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POSSIBLE ZINC DIETARY SUPPLEMENT ONTO RED GRAPE POMACE (*VITIS VINIFERA* L.) SUPPORT

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ABSTRACT. This paper presents a report about the extraction of resveratrol with ethanol (EtOH) from red grape pomace (RGP) *Vitis vinifera* L. (Cluj, Transylvania region, Romania) and obtaining a dietary supplement with zinc on grape pomace support. The concentration of resveratrol (Rv) from the extract was spectrophotometrically determined at 305 nm wavelength, and was found to be 145 mg Rv/L. The material resulting after the extraction of resveratrol was processed to obtain a zinc dietary supplement support. The thermodynamic parameters, including Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of Zn^{2+} biosorption were calculated and the results indicate that the process is endothermic and spontaneous. The Zn^{2+} biosorption kinetics was analysed using pseudo-first- and pseudo-second-order models. The results indicate that biosorption of Zn^{2+} aqueous solution onto grape pomace support is best described by the pseudo-second-order model.

Keywords: *zinc, resveratrol, red grape pomace, food supplement, biosorption, kinetics*

INTRODUCTION

Zinc is an essential trace element for all forms of life. This metal plays important roles in growth and development, has an immune function, and is essential for neurotransmission, vision, reproduction, or intestinal ion transport. Many proteins in humans have functional zinc-binding sites, over 50 enzymes depend on the vital chemical reactions catalysed by zinc. Zinc may have a regulatory function, modulating the activity of cell-signalling enzymes and transcription factors [1-5].

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Clinical zinc deficiency in humans was first described in 1961, when the consumption of diets with low zinc bioavailability due to high phytate content was associated with adolescent nutritional dwarfism in the Middle East. Zinc insufficiency has been recognized by experts as an important public health issue, especially in low-resource countries [6-14].

The elderly population above the age of 60–65 years shows a higher risk of developing nutritional disorders caused by the ageing process, and zinc deficiency is an important factor in the origin of certain common diseases that affect and cause morbidity among this age group [15].

Zinc deficiency in humans is quite prevalent, affecting over two billion people [16]. Nutritional zinc deficiency is widespread throughout developing countries.

Therefore, the production of food supplements based on zinc is a field of interest in recent years.

Zinc supplements including zinc acetate, zinc gluconate, zinc picolinate, and zinc sulphate are commercially available. The recommended dietary allowance for adult men and women is 11 mg/day and 8 mg/day of zinc, respectively. Long-term consumption of zinc in excess of the tolerable upper intake level (UL, 40 mg/day for adults). Zinc bioavailability is relatively high in meat, eggs, and seafood; zinc is less bioavailable from whole grains and legumes, due to their high content in phytate that inhibits zinc absorption [17-23].

Grape pomace is a waste which, due to the significant quantities of wine produced throughout the world, pollutes the environment.

Discharging grape pomaces were shown to have a negative impact on flora and fauna due to their high pollution load [24]. Using grape pomace as fertilizer inhibits seeds germination, and the presence of lignin prevents the waste to be used as animal feed, reducing digestibility [25].

The red grape pomace (RGP) is a form of biomass that together with other organic residues from wine production can be used to obtain food supplements or to obtain bioethanol. It is composed of: bark, stems, seeds and moisture, but also of other components, among the main constituents would be organic acids and polyphenols, unsaturated lipids and sterols, vitamins and antioxidants, mineral elements (potassium, calcium, magnesium, iron, etc.), which gives it the quality of a functional ingredient.

Resveratrol (3,5,4'-trihydroxystilbene) and piceid (3,5,4'-trihydroxystilbene-3-β-D-glucoside) are two of the major stilbene phytoalexins which remain in significant quantities in grape pomace, after wine production. Therefore, their extraction from the RGP is an essential step for obtaining products with high antioxidant properties, before using the biomass as a support for zinc biosorption.

