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Valorization of grape seed waste for use in the production of antioxidant soaps and as an adsorbent for a textile dye

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Abstract*– In most cases, waste from the wine industry is wasted, generating environmental pollution. For this reason, the objective of this research was to prepare soaps from the oil of these seeds for subsequent determination of the antioxidant capacity by the 2,2-Diphenyl-1-picrylhydrazyl (DPPH) assay, and with the residues generated from the extraction of the oil, the adsorbent potential of this residue for an anionic textile dye was evaluated. The results showed that the prepared liquid soap presented an antioxidant capacity corresponding to an IC_{50} of 3.33%. Higher antioxidant capacity was obtained in the solid soap with an IC_{50} of 0.075%. After the adsorption study of the anionic green acid dye 25 (AG25) with defatted grape seed residues, it was possible to remove 100% of the color from water contaminated with AG25 at a concentration of 30 mg/L at pH=2, a dosage of 0.5 g/L, and an agitation speed of 300 rpm for 120 minutes. The pseudo second order kinetic model was a better fit for the dye removal process thus evidencing that the adsorption mechanism involved is chemisorption. The results of the FTIR-ATR analysis showed that the original grape residue has OH, C-H, and C=O groups that are characteristic of the presence of oil in the seed, and after oil extraction the intensity of the vibrations of the C=O and C-H groups are reduced because the residue was defatted. After the adsorption of AG25, the C-H vibration became less intense. Finally, the point of zero charge of the grape seed variety Italia was 4.67, so the interaction between adsorbate-adsorbent would correspond to electrostatic attractions. The present study has shown that the grape seed variety Italia is a waste with biorefinery potential as it possesses antioxidant compounds found in soaps, which could economically benefit the wine industries, and at the same time, the degreased waste has a high capacity to remove dyes, being an environmentally friendly alternative that can be considered for the treatment of textile wastewater.

Keywords*-- Grape seed, antioxidant capacity, soap, textile dye, acid green 25.

I. Introduction

Synthetic dyes represent a relatively large group of organic chemical compounds found in our daily lives [1]. Dyeing industries discharge about 7.5 metric tons per year of dye-laden wastewater [2]. Wastewater-containing dyes are one of the main threats to the environment [3]. Textile dye pollution is such a serious problem that the United Nations Environment Programme (UNEP) found that not only is fabric dyeing the second largest water pollutant, but that the fashion industry alone produces 20 % of the world's wastewater, with these toxic chemicals contributing to the increasing level of pollution, which has a detrimental effect on marine life and the aquatic ecosystem[4], [5]. Several technologies for the removal of textile dyes have been proposed, such as heterogeneous photocatalysis using semiconductors as the TiO_2 [6] and some novel studies have developed materials based on nanotechnology achieving efficient results [7]. On the other hand, biodegradation processes have also been developed using bacteria [8]–[10] and algae [11]–[13] with promising results, however, the problem with these methodologies is their difficult application and scaling to real environments. Another efficient and easy-to-implement alternative is adsorption [14]. Adsorption processes are increasingly used because in this process the dye molecules are adsorbed on the surface of the material using a series of mechanisms that are specific to each adsorbent used [15].

Another important problem to be addressed stems from the wine industry, which is developing worldwide [16] representing an important economic activity that was affected by the COVID-19 pandemic [17]. In particular, the problem is that approximately 20 % of the grapes, including the seed, stalk, and skins, are not used in wine production and therefore end up in landfills [18] generating pollution. Given this, the interest in the valorization of agricultural residues seems to be sustainable because they are renewable resources. [19]. Grape pomace is one of the most abundant solid by-products generated during winemaking. Many products are recovered from grape pomace, such as ethanol, tartrates, citric acid, grape seed oil, hydrocolloids, bioactive compounds, and, dietary fiber [20]. Therefore, there is great interest in the valorization of grape pomace, an agricultural waste that is produced in large quantities every year [21]. Seed oil, in general, could be applied in the elaboration of soaps [22] since any saponifiable oil can be used for soap making, however, the soap obtained will have the physicochemical characteristics of the oil's origin [23], considering this, grape seeds present in their composition phytochemical compounds with important antioxidant activity [24], which in a study was

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taken into account for the elaboration of a facial cream [25]. In this sense, taking advantage of grape oil could be an alternative to generate greater economic income [26] by manufacturing high-demand products such as soaps, which are. For this reason, one of the objectives of this study was to evaluate the antioxidant capacity of soaps (liquid and solid) made from grape seeds of the Italia variety obtained from a wine industry in the city of Arequipa, Peru. The production of soap would leave a residue of defatted seeds, therefore, the second objective of this research was to give an added value to this second residue as a promising adsorbent of a textile dye used in the textile industry in Arequipa (Acid Green 25), because research has shown that grape residues are effective in removing dyes such as methylene blue [27], [28], wastewater dye [29] and Reactive Black 5 [30].

II. Materials and Methods

A. Reagents and equipment

All reagents used in the present research were purchased from Merck. Acid Green 25 dye (AG25) was purchased from Sigma Aldrich. 2,2-Diphenyl-1-Picrylhydrazyl (DPPH) and Trolox were obtained from Merck. Quantification of AG25 dye and determination of antioxidant capacity were performed on Thermo Scientific Genesys 150 UV-Vis spectrophotometer.

B. Seed collection and pressing

Italia grape skin waste was collected from a wine company in the district of Vitor, located in the province and department of Arequipa, Peru. Once collected, these residues were washed with abundant distilled water and the seeds were carefully separated. The seeds were dried in an oven at 40 °C for 48 hours. Subsequently, the seeds were taken to a mechanical press of the Kodama S.A.C. Research Center. After pressing, the oil was obtained and used for the elaboration of the soaps and the determination of their antioxidant capacity (Figure 1). As shown in Figure 1, a post-pressing residue of seeds is generated in the form of bars (Residue).

