used to fit the experimental data, pseudo-first-order and pseudo-second-order (Fig. 9). The parameters were estimated by non-linear regression analysis using Least Squares method implemented in Scientist software. The pseudo-first-order model is one of the most widely used rate equations to describe the adsorption of an adsorbate from given liquid phase, Eq. (13):

$$\frac{dq_t}{dt} = k_f \cdot (q_e - q_t) \quad (13)$$

where  $q_t$  and  $q_e$  (mg g<sup>-1</sup>) are amount of Cr(VI) adsorbed at time  $t$  and equilibrium, and  $k_f$  is pseudo-first-order rate constant (min<sup>-1</sup>). The pseudo-second-order model is based on the assumption that the rate-limiting step may be a chemical sorption involving forces through the sharing or exchange of electrons between adsorbents and adsorbate<sup>23</sup>, Eq. (14):

$$\frac{dq_t}{dt} = k_s \cdot (q_e - q_t)^2 \quad (14)$$

where  $k_s$  is pseudo-second-order rate constant (g mg<sup>-1</sup> min<sup>-1</sup>). The best-fit model was selected

Table 3 – Characteristic parameters of the different kinetic models estimated by non-linear regression for Cr(VI) adsorption on grape waste (a) and olive waste (b)

(a) Grape waste		Pseudo-first model			Pseudo-second model		
$\gamma_0/\text{mg dm}^{-3}$	$q_e/\text{mg g}^{-1}$	$q_{e,\text{calc}}/\text{mg g}^{-1}$	$k_f/\text{min}^{-1}$	$R^2/-$	$q_{e,\text{calc}}/\text{mg g}^{-1}$	$k_s/\text{g mg}^{-1} \text{ min}^{-1}$	$R^2/-$
20	15.9	15.2	0.079	0.977	15.6	0.43	0.982
40	29.9	29.1	0.052	0.989	27.7	0.37	0.963
60	66.5	61.5	0.031	0.951	62.9	0.24	0.976
80	83.6	76.7	0.027	0.892	81.0	0.19	0.971
100	98.3	98.1	0.024	0.993	98.2	0.12	0.999
120	104.3	103.3	0.022	0.977	104.5	0.11	0.997
(b) Olive waste		Pseudo-first model			Pseudo-second model		
$\gamma_0/\text{mg dm}^{-3}$	$q_e/\text{mg g}^{-1}$	$q_{e,\text{calc}}/\text{mg g}^{-1}$	$k_f/\text{min}^{-1}$	$R^2/-$	$q_{e,\text{calc}}/\text{mg g}^{-1}$	$k_s/\text{g mg}^{-1} \text{ min}^{-1}$	$R^2/-$
20	14.7	14.5	0.075	0.968	14.6	0.44	0.983
40	34.6	33.9	0.071	0.984	33.9	0.34	0.983
60	64.7	61.5	0.029	0.961	63.9	0.24	0.989
80	86.7	82.9	0.035	0.973	87.6	0.07	0.986
100	95.3	95.3	0.019	0.987	96.4	0.06	0.978
120	99.9	97.3	0.018	0.978	100.5	0.06	0.991