Consulting the literature it was found that grape pomace contains significant amounts of substances that can be considered beneficial to health [26, 27]. The most abundant in grape pomace are dietary fibres that are present in high levels (up to 85% depending upon the grape variety) and polyphenolic compounds that mainly (about 70%) remain in pomace after the winemaking process [27].

The proximate composition of RGP based on dry weight (quantity g/100 g) is: pH 3.6, ash, 6.8 wt %, humidity 74.3 w/w, residual sugars 1.6 % w/w, cellulose 19.6% w/w, hemicellulose 12.0 % w/w, protein 10.4 % w/w [28].

The aims of this study are to perform the extraction of resveratrol from red grape pomace (RGP) originating from the organic residues resulting from *Vitis vinifera* L. wine production (Cluj, Transylvania region) and, also, to study the Zn^{2+} biosorption onto RGP support in order to obtain a possible dietary supplement.

RESULTS AND DISCUSSION

Characterization of red grape pomace (RGP) biosorbent

The graphs from figure 1 showed different sample appearances before (a) and after (b, c) wine production.

a **(b)** **(c)**

Figure 1. Different grape types - (a). Residual grape pomace biomass, resulting from the wine processing of white grapes - (b) and red grapes (RGP) - (c).

The results of elemental analysis showed the presence of C (59.62%), N (3.1%), O (29.4%), Na (0.7%), Mg (0.1%), P (0.07%), K (0.31), Zn (0.21%) from RGP. The high carbon content of biomass makes RGP a good precursor material for biosorbents. Our results are in good agreement with the literature data [29].

The real density of RGP reflects the ratio of the mass material to its volume, without taking into account pore volume. The real density of RGP was also determined, resulting in an average particle diameter of 1.0-1.6 mm. Particle size was gravimetrically determined [30].

The apparent density of a biosorbent expresses the ratio of the mass of the material to its volume, including the volume of the pores. The apparent density of RGP obtained, with 1.0-1.6 mm, is gravimetrically determined. The porosity of RGP reflects the ratio between the pores volume and the total volume of material. The establishing of RGP specific surface area, with 1.0-1.6 mm, is achieved by using the gravimetric method for the desorption isotherm determination.

The BET equation will be used to calculate the specific surface area of the RGP biomass [13, 14, 17]. The results for physico-chemical characterization of RGP are: S_{BET} 324.3 m^2/g, apparent density 1.234 g/cm^3, real density 0.892 g/cm^3, porosity 38.34%.

A defining feature of the adsorption process is the porosity of the RGP. The higher its value is, the higher the adsorption capacity of material is.

Extraction of resveratrol from red grape pomace

Resveratrol (3,5,4'-trihydroxystilbene), (Rv), is a stilbenol, a polyphenol and a member of resorcinols, in which the phenyl groups are substituted at the positions 3, 5, and 4' by hydroxyl groups. It has a role as a phytoalexin, an antioxidant and a glioma-associated oncogene inhibitor, figure 2.

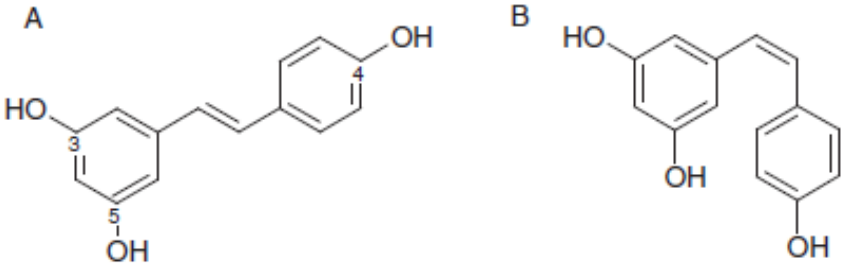

Figure 2. The chemical structure *trans*- (A) and *cis*- (B) of Rv.

The RGP *Vitis vinifera* (Cluj, Transylvania region) was treated with 96% EtOH, for 24 hours to extract Rv. To determine the extracted polyphenolic components, the Janway 6305 spectrophotometer was used, the UV-VIS spectrum was obtained for the wavelength range between 190- and 800 nm, figure 3.