C. Solid soap production

The production of solid soap is schematized by the operation process chart shown in Figure 2. This process consisted of weighing 100 g of grape seed oil in a beaker. The oil was then heated to 80 °C and a 25 % sodium hydroxide solution was slowly added, maintaining constant mixing for 15 min or until saponification. It was then placed in soap molds and cured for 3 months. After this time, the antioxidant capacity of the solid soap was evaluated.

D. Production of liquid soap

The production of liquid soap is schematized using the operation process chart shown in Figure 3. The process consisted of weighing 100 g of grape seed oil in a beaker. Then, it was heated to 80 °C and 25 % potassium hydroxide was slowly added, mixing constantly for 15 min or until saponification, then, gelatinization was carried out by stirring at 50 °C for 45 min until a creamy texture was obtained, then the temperature was reduced to 30 °C and stirred for 15 min, then, the gelatinization was carried out by stirring at 50 °C for 45 min until a creamy texture was obtained. It was allowed to cool and taken to a container for curing for 5 days obtaining a soft and easily malleable soap. The soft soap was dissolved with a suitable amount of distilled water at 80 °C and placed in a container for curing for 5 days. Volumes of 100 mL of water were added for 3 days to hydrate the mixture and finally, the liquid soap was obtained and evaluated for its antioxidant capacity.

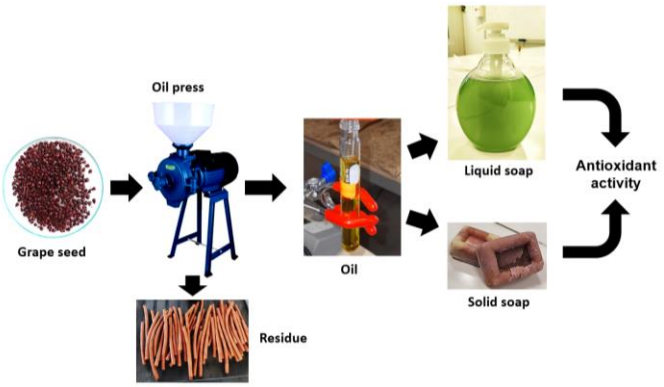

Fig. 1. Oil extraction process by pressing, obtaining mechanical soap, and final analysis of each soap.

E. Evaluation of antioxidant capacity

For the determination of the antioxidant capacity, the DPPH assay described by Atolani *et al.*[31] with some modifications. The test consisted of preparing solid soap solutions at concentrations of 0.25 to 3 % and for liquid soap, it was from 2.5 to 30 %. 100 µL of each solution was measured in a glass container covered with aluminum foil to which 3 mL of a 0.05 mg/mL DPPH solution was added (initial absorbance = 1.4252). Se dejó reaccionar por una hora en la oscuridad. Posterior al tiempo se procedió a medir las absorbancias finales a 517 nm por espectrometría a las cuales se les denominó absorbancia de la muestra. DPPH radical scavenging potential was expressed as a percentage of DPPH radicals scavenged. Trolox at concentrations of 0.1 to 1 mM was used as a standard for comparison. The DPPH solution without a sample was considered as a control. Antioxidant capacity was determined using Equation 1:

$$\%AC = \frac{A_{Control} - A_{sample}}{A_{Control}} \times 100 \quad (1)$$

The concentration of solid or liquid soap capable of scavenging 50 % of DPPH radicals was considered as IC_{50} which was calculated in GraphPad Prism 8 software [32].