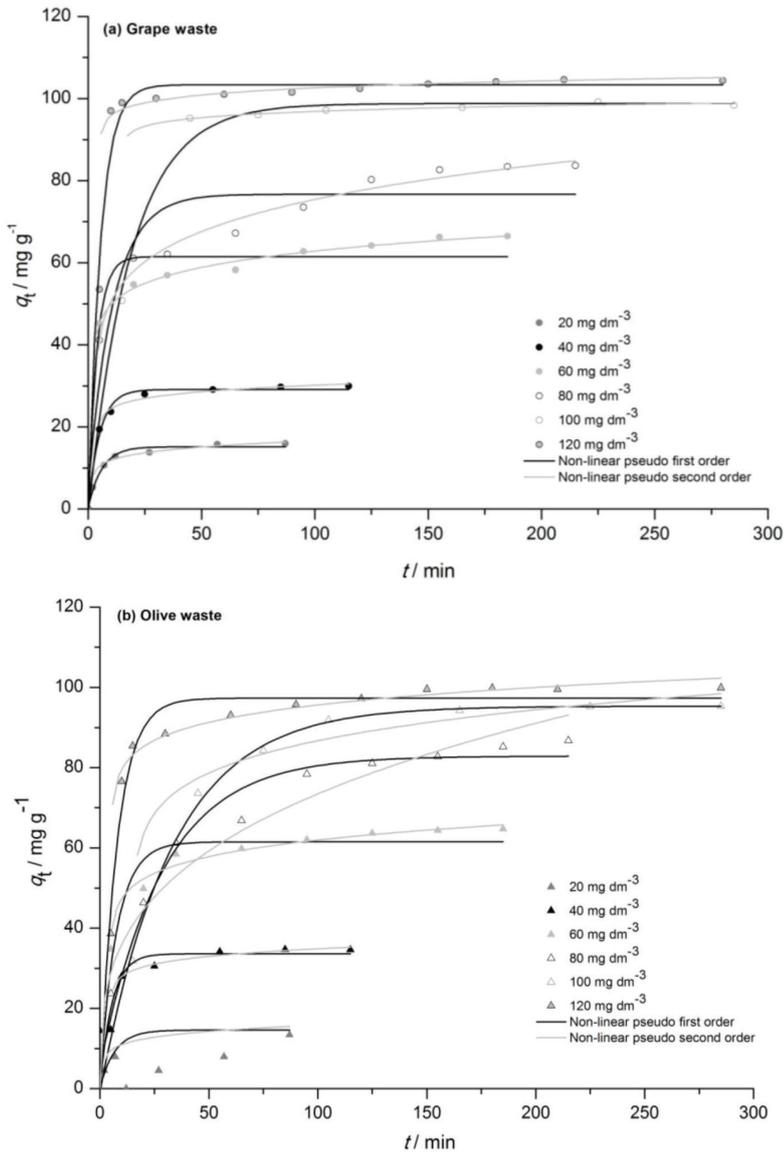


Fig. 9 – Experimental data and fitted non-linear forms of pseudo-first-order and pseudo-second-order equations for the adsorption of Cr(VI) on grape waste (a) and olive waste (b) ( $m = 0.05$  g,  $V_0 = 100$   $\text{cm}^3$ ,  $\text{pH} = 2$  and  $T = 20$  °C)

based on regression coefficient ( $R^2$ ). From Table 3 and Fig. 9, it may be seen that the pseudo-second-order kinetics model better described the experimental values than pseudo-first-order, but in both cases the regression coefficient is above 0.95, indicating that these two models can be applied for the entire concentration range of adsorption process. The good agreement between obtained experimental results with pseudo-first-order and pseudo-second-order, and Langmuir and Freundlich models, suggest that adsorption of Cr(VI) on grape and olive waste is a complex process, involving more than one mechanism<sup>18</sup>.

### Thermodynamic studies

Thermodynamic parameters were determined to confirm the adsorption nature of the present

study. The thermodynamic constants, free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated to evaluate the thermodynamic feasibility of the process, and to confirm the nature of the adsorption process<sup>24</sup>. The Gibb's free energy change of the process is related to the  $K_c$  by the following equation, Eq. (15):

$$\Delta G^\circ = -RT \ln K_c \quad (15)$$

where  $T$  is temperature in K,  $R$  the ideal gas constant ( $8.314$   $\text{J mol}^{-1} \text{K}^{-1}$ ), and  $K_c$  is the thermodynamic equilibrium constant, which is defined as, Eq. (16):

$$K_c = \frac{\gamma_0 - \gamma_e}{\gamma_e} \quad (16)$$

where  $\gamma_0$  is initial concentration of ammonium solution,  $\text{mg dm}^{-3}$ , and  $\gamma_e$  is the equilibrium concentration of solution,  $\text{mg dm}^{-3}$ . According to thermodynamics, the Gibb's free energy is also related to the enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) at constant temperature by the Van't Hoff equation, Eq. (17):

$$\ln K_c = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (17)$$

In order to determine the thermodynamic parameters, experiments were carried out at different temperatures in the range of 20–50 °C (Fig. 10). The values of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were calculated from the slope and intercept of the plot  $\ln K_c$  versus  $T^{-1}$ . The calculated values are listed in Table 4.

