Original Article
Food Science and Technology

ISSN 0101-2061 (Print)
ISSN 1678-457X (Online)

DOI: https://doi.org/10.1590/fst.39322

CC BY

The research of effect of diluents to the amount of pesticide residues in wine

Fataliyev Hasil KAMALADDIN[1], Agayeva Sudaba GALIB[1*], Haydarov Elnur ELMAN[1], Aliyeva Shalala ELXAN[1], Askarova Irada MAMMADTAGI[1], Hasanova Aybaniz ABBASGULU[1], Cafarova Konul TOFIG[1]

Abstract

The effect of various substances on the composition and quality of wine has been studied. Only imazalil residue was 0.35 µg/dm^3, in course of use the activated coal in a dose of 300 mg/dm^3 and no other pesticides were found. The pesticide residue was totally over during the next use of doses (450 & 600 mg/dm^3) of the activated coal. So, the dose of activated coal of 450 mg/dm^3 is sufficient to remove totally the residue of pesticide out of wine examples. The more significant dose of bentonite was 600 mg/dm^3. In this case, the most affected one was imazalil. İncreasing the dose of casein from 150 mg/dm^3 up to 600 mg/dm^3 is observed decreasing with about 5-10 times of the different pesticide residue but these doses weren`t enough to remove the pesticide totally/ we can see show α-endosulfan (about 10 times) and pencondzolen (about 6 times) among highly affected pesticide residues. The weakest effect was PVPP and the strongest one was attributed to activated coal during the removing process of pesticides residues by diluents.

Keywords: juice; wine; dilution; bentonite; activated coal; pesticide.

Practical Application: In juice and wine production is encountered to the different pesticide residues transplanted from grape. Those residues created base to various discomforts and sickness in human body. Therefore, the removal of them have practical implications. The removal of pesticide residue having use the traditional adhesive substance and diluent, can be used in family farm engaged in juice and wine production as well as processing plants.

1 Introduction

There are turbidity and sedimentation on wine making, storage & transportation for some reasons especially in sales outlets. It`s important that the wine is to various process in order to remove that challenging. One of the concern factors is pesticide residue collected from grape in wine, environment and other reasons. Depend on the reasons because turbidity is grouped having biological, biochemical, and physical & physicochemical (Fataliyev, 2011; Fataliyev et al., 2019).

The biological turbidity is connected with the develop of the yeast and yeas like fungus. Studies show that 85-98% of sediments in white table wine may consist of yeast cell. The turbidity too which takes place connected with the activities of pathogen microorganism is included biological turbidity too. The biochemical turbidity occurs presence of free air oxygen to phenol combination and effect of oxidizing ferments (Kishkovsky & Skurikhin, 1988; Gnilomedova et al., 2020).

Physicochemical turbidity occurs out of various reasons and this kind of turbidity is consisting of crystal and colloid. The dangerous of crystal turbidity is increasing in modern period. This is primarily due to the fact that the wine is filled in an earlier stage. On the other hand, the implementation of various minerals or winemaking process is accelerated the enlarging wine by calcium during use the reinforced concrete reservations over fermentation and storage. And the multi-layer filtration removes naturals inhibitors out of wine (Vinogradov et al., 2013; Zagoruiko & Chursina, 2016).

The density of pesticides and the maximum residue limitation, the collecting of pesticide residue in human bload, the assessment of the pesticide effect, the contuct between pesticides and food poisoning, the use of biopesticides are brought to agenda on food product during conducted research (Fazal et al., 2022; Lopes & Nascimento, 2021). The serious cardiovascular diseases risks are observed having increase the concentration of toxic pollutants (Khwaja et al., 2023). Thirty-one pesticide residues have been studied in berries and it was noted that the 23 pesticide residues didn't commite a potential threat to human health (Xing et al., 2022). In other research, the therapeutic properties (Shimoga & Kim, 2022) of alcohol beverages as food and the dietary effect (Mammadova et al., 2020) of producing products of grape pesticide have been noted.