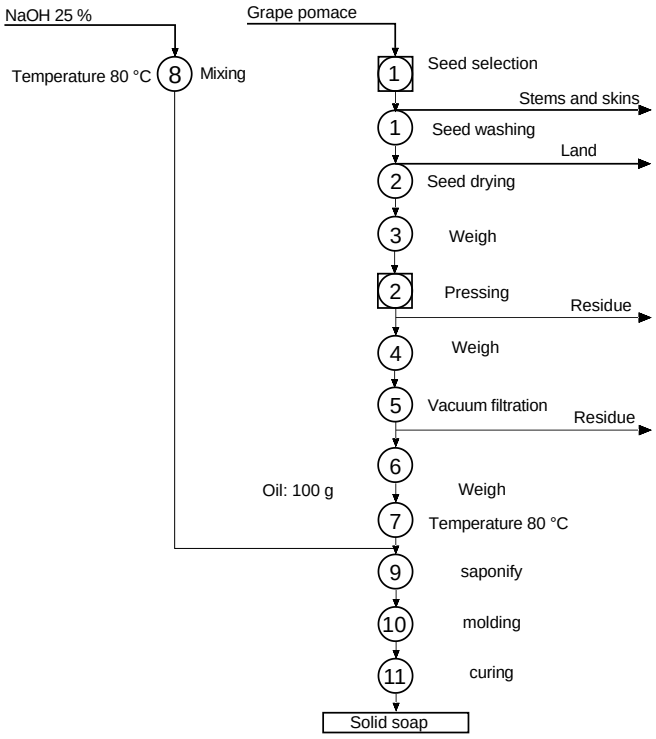

Fig. 2. Operation process chart for the production of solid soap

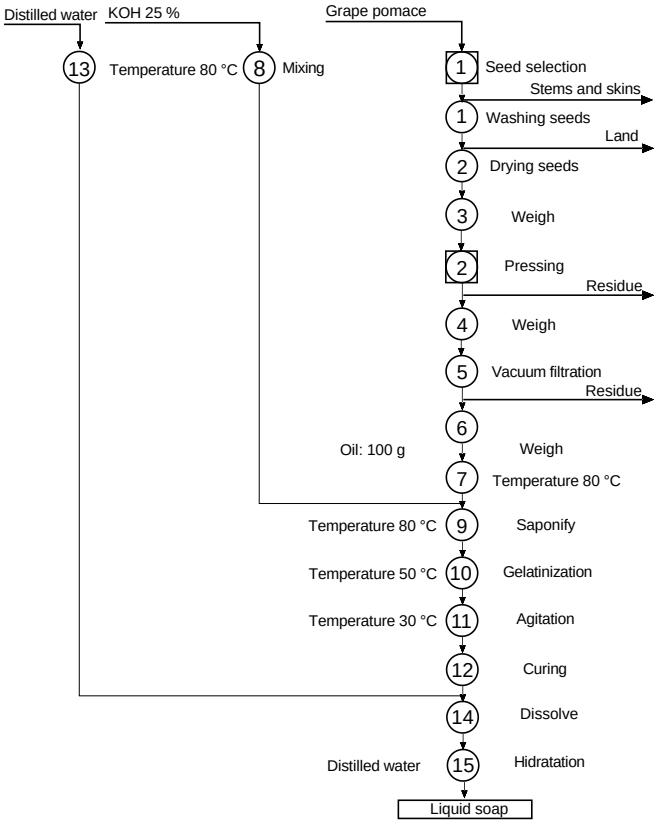

Fig. 3. Operation process chart for the production of liquid soap

F. Acid green 25 dye adsorption study

For the adsorption study, the residue generated in the pressing process was used; however, for the adsorption of the dye, it was necessary to carry out an additional process. The rods were pulverized in a blade mill, then 20 g of the pulverized residue was weighed in a cellulose cartridge and subsequently placed in the extraction chamber of a Soxhlet [33] where extraction was carried out with diethyl ether for 6 hours to remove the remaining oil from the residue. The degreased grape residue was exposed to room temperature to evaporate the solvent and then used for AG25 dye removal studies. The whole process is schematized in Figure 4. Equation 2 was used for the quantification of AG25:

$$y = 0.017x + 0.0058 \quad (2)$$

Where "x" is the concentration of AG25 in mg/L and "y" is the absorbance at 605 nm. The coefficient of determination R^2 of the calibration graph was 0.9995 at dye concentrations from 0.5 to 30 mg/L.

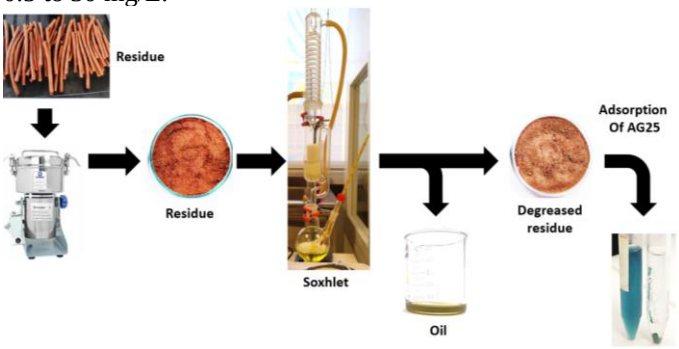

Fig. 4. Preparation process of defatted grape seed residue for subsequent use in the adsorption of acid green 25 dye (AG25).

The adsorption study of AG25 on defatted grape seeds was carried out in a batch agitation system. The procedure consisted of measuring 100 mL of the dye at an initial concentration of 30 mg/L in a 250 mL beaker. Then, the pH was fit to 2 with 0.1 N HCl and 0.1 N NaOH, subsequently, agitation was started at 300 rpm and 0.05 g of the adsorbent was added (dosage=0.5 g/L). The system was stirred for 120 minutes and samples were taken at 0, 5, 10, 15, 30, 60, and 120 minutes. Water samples were centrifuged at 6000 rpm for 10 min and the supernatant was analyzed by spectrophotometry at 605 nm.

Concentrations were calculated using equation 2 and then the percentage removal rate (*%R*) was calculated using equation 3 [34]:

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \quad (3)$$

Where "C_i" is the initial concentration of the AG25 in mg/L and "C_f" is the final concentration of the AG25 in mg/L.

Subsequently, the kinetics of the adsorption process was evaluated. For this purpose, the adsorption capacity "q_t" was calculated with equation 4:

$$q_t = \frac{C_i - C_f}{m} \times V \quad (4)$$

Where "m" is the mass of grape seed powder in grams and "V" is the volume of the agitation system in liters.

The kinetics of the process was evaluated considering the pseudo first order and pseudo second order kinetic model presented in equations 5 and 6 respectively.

$$q_t = q_e(1 - e^{k_1 t}) \quad (5)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t} \quad (6)$$

Where "k_1" is the first order rate constant, "q_t" is the adsorption capacity at time "t" and "q_e" is the adsorption capacity at equilibrium, and "k_2" is the rate constant of the pseudo second order model [35].

G. Characterization of the adsorbent

FTIR-ATR analysis was performed on the Agilent Cary 630 ATR-FTIR analyzer [36]. The grape seed pulverized before and after oil extraction was analyzed. Likewise, the analysis was performed after the adsorption of the dye with the defatted residue.

On the other hand, the point of zero charge (pH_{PZC}) was calculated. For this, we used the procedure developed by Choquenaira-Quispe *et al.* [37]. The procedure consisted of measuring in 100 mL beakers a volume of 50 mL of a 0.1 M $NaNO_3$ solution. Subsequently, the pH was fit with 0.1 M HNO_3 and 0.1 M NaOH at pH 2, 3, 4, 5, 5, 6, 7, 8, 9, 10, and 11. Then, 0.05 g of the defatted pulverized residue was added and it was left stirring with the aid of magnetic stirrers for 24 hours. At the end of this time, the final pH (pH_f) of the solutions was measured. The calculation of the pH_{PZC} was performed by plotting the initial pH (pH_i) vs. the ΔpH. The latter was calculated with equation 7:

$$\Delta pH = pH_i - pH_f \quad (7)$$

III. Results and Discussion

A. Antioxidant capacity in soaps

Figure 5 shows the liquid soap to which 2 drops of green food dye were added, and the solid soap is also shown.