To determine the Rv content from the RGP extract, it was worked at 305 nm, with a dilution of 1:100.

The spectrophotometer was calibrated, using standard solutions in the concentration range 0.1 – 1 × 10^{-4} M. With the absorbance values measured at 305 nm, the concentration of Rv in the alcoholic solution was calculated, this being 145 mg / L, for a ratio of mass of RGP / solvent of 1:20.

The effect of zinc ions concentration on the biosorption process

The experiments were conducted using 100 mL Zn^{2+} aqueous solutions with the Zn^{2+} concentrations between 181–341 mg Zn^{2+}/L, in batch conditions, with magnetic stirring at 200 rpm, at room temperature (T=293K, 20°C) and 2 g RGP biosorbent, with grain size of 0.6-1.0 mm. The variation of the Zn^{2+} concentration over time, until the equilibrium is established (constant residual concentration of Zn^{2+}) is presented in figure 4.

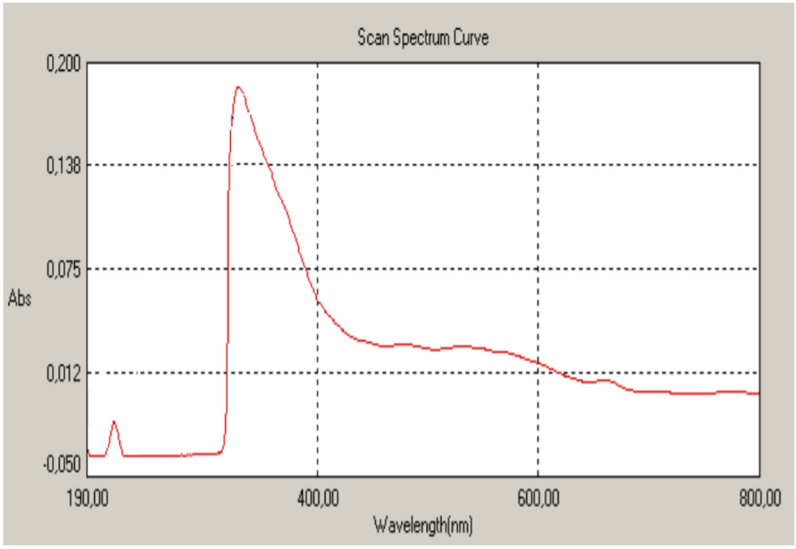

Figure 3. UV-VIS spectrum of the red grape extract (extraction in EtOH, 20°C (293K), dilution 1:100).

From the recorded experimental results, it was possible to reach equilibrium after about 90 minutes, the maximum adsorption capacity of Zn^{2+} on the obtained biomass being 11.92 mg Zn^{2+}/g (for initial concentration 341 mg Zn^{2+}/L), the efficiency calculated based on values obtained from experimental data being 88%