The numerous research has been implemented on purpose of to increase the quality of wine and the way to remove the substances which are sources of unstable and some of turbidity have been processed (Mikhaylovna et al., 2020; Taran et al., 2015; Aghayeva, 2020). Z.N.Kishkovski, Riberro-Gayon, N.A.Mexuzla, V.A.Zaguroyko, N.V.Gnilomedova, N.M.Aqeeva, N.Q.Taran, V.A.Vinoqradov have investigated on this field. But those research weren't mainly on the level of covering the matters which connected with removing the turbidity and the indicators

Received 18 Apr., 2022
Accepted 01 June, 2022
[1] *Azerbaijan State Agrarian University – ASAU, Ganja, Azerbaijan*
*Corresponding author: aqayeva_90@bk.ru

about quality of stabilization of wine especially there weren`t any of research connected with removing the pesticide residue in terms of safety of wine in our country.

The purpose of the research is to study the influence to the amount of pesticide residue of diluents in wine.

2 Materials and methods

The research object is grape varieties growing in the regions, juice, wine, auxiliary materials, technology and technological means. Bentonite, gelatin, kieselsol, tannin and activated coal are used as auxiliary materials.

Juice and wine materials made from aboriginal Bayanshira and Madrasa grape varieties were used during research process. As diluents substances Bentonit, gelatin, kieselsol, PVPP Erbslöh GmbH (Geisenbelium, Germany) company; activated coal, Merks KGaA (Darmstadt, Germany) company, casein Latfort (Bordeaux, France) company have been used.

The insecticide α-endosulfan made by Ehrensorfer GmbH against to insects, penconazole and imazalil fungicide against to fungus and tetradifon acaroid against to ticks are used in research.

Wine examples have been made in micro-winemaking condition over the sorts and collected in 10 l, tanks. Wine examples are shared to 100 mL cylinders in order to test. Nothing is added besides wine to the cylinders taken as a control.

Because the tests are performed on 4 pesticides, taking various doses into the account for each of pesticides are divided into cylinders. The research is in following scheme.

The control with the process of wine examples on various variants is implemented without absorbent having increase the dose of polyvinylpolypirrolidine (130, 190, 250 mg/dm^3) consist of different diluent (activated coal, bentonite, casein) in individual (150, 300, 450, 600 mg/dm^3).

In order to clarify the influence to residue of pesticide of the mixture of kieselsol and gelatin, a) 0.25 mL/L kieselsol + 525 mg/L gelatin; b) 0.35 mL/L kieselsol + 50 mg/L gelatin; c) 0.60 mL/L kieselsol + 75 mg/L gelatin have been added and researched.

As we see, 5 cylinders and used for one dilute/if we consider that 4 pesticides have been taken, then 20 cylinders have to be taken. The cylinders are chosen for each diluents in accordance with this scheme.

The analysis of pesticide is conducted by using the instrument of gas chromatography HP Agilent 6890 model.

On the basis of using chromatography method is modificated the way as a main base which Wong and his employees used. (Wong et al.2003)

3 Results and discussion

The connected process with the effect of physical and chemical, physicochemical and mechanical substances in the conducted diluent process of wine is agenda for years. In terms of that, the influence to pesticide of diluents became the special research abject and the research with various pesticide are carrying out. On this purpose, the experiments were conducted with diluent widely used in winemaking.

It`s obvious that casein has a sedimentation quality in sour environment and it takes special role with its positive load in negative loaded sedimentation of substance (particles) in wine, at the same time casein has the ability to remove bad smell like some other diluent. So we have implemented the researches in order to determine the dilution and remove the side smell, the use of casein and the influence to pesticide residue of it (Schedule 1).

It`s clear from the Schedule 1 that, the decrement has been observed in the amount of the consistency of increasing dose and pesticide residue in 4 different dose during the working process of casein. But it not possible to remove totally the pesticide residue even in the highest dose of casein. Along with that the decrease has been observed about 5-10 times of different pesticide residue with the increase of casein dose from 150 mg/dm^3 up to 600 mg/dm^3. But that dose wasn`t enough in order to remove completely out of pesticide.

We can show α-endosulfan (about 10 times) and pencondzolen (about 6 times) among highly effected pesticide residues. The effect of casein on other pesticide residue is weaker.

Studies show that when bentonite is added to the wine in order to dilute, the calcium, sodium and magnesium ions in the bentonite pass into the wine and the dilution combines with the molecule of positive loaded protein. So, the protein which is able to create the turbid in wine settles as a small layers and is removed out of material. At the same time anthocyan cations react and makes a substantial impact to purify the color of the red wine. Though there are some sources of bentonite in Azerbaijan, there are not sufficiently researches yet.

The results of researches connected with changes of amount of pesticide on the process of dilution by bentonite are given below (Schedule 2).