Table 1 shows the results of the analysis of the antioxidant capacity of both soaps, finding that the liquid soap presented an IC_{50} of 3.33 % and the solid soap of 0.075 %, also, these results were compared with the Trolox, finding an IC_{50} of 0.02 % for the latter. These tests show that the soap exhibits antioxidant activity. In a similar study, they prepared a transparent soap from Ganoderma with antioxidant properties with an IC_{50} of 1.53 mg/mL equivalent to 0.15 % [38]. Compared to this study, grape seed oil solid soap would exhibit a higher antioxidant capacity than Ganoderma soap. Antioxidant capacity would be related to the concentration of phenolic compounds and other components [39] present in the seed oil, which could also be indicative of the properties of the soap [40]. Complementary studies could be carried out based on these results, such as the determination of the antibacterial effect to determine the effectiveness of both soaps against pathogenic microorganisms [41].

Fig. 5. Solid and liquid soap obtained from grape seeds of the Italia variety.

TABLE I
ANTIOXIDANT CAPACITY OF GRAPE SEED OIL LIQUID AND SOLID SOAP, ITALIAN GRAPE SEED OIL VARIETY

Product	IC_{50}
Liquid soap	3.33 %
Solid soap	0.075 %
Trolox	0.71 mM (0.02 %)

B. Adsorption study

Figure 6 shows the percentage of AG25 removal concerning the agitation time, showing that 100 % of the color of the solution was removed after 120 minutes. This figure also shows the initial color of the dye AG25 of 30 mg/L, and it is also noted that the color of the dye decreases as a function of the agitation time.

Figure 7 shows the fit plots of the removal process to the pseudo first order and pseudo second order mathematical models. It is observed that graphically the pseudo second order model would fit the process better.

The parameter values of the pseudo first order and pseudo second order models are presented in Table II where it is observed that the adsorption process fits a pseudo second order model with a coefficient R^2 is 0.9968 which is higher

than the coefficient value of the pseudo first order model (R^2=0.993). These results indicate that the adsorption process would correspond to chemisorption mechanisms. According to the pseudo second order model, the adsorption capacity at equilibrium q_e is 57.06 mg/g.

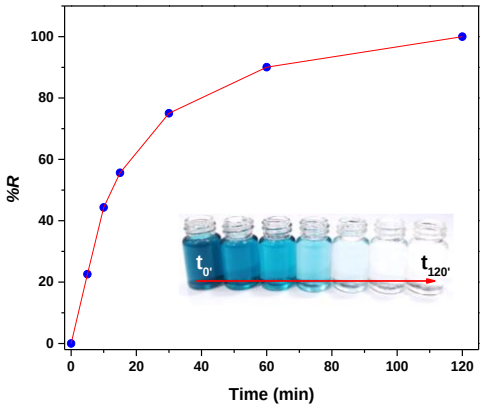

Fig. 6. Adsorption of Acid Green 25 on defatted grape seeds as a function of agitation time.

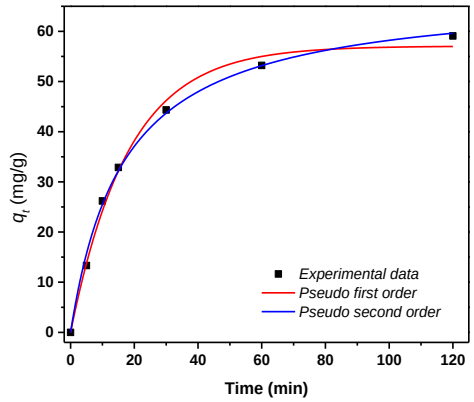

Fig. 7. Pseudo first order and pseudo second order kinetic modeling of the adsorption of the dye Acid Green 25 on the degreased grape seed.

Compared to other studies where other biosorbents were used to remove AG25 some reported lower removal capacities as in the studies of Jain *et al.* [42] which found that the alkali modification of *Prunus Dulcis* increases the adsorption capacity of AG25 up to 28.57 mg/g. Likewise, Ayad *et al.* [43], found that a polyaniline nanotubes salt/silica composite exhibited a 2.7 mg/g, and Yap *et al.*[44] found a capacity of 31.35 mg/g when using kaolin as an adsorbent.

On the other hand, other studies have achieved higher removal capacities, such as the studies of Parimalam *et al.* [45] which evaluated the removal of this dye with activated charcoal of *Ananas Comosus* finding a capacity of 182.6 mg/g, and Kalotra *et al.* [46] which found a removal capacity of 518 mg/g using carbon aerogel powder. With these results, further studies could continue with the aim of chemically or physically modifying the grape residue to prepare activated carbon to improve the adsorption capacity of defatted grape seeds.