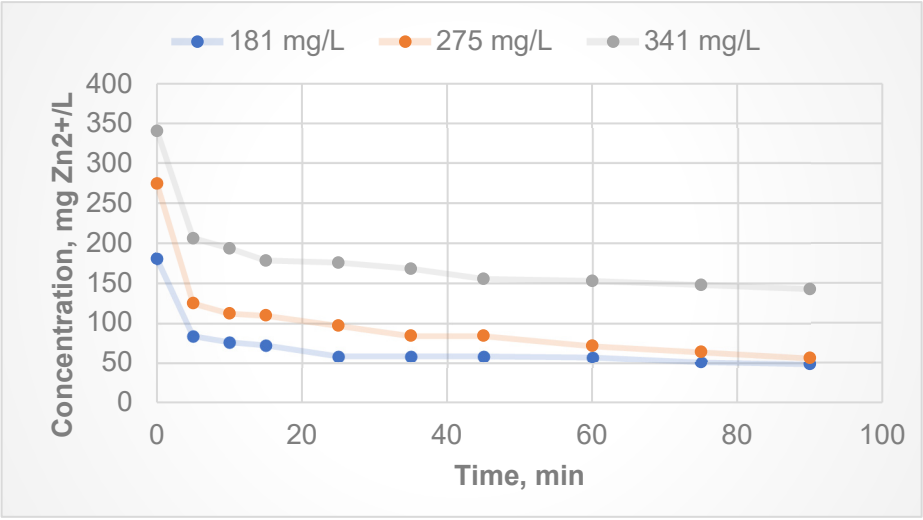

Figure 4. The influence of the initial Zn^{2+} concentration over the time evolution for biosorption onto RGP (181–341 mg Zn^{2+}/L, 2 g RGP, 0.6-1.0 mm, 293 K, pH= 6.3, 200 rpm).

The effect of the stirring rate

The study was conducted under the following conditions: room temperature (293K, 20°C), concentration of zinc solution 275 mg Zn^{2+}/L, grain size of RGP 0.6 - 1 mm, the ratio of addition of biomass/volume of zinc solution is 2 g RGP/100 mL; the stirring rates were 200, 300 and 400 rpm.

From the data collected after the experiment it can be seen that, after about 90 minutes, equilibrium is reached (until constant residual concentration), the adsorption capacity of the prepared biomaterial RGP being 10.94 mg Zn^{2+}/g for experiments conducted at 300 rpm. As the stirring rate increases from 200 to 300 rpm, the liquid layer around the adsorbent particles decreases and the amount of Zn^{2+} retained on the surface of the adsorbent material increases. If the experiment is carried out at 400 rpm, a decrease of adsorption capacity (q_e, mg/g) is observed, as a result of the increase of mechanical disorder, which probably leads to a slower establishment of the biosorption conditions, and, consequently, to a decrease of the biosorption efficiency (E, %), figure 5.

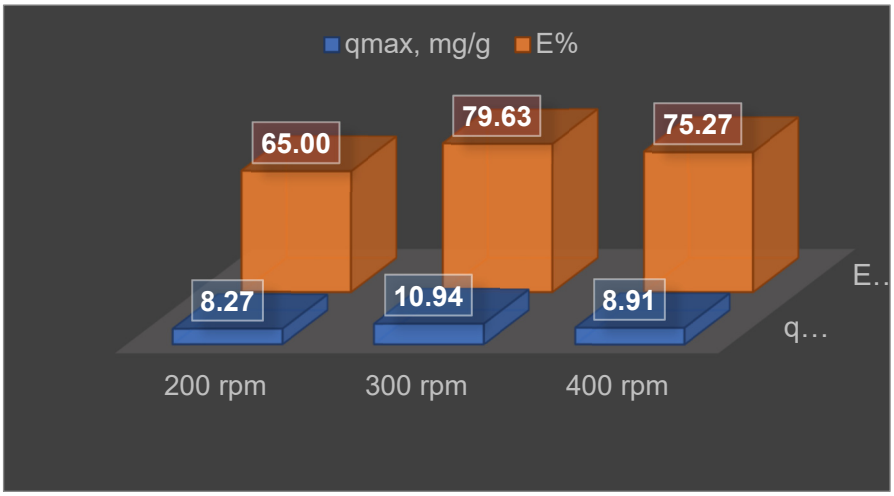

Figure 5. The maximum efficiency and adsorption capacity for Zn^{2+} biosorption process onto RGP biomass; the influence of stirring rate.

The effect of the grain size of RGP biosorbent

This study was performed under the following conditions: the room temperature (293K, 20°C), the concentration of zinc solution was 224 mg Zn^{2+}/L, magnetic stirring rate 300 rpm, grain size biomass granulation 0.4-0.6, 0.6 - 1 mm and >1mm, the ratio of RGP biomass/volume of zinc solution was 2 g RGP/100 mL Zn^{2+} solution.

The study of the particle granulation influence on the biosorption process revealed that, for the RGP material with granulation between 0.6–1 mm, the maximum adsorption capacity was 6.89 mg Zn^{2+}/g.