Schedule 1. The effect of casein on the amount of pesticide residues in wine.

The variants of experience	Pesticides, μq/dm^3			
	İmazalil	Tetradifon	Pencondzole	α-endosulfan
Control	155.31	145.56	128.55	135.44
Casein, mg/dm^3: 150	55.10	83.60	45.20	36.51
300	50.00	80.10	28.52	27.16
450	46.22	71.16	24.30	16.22
600	42.10	67.00	20.10	14.11

As we see, in the control variants, during wasn`t used the bentonite the initial amount of pesticide residue was maintained. The amount of pesticide residue too has got figures used in various doses of bentonite. The highest dose of bentonite (600 mg/dm^3) more attracts with removing the pesticide residue among the variants.

This time, the most affected one was imazalil from pesticide residue. However, it`s amount too was level of 19.32 mg/dm^3.

Having exist the resources of bentonite in Azerbaijan make possible to use accordance with this diluent in future.

Let`s note it for information that they usually exposure the bentonite to processing in industry in order to use the bentonite mineral taking out of enclosure. First of all, this is drying, crushing and activation by various method. The important character of bentonite is to protect the natural crystal structure during industrial use.

The research has been carried out on 4 variants on order to study the effect of polyvinylpolypirrolidin to the amount of pesticide residue in the wine. There was no use PVPP on control variant but added different dose of it on experiment of variants (Schedule 3).

It was found that the amount of pesticide residue in the control variant varies between 122-155 mg/dm^3. α-endosulfan was the most decreased of the pesticide residues during added 130 mg/dm^3 PVPP into the wine material on the experiment variant and the amount of it decreased from 131μg/dm^3 to 3 μg/dm^3 in control variant. When the dose of PCPP increased up to 190 mg/dm^3 α-endosulfan decreased to 0.2 μg/dm^3 and in dose of 250 mg/dm^3 of preparation, it was 0. The other reduction on the dose of 190 mg/dm^3, α-endosulfan has been observed in penconazole and imazalil pesticide. I general comparison, the best dose has been discovered in 130 mg/dm^3.

The appearance was a bit different during the effect of kieselsol and gelatin to the amount pesticide residue. So, in this case, compared to control a significant reduction in the majority of pesticides was observed in the first experimental variant (Schedule 4).

As can be seen, in this case the most decrease was observed in α-endosulfan and penconazole pesticide.

The active coal is used in order to remove the phenol combination, color pigments and bad fragranced substances in winemaking. The substance can be easily soluble in water is absorbed by active coal.

Having use the various dose of active coal, the impact to the amount of the pesticide of the dilution process in given (Schedule 5).

As can be seen, compared to control serious reduction pesticide residue is observed on the examples processing by active coal. If there was imazalil residue 8.9 μ/dm^3, tetradifon 0.09 μ/dm^3 and penconazole 0.02 μ/dm^3, α-endosufan wasn`t found during use the active coal in the dose of 150 mg/dm^3.

Schedule 2. The effect of bentonite to the amount of pesticide reside in wine.

The variants of experience	Pesticides, μq/dm^3			
	İmazalil	Tetradifon	Pencondzole	α-endosulfan
Control	155.31	145.56	128.55	135.44
Bentonite, mg/dm^3: 150	75.34	91.3	77.42	74.36
300	38.21	86.21	69.55	72.81
450	19.32	85.36	57.31	59.25
600	1.05	86.10	12.45	57.16

Schedule 3. The effect of polyvinylpolypirrolidin to the amount of pesticide residue in wine.

The variants of experience	Pesticides, μ q/dm^3			
	İmazalil	Tetradifon	Penconazole	α -endosulfan
Control	155	144	122	131
PVPP, mg/dm^3:				
130	61	109	25.0	3.0
190	73	111	18.0	0.2
250	72	120	26.0	0.0

Schedule 4. The effect of the kieselsol-gelatin mixture to the amount of pesticide.

The variants of experience	Pesticides, μq/dm^3			
	İmazalil	Tetradiphon	Penconazol	α -endosulfan
Control	155	144	122	131
A	36	115	1.50	0.03
B	65	106	6.60	0.0
C	61	114	1.40	0.0

Schedule 5. The impact of the active coal of the amount of pesticide in wine.