TABLE II
PARAMETER VALUES OF THE PSEUDO FIRST ORDER, PSEUDO SECOND ORDER KINETIC MODELS FOR THE ADSORPTION PROCESS OF ACID GREEN 25

Model	**Parameter**	**Value**
	q_{exp}, (mg/g)	59.09
Pseudo first order	k_1 (min^{-1})	0.055
	$q_{e,cal}$ (mg/g)	57.06
	R^2	0.993
Pseudo second order	k_2 (g $mg^{-1}min^{-1}$)	0.0009
	$q_{e,cal}$ (mg/g)	67.87
	R^2	0.9968

C. *Characterization*

Figure 8 shows the FTIR-ATR spectra of Italian grape seed in the various processes studied. Figure 8A shows the presence of -OH groups at 3300 cm^{-1} that could correspond to the hydroxyls of the polyphenols or hydroxyls of the fatty acids of the oil present in the seed. On the other hand, there are characteristic C-H vibrations at 2800, 2900, and 3000 cm^{-1} present in alkanes, which could correspond to the hydrocarbon chain of the fatty acids. Likewise, vibrations are also observed at 1640 cm^{-1} corresponding to C=C groups. At 1750 cm^{-1} the vibration of the C=O groups of the carboxylic acids present in the fatty acids of the seed oil is observed. On the other hand, Figure 8B shows the FTIR spectrum of defatted Italia grape seed, it is observed that there is the presence of -OH groups at 3300 cm^{-1} that could correspond to the hydroxyls of the polyphenols present in the seed, on the other hand, there are characteristic C-H vibrations at 2800 and 2900 cm^{-1}. Also, a small vibration at 1750 cm^{-1} of the carboxyl groups is not present ensuring that the residue was efficiently degreased. Figure 8C shows the FTIR spectrum of defatted Italia grape seed after the VA25 dye removal process, where it is observed that the characteristic C-H vibrations at 2800 and 2900 cm^{-1} decreased when compared to the spectrum in Figure 8B, this could be due to the presence of the adsorbed dye in the defatted seeds.

Finally, the point of zero charge was determined (pH_{PZC}). Figure 9 shows the graph corresponding to the determination of the pH_{PZC}, which gives a value of pH_{PZC}=4.67, this value was taken from the pH value when the ΔpH is zero. In comparison with other studies, it was found that Ahmed *et al.* [47] used Jaca leaf to remove methylene blue and found a pH_{PZC} of 3.9, in this study the percentage of removal was favored at pH lower than the pH_{PZC}. Nasiruddin Khan *et al.* [48] explain that adsorption given below the pH_{PZC} indicates protonation of the adsorbent favoring electrostatic interactions. Then, the grape seed by removing the AG25 below the value of the pH_{PZC}=4.67 would indicate electrostatic interactions between AG25 (anionic dye) and positively charged grape seed lignin at pH=2.

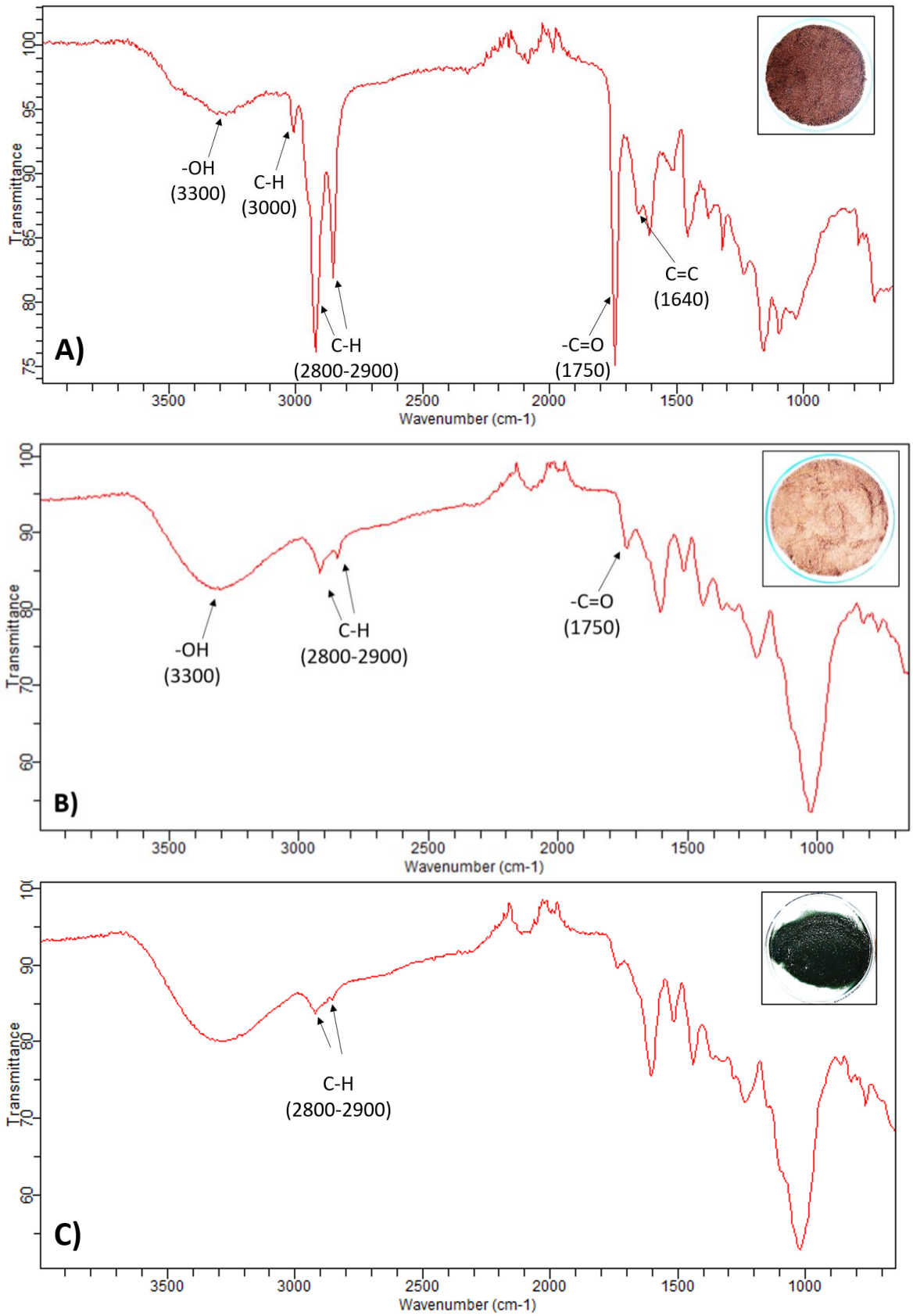

Fig. 8. FTIR spectra of grape seed Italy (A) unprocessed, (B) defatted and (C) defatted after adsorption of acid green 25 dye.