The increase of the RGP granulation leads to a decrease of the specific surface of the adsorbent material, which determines the decrease of the adsorption capacity (6.49 mg Zn^{2+}/g for grain size >1 mm), figure 6.

The influence of temperature on the biosorption process. Thermodynamic

The Zn^{2+} biosorption onto RGP was conducted using three different temperatures (20°C, 30°C and 40°C). It was observed that an increase in temperature leads to an increase in the biosorption efficiency, suggesting that the adsorption process is endothermic. Higher temperatures conduct to a decrease in biosorption efficiency, due to the fact that, after 40°C (313 K) desorption process begin, figure 7.

Similar results were reported in literature for the biosorption of Zn^{2+} onto different vegetal fibres wastes, [31].

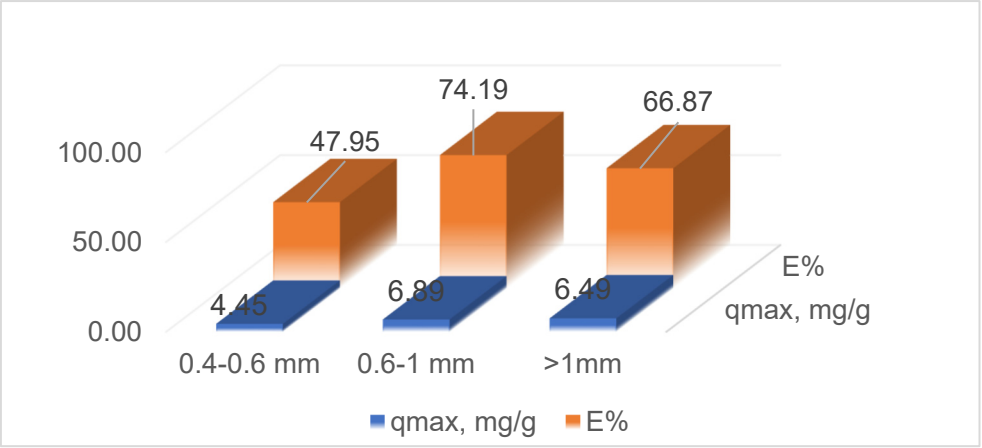

Figure 6. The effect of grain size biosorbent over the amount of Zn^{2+} uptake onto RGP biosorption (224 mg Zn^{2+}/L, 300 rpm, grain size biomass granulation 0.4-0.6, 0.6-1 mm, >1 mm, 2 g RGP/ 100 mL).

For each experiment, performed at a certain temperature, values of biosorption capacity (q_e) and Zn^{2+} concentration in solution, at equilibrium (C_e) were determined.

The equilibrium constant Kd, of the biosorption process, calculated as q_e/C_e, can be used to estimate the thermodynamic parameters, due to its dependence on temperature.

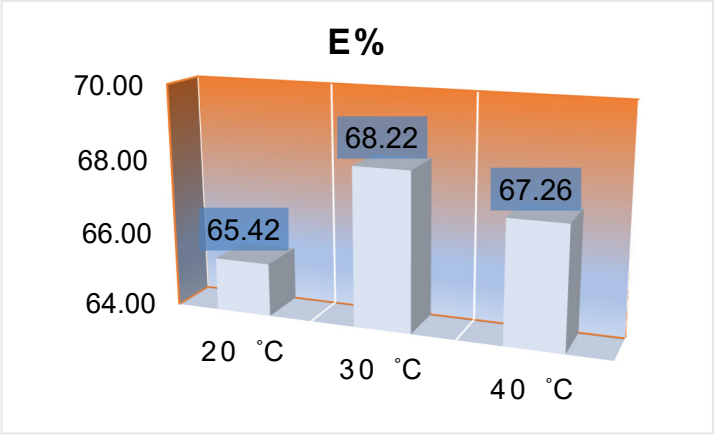

Figure 7. The influence of temperature over the adsorption efficiency of Zn^{2+} onto RGP (272 mg Zn^{2+}/L, 300 rpm, grain size biomass 0.6 - 1 mm, 2 g RGP/ 100 mL).