The variants of experience	Pesticides, μq/dm^3			
	İmazilil (Fungisid)	Tetradiphon (akarsid)	Penconazole (fung)	α-endosülfan (inseksid)
Control	155.31	145.56	128.55	135.44
Active coal, mq/dm^3: 150	8.96	0.09	0.02	0.00
300	0.35	0.00	0.00	0.00
450	0.00	0.00	0.00	0.00
600	0.00	0.00	0.00	0.00

During use the active coal dose of 300 mg/dm^3 (third variant) there was only imazalil residue 0.35 μg/dm^3 but no other pesticides be found.

And in course of the use of the next dose (450 and 600 mg/dm^3) of active coal, the pesticide residue wasn`t found at all. It turns out that the dose 450 mg/dm^3 of active coal is enough to remove the pesticide residue totally out of wine examples.

The substances of polyphenol, protein, pectin and metal are related in them an in combination groups which cause the turbidity in red and pink wine. Polyphenols and proteins (about 20%) are more reasonable in terms of specific gravity of the turbidity they cause. The found double combination in wine polyphenol and protein make a complex with each other and spoil the commodity appearance of the product.

Having possess both the polyphenol and too much protein of wine are significant in terms of the option of the substances of dilution and to diluent. It is necessary to use properly from the diluent subsidiary material in order to prevent the formation complex of phenol and protein/ the combination which isn`t be able to remove by filtration, but leaves easily by the complex which the diluent substances create. As a result, the wine is transparent. The different combination group and the effective mechanism are existing to effect of each of them of diluent adhesives substances used in this process.

Along with the natural adhesive, the subsidiary materials out of synthetically like bentonite and gelatin are used in order to remove the polyphenol. We may note that the most important of them is polivynilpolipirrolide (PVPP). Along with removing the PVPP polyphenol. PVPP is using on purpose of transparentize too along with removing polyphenol. When we talk about its impact mechanism to polyphenol, we need to note than PVPP is adsorption skilled having create hydrogen contact.

The conducted results of the experiments with diluent substances most commonly used in winemaking in the examples of the pink wine are given below (Schedule 6).

The change of amount of phenol combination has been observed in course of researches conducted on purpose of removing the substances can make turbidity in the colored (red and pink) wine. The dose of bentonite increased to1.0; 1.5 g/dm^3 from 0.5 g/dm^3 that the amount removing of anthocyan and polyphenol out of the wine has increased too whine. But there was no visible growth in the next dose. So, we have used a dose of 1.5 g/dm^3 of bentonite in the subsequent researches.

As can be seen, the process with PVPP in dose of 1.0 g/dm^3 has been observed with much more decrease in the amount of phenolic combination and anthocyan. If the total amount of phenol compounds in the primary wine material was 340 mg/dm^{3}and anthocyan 70 mg/dm^3, the same indicators was 274 μg/dm^3 and 58 μg/dm^3 by the process of PVPP.

According to the degree of effect on phenolic compounds, we should note the next adhesive is bentonite. As we see the dose of 1.5 g/dm^3 in the general amount of phenol compounds and 10 mg/dm^3 amount of anthocyan has been observed with reduction. In terms of impact, gelatin was next (302 mg/dm^3 and 58 mg/dm^3) and albumin was last (phenol combinations 310 mg/dm^3, anthocyan 63 mg/dm^3).

The substances of dilution used in winemaking is used in order to remove some of unwanted compounds impacting the organoleptic features of wine too, along with on purpose to stabilize and transparentize the juice and wine.

In the process of studying the effect of various stabilizers on the antioxidant activity of wine samples, sour wine samples out of grape varieties were processed with different doses of gelatin. It was known that, unlike the control samples organized of the antioxidant activity 196, the same examples used out of gelatin a little bit decreased and then a further decrease was observed at a dose of 5 g/100 sm^3 of gelatin. In this case the activity of antioxidant organized 176.4.

The dose of bentonite used range from 10 to 35 g/dal and the decrease of antioxidant activity has been observed by increase of dose. The resemble case has been observed during used process of activated coal too. The decrease in antioxidant activity was more manifested at a dose of 4,0-4,5 kg/50 dal of activated charcoal.