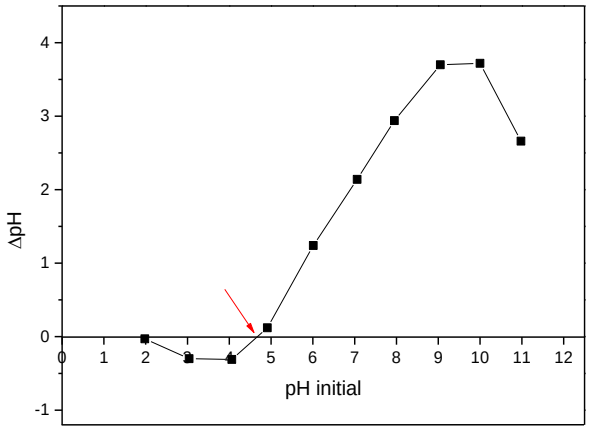

Fig. 9. Graph for point of zero charge calculation.

IV. CONCLUSIONS

Soaps were prepared from the grape seed oil of the Italia variety. Liquid soap showed higher antioxidant capacity than liquid soap. It was demonstrated that grape seed oil is a product that can be used for the preparation of soaps that would preserve the antioxidant properties of the oil. It has been demonstrated that the residues generated from the extraction of grape seed oil of the Italia variety have a high potential as adsorbents of the dye AG25, removing 100 % of a 30 mg/L solution. The point of zero charge of the defatted seeds was 4.67. The adsorption process would be based on electrostatic attractions. The pseudo second order model fitted the adsorption process best suggesting that the adsorption process corresponds to chemisorption. This study could initiate the incorporation of cosmetic manufacturing processes in the wine industry to generate greater economic income.

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REFERENCES

[1] M. Belhachemi, «Chapter 14 - Adsorption of organic compounds on activated carbons», *Sorbents Materials for Controlling Environmental Pollution*, A. Núñez-Delgado, Ed., Elsevier, 2021, pp. 355-385. doi: 10.1016/B978-0-12-820042-1.00006-7.

[2] K. Maheshwari, M. Agrawal, y A. B. Gupta, «Dye Pollution in Water and Wastewater», *Novel Materials for Dye-containing Wastewater Treatment*, S. S. Muthu y A. Khadir, Eds., Sustainable Textiles: Production, Processing, Manufacturing & Chemistry. Singapore: Springer, 2021, pp. 1-25. doi: 10.1007/978-981-16-2892-4_1.

[3] P. V. Nidheesh, R. Gandhimathi, y S. T. Ramesh, «Degradation of dyes from aqueous solution by Fenton processes: a review», *Environ Sci Pollut Res*, vol. 20, n.º 4, pp. 2099-2132, 2013, doi: 10.1007/s11356-012-1385-z.

[4] R. Kant, «Textile dyeing industry an environmental hazard», vol. 2012, 2011, doi: 10.4236/ns.2012.41004.

[5] European Commission, «Smart innovative system for recycling wastewater and creating closed loops in textile manufacturing industrial processes | Waste2Fresh Project | Fact Sheet | H2020», *CORDIS | European Commission*, 2020. https://cordis.europa.eu/project/id/958491

[6] A. Rafiq *et al.*, «Photocatalytic degradation of dyes using semiconductor photocatalysts to clean industrial water pollution», *Journal of Industrial and Engineering Chemistry*, vol. 97, pp. 111-128, 2021, doi: 10.1016/j.jiec.2021.02.017.

[7] V. Batra, I. Kaur, D. Pathania, Sonu, y V. Chaudhary, «Efficient dye degradation strategies using green synthesized ZnO-based nanoplatforms: A review», *Applied Surface Science Advances*, vol. 11, p. 100314, oct. 2022, doi: 10.1016/j.apsadv.2022.100314.

[8] R. Jamee y R. Siddique, «Biodegradation of Synthetic Dyes of Textile Effluent by Microorganisms: An Environmentally and Economically Sustainable Approach», *Eur J Microbiol Immunol (Bp)*, vol. 9, n.º 4, pp. 114-118, 2019, doi: 10.1556/1886.2019.00018.

[9] S. Afrin *et al.*, «The degradation of textile industry dyes using the effective bacterial consortium», *Heliyon*, vol. 7, n.º 10, p. e08102, 2021, doi: 10.1016/j.heliyon.2021.e08102.

[10]A. Mishra *et al.*, «An Integrative Approach to Study Bacterial Enzymatic Degradation of Toxic Dyes», *Frontiers in Microbiology*, vol. 12, 2022. [En línea]. Disponible en: https://www.frontiersin.org/articles/10.3389/fmicb.2021.802544

[11]T. Ishchi y G. Sibi, «Azo Dye Degradation by Chlorella vulgaris: Optimization and Kinetics», *International Journal of Biological Chemistry*, vol. 14, n.º 1, pp. 1-7, 2020, doi: 10.17311/ijbc.2020.1.7.

[12]A. Ayele, D. Getachew, M. Kamaraj, y A. Suresh, «Phycoremediation of Synthetic Dyes: An Effective and Eco-Friendly Algal Technology for the Dye Abatement», *Journal of Chemistry*, vol. 2021, p. e9923643, 2021, doi: 10.1155/2021/9923643.