In order to describe the thermodynamic behaviour of the biosorption of Zn^{2+} onto RGP biomass, standard thermodynamic parameters, including the changes in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations:

$$\Delta G^o = -RTlnK_d \quad (1)$$

$$\Delta \mathrm{G^o} = \Delta \mathrm{H^o} - \mathrm{T}\Delta \mathrm{S^o} \quad (2)$$

where, R is the universal gas constant (8.314×10-3 kJ/K·mol), T is absolute temperature (K), and Kd is the distribution coefficient (L/g) calculated as q_e/C_e, where q_e is biosorption capacity (mg/g) and C_e is Zn^{2+} concentration in solution at equilibrium.

The ΔH° and ΔS° parameters were estimated from the following equation:

$$\mathrm{Kd} = \mathrm{qe/Ce} \quad (3)$$

from the slope and intercept of the lnKd versus 1/T plot [13, 32].

The plot of ln(Kd) as a function of 1/T (Figure 8) yields a straight line (R^2 =0.999) from which ΔH° and ΔS° were calculated, Table 1. The values of ΔG° for Zn^{2+} biosorption onto RGP were found to be negative for the experimental range of temperatures (Table 1) corresponding to a favourable process.

Table 1. The thermodynamic parameters for Zn^{2+} biosorption onto RGP biomass, at various temperatures.

Biomas	**∆H° (kJ/mol)**	**∆S° (kJ/K*mol)**	**∆G° (kJ/mol)**		
RGP	9.150	0.31	293K	303K	313K
			-1.996	-5.187	-8.378

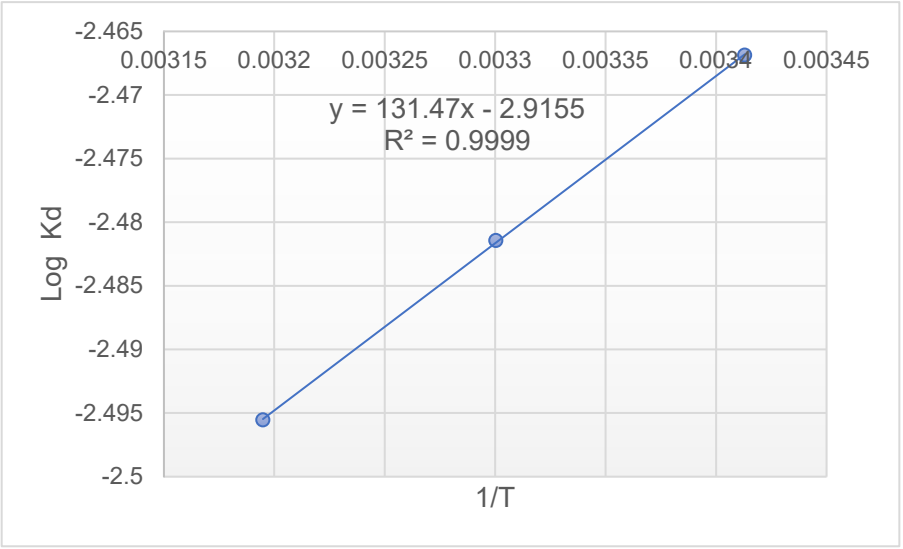

Figure 8. Plot of lnKd versus 1/T for Zn^{2+} biosorption onto RGP (Ci = 272 mg Zn^{2+}/L, 2 g RGP, 0.6 < d < 1.0 mm, 300 rpm).

Furthermore, the decrease in the values of ΔG° with temperature increasing indicates that the biosorption is more favoured at higher temperatures.

The positive value of ΔH° (Table 1) confirms the endothermic nature of the overall biosorption process. This means that, as the temperature increases, more energy is available to enhance the biosorption, but, until 40°C, desorption process begin. Our results are in good agreement with other literature data [30-32].

The endothermic process shows that the diffusion from bulk solution to RGP biosorbent surface may require energy to overcome interaction of dissolved ions with solvation molecules.