Fig. 10 shows the influence of temperature (20, 30 and 50 °C) on the adsorption of Cr(VI) ions on grape and olive waste. The amount of Cr(VI) removed from aqueous solution by adsorption on grape and olive waste increased as temperature increased from 20 to 50 °C. The positive values of  $\Delta H^\circ$  for grape and olive waste indicated the endothermic nature of the process. The small values of enthalpy indicates the physical adsorption of Cr(VI) on grape and olive waste<sup>32</sup>. Changes in entropy,  $\Delta S^\circ$ , for grape and olive waste was found to be 10.13 and 7.23  $\text{J mol}^{-1} \text{K}^{-1}$ , respectively, for Cr(VI) removal from aqueous solution. This result implied that Cr(VI) ions on solid phase (surface of adsorbent) were in a much more chaotic distribution compared to the relatively ordered state of bulk phase (aqueous solution)<sup>23</sup>. The negative values of  $\Delta G^\circ$  for investigated adsorbents confirmed the feasibility and spontaneous nature of the adsorption process.

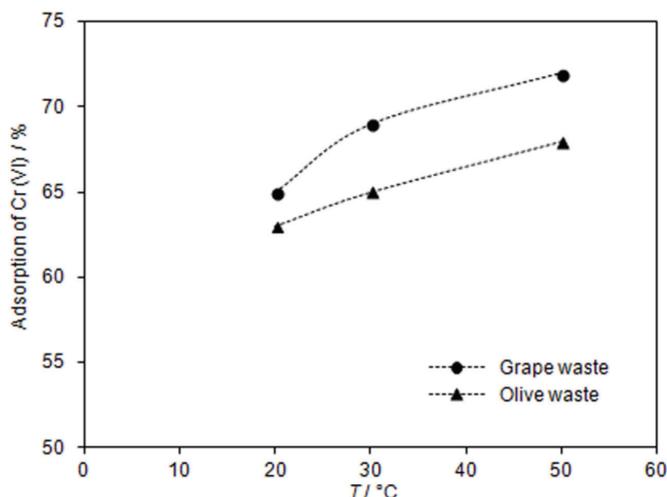


Fig. 10 – Effect of temperature on Cr(VI) adsorption on grape and olive waste ( $\gamma_0 = 50 \text{ mg dm}^{-3}$ ,  $V_0 = 100 \text{ cm}^3$ ,  $\text{pH} = 2$ ,  $m = 0.05 \text{ g}$ ,  $t = 160 \text{ min}$ )

Table 4 – Thermodynamic parameters for the adsorption of Cr(VI) on grape and olive waste

Adsorbent	T/K	$K_c$ /–	$\Delta G$ / kJ mol <sup>-1</sup>	$\Delta H$ / kJ mol <sup>-1</sup>	$\Delta S$ / J mol <sup>-1</sup> K <sup>-1</sup>
Grape waste	293.15	1.94	-1.62		
	303.15	2.33	-2.13	0.092	10.13
	323.15	2.71	-2.68		
Olive waste	293.15	1.86	-1.51	0.043	
	303.15	1.95	-1.68		7.23
	323.15	2.18	-2.09		

## Conclusions

From the obtained experimental results and their evaluation, it may be concluded that grape and olive waste are better adsorbents than natural and modified zeolite for removal Cr(VI) ions from aqueous solution. The equilibrium data were analyzed using Freundlich and Langmuir isotherms. The Langmuir isotherm provided the best fit for the sorption of Cr(VI) on grape and olive waste. The maximum adsorption capacity of Cr(VI) on grape and olive waste was  $108.12 \text{ mg g}^{-1}$  and  $100.47 \text{ mg g}^{-1}$ , respectively, at pH 2. Kinetic studies suggested that pseudo-second-order kinetics model better described the experimental values than pseudo-first-order.