[13]R. A. Hamouda, N. E.-A. El-Naggar, y G. W. Abou-El-Souod, «Simultaneous bioremediation of Disperse orange-2RL Azo dye and fatty acids production by Scenedesmus obliquus cultured under mixotrophic and heterotrophic conditions», *Sci Rep*, vol. 12, n.º 1, Art. n.º 1, 2022, doi: 10.1038/s41598-022-22825-6.

[14]Y. Dai, N. Zhang, C. Xing, Q. Cui, y Q. Sun, «The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: A review», *Chemosphere*, vol. 223, pp. 12-27, 2019, doi: 10.1016/j.chemosphere.2019.01.161.

[15]M. Shahadat, S. F. Azha, S. Ismail, Z. A. Shaikh, y S. A. Wazed, «16 - Treatment of industrial dyes using chitosan-supported nanocomposite adsorbents», en *The Impact and Prospects of Green Chemistry for Textile Technology*, Shahid-

ul-Islam y B. S. Butola, Eds., en The Textile Institute Book Series. Woodhead Publishing, 2019, pp. 509-539. doi: 10.1016/B978-0-08-102491-1.00016-2.
[16]Y. Ding y C. Lin, «A Study on the Model of Experience Activities in Wineries», en *Cross-Cultural Design*, P.-L. P. Rau, Ed., en Lecture Notes in Computer Science. Cham: Springer Nature Switzerland, 2023, pp. 129-140. doi: 10.1007/978-3-031-35946-0_11.
[17]F. Synák, «Problems and Opportunities within the Wine Industry in Terms of the COVID-19 Pandemic», *Agriculture*, vol. 13, n.º 3, Art. n.º 3, 2023, doi: 10.3390/agriculture13030731.
[18]H. Apel, «Husker researchers explore ways to repurpose grape waste». https://news.unl.edu/newsrooms/today/article/husker-researchers-explore-ways-to-repurpose-grape-waste/.
[19]A. Kovalcik *et al.*, «Grape winery waste as a promising feedstock for the production of polyhydroxyalkanoates and other value-added products», *Food and Bioproducts Processing*, vol. 124, pp. 1-10, 2020, doi: 10.1016/j.fbp.2020.08.003.
[20]M. Spinei y M. Oroian, «The Potential of Grape Pomace Varieties as a Dietary Source of Pectic Substances», *Foods*, vol. 10, n.º 4, Art. n.º 4, 2021, doi: 10.3390/foods10040867.
[21]M. Ferri *et al.*, «From winery waste to bioactive compounds and new polymeric biocomposites: A contribution to the circular economy concept», *Journal of Advanced Research*, vol. 24, pp. 1-11, 2020, doi: 10.1016/j.jare.2020.02.015.
[22]H. Y. Nchimbi, «Quantitative and qualitative assessment on the suitability of seed oil from water plant (Trichilia emetica) for soap making», *Saudi Journal of Biological Sciences*, vol. 27, n.º 11, pp. 3161-3168, 2020, doi: 10.1016/j.sjbs.2020.07.019.
[23]E. D. George y D. J. Raymond, «3 - Formulation of Traditional Soap Cleansing Systems», en *Soap Manufacturing Technology (Second Edition)*, L. Spitz, Ed., AOCS Press, 2016, pp. 55-72. doi: 10.1016/B978-1-63067-065-8.50003-7.
[24]G. K. Jayaprakasha, R. P. Singh, y K. K. Sakariah, «Antioxidant activity of grape seed (Vitis vinifera) extracts on peroxidation models in vitro», *Food Chemistry*, vol. 73, n.º 3, pp. 285-290, 2001, doi: 10.1016/S0308-8146(00)00298-3.
[25]Y. Supriadi y N. Khoirin, «Formulation and Evaluation of Grape Seed Oil (Vitis Vinifera, L) Facial Cream with Variations in The Concentration of Stearic Acid as an Emulsifier», *Journal of Health Sciences and Medical Development*, vol. 1, n.º 01, Art. n.º 01, 2022, doi: 10.56741/hesmed.v1i01.32.
[26]Q. Jin, S. F. O'Keefe, A. C. Stewart, A. P. Neilson, Y.-T. Kim, y H. Huang, «Techno-economic analysis of a grape pomace biorefinery: Production of seed oil, polyphenols, and biochar», *Food and Bioproducts Processing*, vol. 127, pp. 139-151, 2021, doi: 10.1016/j.fbp.2021.02.002.
[27]S. A. Mousavi, A. Mahmoudi, S. Amiri, P. Darvishi, y E. Noori, «Methylene blue removal using grape leaves waste: optimization and modeling», *Appl Water Sci*, vol. 12, n.º 5, p. 112, 2022, doi: 10.1007/s13201-022-01648-w.
[28]R. Davarnejad, S. Afshar, y P. Etehadfar, «Activated carbon blended with grape stalks powder: Properties modification and its application in a dye adsorption», *Arabian Journal of Chemistry*, vol. 13, 2020, doi: 10.1016/j.arabjc.2020.03.025.
[29]A. Caridi, R. Sidari, L. Kraková, T. Kuchta, y D. Pangallo, «Assessment of color adsorption by yeast using Grape Skin Agar and impact on red wine color», *OENO One*, vol. 49, n.º 3, Art. n.º 3, 2015, doi: 10.20870/oeno-one.2015.49.3.81.
[30]M. Afsharnia, H. Biglari, A. Javid, y F. Zabihi, «Removal of Reactive Black 5 dye from Aqueous Solutions by Adsorption onto Activated Carbon of Grape Seed», *Iranian Journal of Health Sciences*, vol. 5, n.º 4, pp. 48-61, 2017, doi: 10.29252/jhs.5.4.48.
[31]O. Atolani *et al.*, «Chemical characterization, antioxidant, cytotoxicity, Anti-Toxoplasma gondii and antimicrobial potentials of the Citrus sinensis seed oil for sustainable cosmeceutical production», *Heliyon*, vol. 6, n.º 2, 2020, doi: 10.1016/j.heliyon.2020.e03399.
[32]C. B. Adeosun, S. Olaseinde, A. O. Opeifa, y O. Atolani, «Essential oil from the stem bark of Cordia sebestena scavenges free radicals», *Journal of Acute Medicine*, vol. 3, n.º 4, pp. 138-141, 2013, doi: 10.1016/j.jacme.2013.07.002.
[33]E. G. Gonzales-Condori, R. Alvarez-Gonzales, y S. A. Ramírez-Revilla, «Ultrasound-assisted extraction for the determination of α-linolenic and linoleic acid in vegetable oils by high performance liquid chromatography», *Eclética Química Journal*, vol. 46, n.º 2, Art. n.º 2, 2021, doi: 10.26850/1678-4618eqj.v46.2.2021.p57-66.
[34]V. Zea-Linares, B. M. Salazar-Pinto, J. A. Villanueva-Salas, y E. G. Gonzales-Condori, «Optimization of Cd (II) and Pb (II) biosorption using Olea europea endocarp in bimethal solutions», presentado en Proceedings of the LACCEI international Multi-conference for Engineering, Education and Technology, 2021. doi: 10.18687/LACCEI2021.1.1.134.
[35]J. Lin y L. Wang, «Comparison between linear and non-linear forms of pseudo-first-order and pseudo-second-order adsorption kinetic models for the removal of methylene blue by activated carbon», *Front. Environ. Sci. Eng. China*, vol. 3, n.º 3, pp. 320-324, 2009, doi: 10.1007/s11783-009-0030-7.
[36]J. M. Medina-Pérez *et al.*, «Production of Lactobionic Acid Using Gold Nanoparticles Synthesized with Fruit *Myrciaria dubia* Extract», *Journal of Nanotechnology*, vol. 2023, p. e5654802, 2023, doi: 10.1155/2023/5654802.
[37]C. Choquenaira-Quispe, H. R. Yucra Condori, J. A. Villanueva Salas, y E. G. Gonzales-Condori, «In vitro release of aluminum from the geophagic clay "Chacco" in the Peruvian highlands: Chemical characterization and health risk assessment», *Journal of Environmental Science and Health, Part B*, vol. 58, n.º 4, pp. 294-303, 2023, doi: 10.1080/03601234.2022.2161795.
[38]S. N. Hayati *et al.*, «Physicochemical properties, antimicrobial and antioxidant activity of ganoderma