Moreover, the positive value of ΔS° (Table 1) points out the increased randomness at the solid/liquid interface during the biosorption of Zn^{2+} onto RGP [17-19].

Biosorption kinetics

Pseudo-first-order (Lagergren, [33]) and pseudo-second-order (Ho, [34]) models were used to study the biosorption kinetic.

Linear regression was used to determine the best fitting kinetic rate equation (coefficient of determination, R^2).

Lagergren suggested a first-order equation for the adsorption of liquid/solid system based on solid capacity, which can be expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

Integrating equation (4) from the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, gives:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (5)$$

where: q_e and q_t are the amounts of Zn^{2+} biosorbed (mg Zn^{2+}/g) at equilibrium and time t, respectively, k_1 is the rate constant of first order adsorption (1/min).

The pseudo-second-order kinetic model is derived based on the adsorption capacity of the solid phase, expresses as[19]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

Integrating eq. (6) from the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (7)$$

where: q_e and q_t are the amounts of Zn^{2+} biosorbed (mg Zn^{2+}/g) at equilibrium and time t, respectively, k_2 is the rate constant of first order adsorption (g/mg·min).

Equation (7) can be rearranged in linear form, as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e} \quad (8)$$

Because the correlation coefficients are modest (between 0.92 and 0.95), and calculated adsorption capacities values show great differences by comparison to experimental values (values are not shown) it can be concluded that the Zn^{2+} biosorption onto RGP biomass cannot be classified as pseudo-first-order.

The linear plots of t/q_t versus t representation (Figure 9) allows the calculation of k_2, q_e values and the coefficient of determination, R^2 (Table 2), when pseudo-second-order kinetic model was applied for the considered adsorption process.

Table 2. Pseudo-first and pseudo-second order rate constants, calculated and experimental q_e values for Zn^{2+} biosorption onto RGP.

C (mg Zn^{2+}/L)	Pseudo-first order				Pseudo-second order		
	$q_{e\ exp}$ (mg/g)	$q_{e\ calc}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e\ calc}$ (mg/g)	k_2 (g/mg·min)	R^2
181	6.61	4.034	0.034	0.923	6.72	0.046	0.998
275	7.94	6.19	0.033	0.946	9.09	0.026	0.996
341	9.92	7.22	0.029	0.951	10.23	0.022	0.998

Values of 0.996-0.998 for R^2 were obtained for all concentrations considered (181–341 mg Zn^{2+}/L).

In addition, the calculated q_e values are very close to the experimental ones (Table 2).

Therefore, it was concluded that Zn^{2+} biosorption on RGP obey the pseudo-second-order kinetic model.

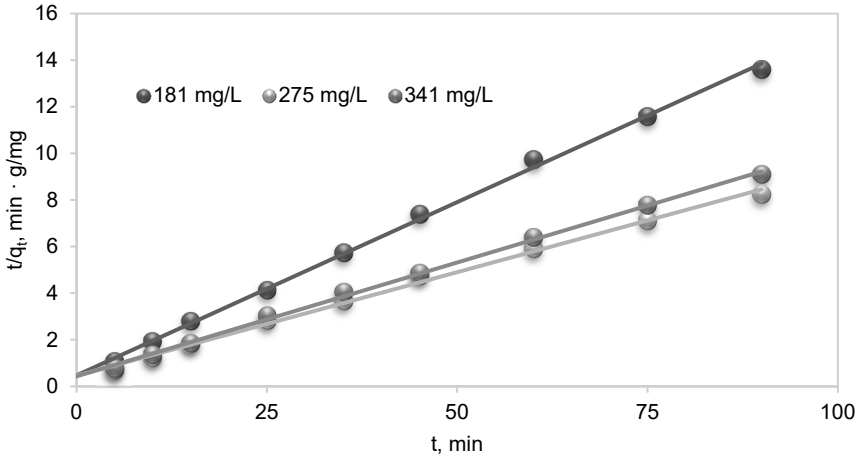

Figure 9. Plots of the pseudo-second-order kinetic model of Zn^{2+} biosorption, onto RGP biomass.