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## References

- Malkoc, E., Nuhoglu, Y., Dundar, M., Adsorption of chromium (VI) on pomace-An olive oil industry waste, *Journal of Hazardous Materials* **B 138** (2006) 142. doi: <https://doi.org/10.1016/j.jhazmat.2006.05.051>
- Leyva-Ramos, R., Jacobo-Azuara, A., Diaz-Flores, P. E., Guerrero-Coronado, R. M., Mendoza-Barron, J., Berber-Mendoza, M. S., Adsorption of chromium (VI) from an aqueous solution on a surfactant-modified zeolite, *Colloids and Surfaces A* **330** (2008) 35. doi: <https://doi.org/10.1016/j.colsurfa.2008.07.025>
- Lu, G., Li, Z., Jiang, W. T., Ackley, C., Fenske, N., Demarco, N., Removal of Cr(VI) from water using Fe(II)-modified natural zeolite, *Chemical Engineering Research and Design* **92** (2014) 384. doi: <https://doi.org/10.1016/j.cherd.2013.08.003>
- Malkoc, E., Nuhoglu, Y., Potential of tea factory waste for chromium (VI) removal from aqueous solutions: Thermodynamic and kinetic studies, *Separation and Purification Technology* **54** (2007) 291. doi: <https://doi.org/10.1016/j.seppur.2006.09.017>
- Miretzky, P., Fernandez Cirelli, A., Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review, *Journal of Hazardous Materials* **180** (2010) 1. doi: <https://doi.org/10.1016/j.jhazmat.2010.04.060>
- Razaei, H., Biosorption of chromium by using *Spirulina* sp., *Arabian Journal of Chemistry* **142** (2013) 1. doi: <https://doi.org/10.1016/j.arabjc.2013.11.008>
- Jayakumar, R., Rajasimman, M., Karthikeyan, C., Sorption of hexavalent chromium from aqueous solution using marine green algae *Halimeda gracilis*: Optimization, equilibrium, kinetic, thermodynamic and desorption studies, *Journal of Environmental Chemical Engineering* **2** (2014) 1261. doi: <https://doi.org/10.1016/j.jece.2014.05.007>
- Shukla, D., Vankar, P. S., Chapter 30 – Role of *Trichoderma* Species in Bioremediation Process: Biosorption Studies on Hexavalent Chromium, *Biotechnology and Biology of Trichoderma* (2014) 405. doi: <https://doi.org/10.1016/B978-0-444-59576-8.00030-8>
- Fiol, N., Escudero, C., Villaescusa, I., Chromium sorption and Cr(VI) reduction to Cr(III) by grape stalks and yohimbe bark, *Bioresource Technology* **99** (2008) 5030. doi: <https://doi.org/10.1016/j.biortech.2007.09.007>
- Vargas, C., Brandão, P. F. B., Ágreda, J., Castillo, E., Bio-adsorption using compost: An alternative for removal of chromium (VI) from aqueous solution, *BioResources* **7** (2012) 2711.
- Poch, J., Villaescusa, I., A model to describe Cr(VI) kinetics biosorption, *Journal of Hazardous Materials* **175** (2010) 770. doi: <https://doi.org/10.1016/j.jhazmat.2009.10.075>
- Aksu, Z., Gönen, F., Demircan, Z., Biosorption of chromium (VI) ions by Mowital B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon, *Process Biochemistry* **38** (2002) 175. doi: [https://doi.org/10.1016/S0032-9592\(02\)00053-5](https://doi.org/10.1016/S0032-9592(02)00053-5)
- Krishnani, K. K., Ayyappan, S., Heavy metals remediation of water using plants and lignocellulosic agrowastes, *Reviews of Environmental Contamination and Toxicology* **188** (2006) 59. doi: [https://doi.org/10.1007/978-0-387-32964-2\\_2](https://doi.org/10.1007/978-0-387-32964-2_2)
- APHA Standard Methods for the examination of Water and Wastewater, 16<sup>th</sup> ed., American Public Health Association, Washington, DC, 1985.