transparent soap», *IOP Conf. Ser.: Earth Environ. Sci.*, vol. 462, n.º 1, p. 012047, 2020, doi: 10.1088/1755-1315/462/1/012047.
[39]O. Adigun *et al.*, «Use of Natural Antioxidants from Newfoundland Wild Berries to Improve the Shelf Life of Natural Herbal Soaps», *Antioxidants (Basel)*, vol. 8, n.º 11, p. 536, 2019, doi: 10.3390/antiox8110536.
[40]M. M. Ircham, A. S. Mubarak, y E. Saputra, «Physical characteristic and antioxidant activities of liquid bath soap with substitution of β-carotene crude extract from Gracilaria sp.», *IOP Conf. Ser.: Earth Environ. Sci.*, vol. 1036, n.º 1, p. 012047, 2022, doi: 10.1088/1755-1315/1036/1/012047.
[41]K. Rambabu *et al.*, «Date-fruit syrup waste extract as a natural additive for soap production with enhanced antioxidant and antibacterial activity», *Environmental Technology & Innovation*, vol. 20, p. 101153, 2020, doi: 10.1016/j.eti.2020.101153.
[42]S. N. Jain y P. R. Gogate, «Efficient removal of Acid Green 25 dye from wastewater using activated Prunus Dulcis as biosorbent: Batch and column studies», *J Environ Manage*, vol. 210, pp. 226-238, 2018, doi: 10.1016/j.jenvman.2018.01.008.
[43]M. M. Ayad y A. A. El-Nasr, «Anionic dye (acid green 25) adsorption from water by using polyaniline nanotubes salt/silica composite», *J Nanostruct Chem*, vol. 3, n.º 1, p. 3, 2012, doi: 10.1186/2193-8865-3-3.
[44]P.-S. Yap y Y.-H. Cheah, «Treatment of crystal violet and acid green 25 using Fenton process», *IOP Conf. Ser.: Mater. Sci. Eng.*, vol. 495, p. 012053, 2019, doi: 10.1088/1757-899X/495/1/012053.
[45]R. Parimalam, V. Raj, y P. Sivakumar, «Removal of Acid Green 25 from Aqueous Solution by Adsorption», *Journal of Chemistry*, vol. 9, pp. 1683-1698, 2011 doi: 10.1155/2012/197235.
[46]S. Kalotra y R. Mehta, «Carbon aerogel and polyaniline/carbon aerogel adsorbents for Acid Green 25 dye: synthesis, characterization and an adsorption study», *Chemical Engineering Communications*, vol. 209, n.º 6, pp. 757-773, 2022, doi: 10.1080/00986445.2021.1919650.
[47]T. Ahmed, W. Noor, O. Faruk, M. C. Bhoumick, y M. T. Uddin, «Removal of methylene blue (MB) from waste water by adsorption on jackfruit leaf powder (JLP) in continuously stirred tank reactor.», *J. Phys.: Conf. Ser.*, vol. 1086, p. 012012, 2018, doi: 10.1088/1742-6596/1086/1/012012.
[48]M. Nasiruddin Khan y A. Sarwar, «Determination of points of zero charge of natural and treated adsorbents», *Surf. Rev. Lett.*, vol. 14, n.º 03, pp. 461-469, 2007, doi: 10.1142/S0218625X07009517.