CONCLUSIONS

The study have shown that resveratrol (Rv) can be separated from grape pomace *Vitis vinifera* L. (Cluj, Transylvania region, Romania) with good efficiency, the extraction of Rv with EtOH from RGP biomass being 145 mg/L. The biosorption of Zn^{2+} aqueous solutions using red grape pomace (RGP) *Vitis vinifera* L. has been investigated under different experimental conditions, in batch mode. Biosorption process followed pseudo-second-order kinetic model. The positive enthalpy ($\Delta H° = 9$, 15 kJ mol-1) change for the adsorption process confirms the endothermic nature of the adsorption. The negative values of $\Delta G°$ suggest the spontaneous nature of the adsorption process.

EXPERIMENTAL SECTION

Preparation and characterization of the biosorbent

The biomass used in this work was red grape pomace, RGP (*Vitis vinifera L.,* Cluj, Transylvania region) from the winemaking process. After fermenting for ten days, the by-product was pressed and collected. The sample was dehydrated in a forced-air-drying oven at 50 °C/24 h.

The RGP was treated with 96% EtOH, for 24 hours to extract Rv [28], washed with water to remove traces of alcohol, dried and then treated with a 5% sodium hydroxide solution for 24 hours, to remove organic matter from carbon matrix (with the role of cleaning the internal channels and holes and obtaining a specific surface as large as possible).

The obtained biomass was washed with distilled water, then dried at 105 °C, for 24 hours. The biomass was ground and sieved. The granulation biosorbent material was obtained: 1.0-1.6 mm, 0.6 - 1.0 mm and 0.2 - 0.6 mm which was stored in plastic containers and used in the determinations of the experiments.

Representative RGP samples were investigated using gravimetric method (humidity, apparent density, real density, porosity humidity) [12] and elemental analysis using a Thermo Finnigan Flash EA 1 Series equipment.

The adsorption capacity of a porous material is correlated with properties, such as surface area, pore volume and porosity, these properties are specific to each material [35-38].

Preparation of Zn^{2+} solutions

The Zn^{2+} stock solution (1000 mg/L) was obtained by dissolving the necessary quantity of solid substance, $ZnSO_4 \times 7H_20$ (analytical purity reagent) in distilled water. From this solution, the solutions with known concentration in 181-341 mg/L range were further prepared.

The study of the biosorption process of the Zn^{2+} onto RGP

To determine the optimal parameters of the zinc ion biosorption process on the RGP (working temperature, biosorbent granulation), the pomace samples was contacted with the zinc solution of different concentrations, under magnetic stirring, using a Heidolph MR Hei device, standard equipped with a probe for recording temperature Heidolph EKT Hei-Con.

To determine the residual zinc concentration, samples were taken at different time intervals: 5, 10, 15, 25, 35, 45, 60, 75 and 90 minutes. Samples were appropriately diluted for spectrophotometric determination of zinc concentration using 100 ml graduated flasks. Zinc reagents were added to the collected samples. 10 minutes after the addition of the reagents, the absorbance readings were taken using the Jenway 6305 molecular absorption spectrophotometer, at a wavelength of 420 nm.

The experiments were repeated three times and concentration values were calculated using averaged concentration values.

The experimental data were used to determine the equilibrium time, the equilibrium concentrations, the amounts adsorbed at equilibrium and the efficiency.

The biosorption process capacity and efficiency was calculated with the equation *(9)* and *(10)*:

$$q = \frac{(C_0 - C_t)}{m} \times \frac{V}{1000} \ (mg/g) \tag{9}$$

$$E\ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{10}$$

where: q – biosorption capacity (mg Zn^{2+}/g);
C_0 – Zn^{2+} initial concentration (mg/L);
C_t – Zn^{2+} time *t* concentration (mg/L);
V – aqueous solution volume (mL);
m – biosorbent quantity (g);
E – efficiency (%)

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