15. Du, G., Li, Z., Liao, L., Hanson, R., Leick, S., Hoepfner, N., Jiang, W.-T., Cr(VI) retention and transport through Fe(III)-coated natural zeolite, *Journal of Hazardous Materials* **221-222**, (2012) 118.  
doi: <https://doi.org/10.1016/j.jhazmat.2012.04.016>
16. Salgado-Gómez, N., Macedo-Miranda, M. G., Olguín, M. T., Chromium (VI) adsorption from sodium chromate and potassium dichromate aqueous system by hexadecyltrimethylammonium-modified zeolite-rich tuff, *Applied Clay Science* **95** (2014) 197.  
doi: <https://doi.org/10.1016/j.clay.2014.04.013>
17. Rangabhashiyam, S., Selvaraju, N., Evaluation of the bio-sorption potential of a novel *Caryota urens* inflorescence waste biomass for the removal of hexavalent chromium from aqueous solution, *Journal of the Taiwan Institute of Chemical Engineers* **47** (2015) 59.  
doi: <https://doi.org/10.1016/j.jtice.2014.09.034>
18. Xie, J., Li, H., Wang, X., Son Ng, I., Lu, Y., Jing, K., Kinetic simulating of Cr(VI) by the waste *Chlorella vulgaris* biomass, *Journal of the Taiwan Institute of Chemical Engineers* **45** (2014) 1773.  
doi: <https://doi.org/10.1016/j.jtice.2014.02.016>
19. Celik, A., Demirbas, A., Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes, *Energy Sources* **27** (2005) 1167.  
doi: <https://doi.org/10.1080/00908310490479583>
20. Elangovan, R., Philip, L., Chandraraj, K., Biosorption of hexavalent and trivalent chromium by palm flower (*Borassus aethiopicum*), *Chemical Engineering Journal* **141** (2008) 99.  
doi: <https://doi.org/10.1016/j.cej.2007.10.026>
21. Chand, R., Narimura, K., Kawakita, H., Ohto, K., Watari, T., Inoue, K., Grape waste as a biosorbent for removing Cr(VI) from aqueous solution, *Journal of Hazardous Materials* **163** (2009) 245.  
doi: <https://doi.org/10.1016/j.jhazmat.2008.06.084>
22. Karthik, R., Meenakshi, S., Removal of hexavalent chromium ions using polyaniline/silica gel composite, *Journal of Water Process Engineering* **1** (2014) 37.  
doi: <https://doi.org/10.1016/j.jwpe.2014.03.001>
23. Kučić, D., Čosić, I., Vuković, M., Briški, F., Sorption kinetic studies of ammonium from aqueous solution on different inorganic and organic media, *Acta Chimica Slovenica* **16** (2013) 109.
24. Finocchio, E., Lodi, A., Solisio, C., Converti, A., Chromium (VI) removal by methylated biomass of *Spirulina platensis*: The effect of methylation process, *Chemical Engineering Journal* **156** (2010) 264.  
doi: <https://doi.org/10.1016/j.cej.2009.10.015>
25. Jain, M., Garg, V. K., Kadirvelu, K., Equilibrium and kinetic studies for sequestration of Cr(VI) from simulated wastewater using sunflower waste biomass, *Journal of Hazardous Materials* **171** (2009) 328.  
doi: <https://doi.org/10.1016/j.jhazmat.2009.06.007>
26. Qu, Y., Zhang, X., Xu, J., Zhang, W., Guo, Y., Removal of hexavalent chromium from wastewater using magnetotactic bacteria, *Separation and Purification Technology* **136** (2014) 10.  
doi: <https://doi.org/10.1016/j.seppur.2014.07.054>
27. Foo, K. Y., Hameed, B. H., Insights into the modeling of adsorption isotherm system, *Chemical Engineering Journal* **156** (2010) 2.  
doi: <https://doi.org/10.1016/j.cej.2009.09.013>
28. Jain, M., Garg, V. K., Kadirvelu, K., Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomass, *Journal of Environmental Management* **91** (2010) 949.  
doi: <https://doi.org/10.1016/j.jenvman.2009.12.002>
29. Mahmoud, M. E., Mohamed, R. H. A., Biosorption and removal of Cr(VI)-Cr(III) from water by eco-friendly gelatin biosorbent, *Journal of Environmental Chemical Engineering* **2** (2014) 715.  
doi: <https://doi.org/10.1016/j.jece.2013.11.011>
30. Chen, C., Evaluation of equilibrium sorption isotherm equations, *The Open Chemical Engineering Journal* **7** (2013) 24.  
doi: <https://doi.org/10.2174/1874123101307010024>
31. Kumara, N. T. R. N., Hamdan, N., Petra, M. I., Tennakoon, K. U., Ekanayake, P., Equilibrium isotherm studies of adsorption of pigments extracted from kuduk-kuduk (*Melastoma malabathricum* L.) pulp onto TiO<sub>2</sub> nanoparticles, *Journal of Chemistry* **2014** (2014) 1.  
doi: <https://doi.org/10.1155/2014/468975>
32. Gomzi, Z., Kemijski reaktori, HINUS, Zagreb, 1998.