It was found that injecting SO_2 in both 40 and 80 mg/dm^3 without the addition of SO_2, with different doses of bentonite and gelatin, had a similar effect on the turbidity index, the amount of protein and phenolic compounds. So in case of conducted process without SO_2, the turbidity changed between 70-79, this indicator was 0.61 and 1.50 in the variants used having injected 40-80 mg/dm^3 SO_2. The main changes have been noticed in the amount of protein is the group of the main substances too which create turbidity. The proteins are 42-47 mg/dm3 in samples treated without injected SO_2, and 33-36 ml/dm^3 in those treated with SO_2 ml/dm^3. In other words, there was a decrease to 9.0-11.0 mg/dm^3. The same case took place in the amount of phenol combination.

Schedule 6. The impact to the amount of phenol combination of some diluent substances in the pink Madrasa wine.

Phenol combination	The initial wine materials, mq/dm^3	Diluent substances and the dose q/dm^3			
		PVPP 1,0	Albumin 0,2	Gelatin 0,2	Bentonit 1,5
The combination of general phenol	340	274	310	302	295
Anthocyans	70	58	63	58	60

As can be seen, the diluent substances used in winemaking use on purpose of clarify and stabilize the wine, also possess the effect on removing some of unwished combination influencing to organoleptic characters of wine.

4 Conclusion

It was revealed in course of research of the impact to various dilution substances in wine, specially to pesticide residue that the serious reduction of pesticide residue is observed in the examples using by the activated coal compared with the control. During used the activated coal in a dose of 150 mg/dm^3, the imazalil residue was 8.9 μg/dm^3, tetradiphon 0.09 μg/dm^3, but no α-endosulfan was found.

Only imazalil residue 0.35 μg/dm^3 was found in course of using the activated coal in a dose of 300 mg/dm^3 but there was no other pesticide residue (variant 3). No pesticide residue was found during the nextuse of the activated coal is sufficient to totally remove the pesticide residue out of the examples of the wine.

Though the increase of dose during the process in 4 different dose and the reduction of the amount of pesticide residue in appropriately were observed, it wasn`t possible to completely remove the pesticide residue even within highest dose. It`s true that the increase of the casein dose from 150 mg/dm^3 up to 600 mg/dm^3 was observed with the decrease 5-10 times of the separate pesticide residue. But this dose wasn`t sufficient to absolutely remove the pesticides. The most affected pesticide residues are α-endosulfan (about 10) and pencandzole (about 6).

The amount of the pesticide residue too has differed in various doses of used bentonite. The most important dose of bentonite was 600 mg/dm^3. At this time the imazalil more exposed to impact, but along with that, the amount of it too was the level of 19.32 μg/dm^3. The doubling dose of bentonite didn`t effective, and even some pesticide residues were found to be higher than the previous variant.

The increase of bentonite dose from 0.5 g/dm^3 up to 1.0; 1.5 g/dm^3 has been displayed that the amount removing plyphenole, as well as anthocyan out of the wine has been increased having arising the dose, but there was no fundamental growth in the next doses. So, we have used a dose of 1.5 g/dm^3 of bentonite in subsequent researches.

The process by PVPP in dose of 1 g/dm^3 was observed with more reduction in phenol and anthocyanin compounds. İf the total amount of phenol compounds in the initial wine material was 340 mg/dm^3 and α-endosulfan 70 mg/dm^3, according to the same indicators were 274 mg/dm^3, 58 mg/dm^3 in the process of PVPP. The weakest impact was PVPP, but the strongest one was activated coal in course of removing the pesticide residue by diluent substances. Casein, bentonite and others diluents are average.

References

Aghayeva, S. Q. (2020). The influence of filtering to content and quality of wine. In A. Y. Prosekov (Eds.), *Collection of abstracts of the all-Russian online conference with international participation* (pp. 3-4). Kemerovo: FSBEİ HE Kemerovo State University. Modern biotechnology: topical issues, innovations and achievements.

Fataliyev, H. K. (2011). *Wine technology*. Baku: Science.

Fataliyev, H. K., Aliyeva, S. E., & Musayev, T. M. (2019). *Biotechnology*. Baku: Ecoprint.

Fazal, A., Ismail, A., Naeem, I., Oliveira, C. A. F., Shaukat, S., Saleem, M. U., Saima, S., Nasir, U., Alam, A., Aslam, Z., & Aslam, R. (2022). Exposure assessment of selected pesticide residues using occurrence data in foods and serum samples in Pakistan. *Food Science and Technology*, 42, e01222. http://dx.doi.org/10.1590/fst.01222.

Gnilomedova, N. V., Chervyak, S. N., & Vesyutova, A. V. (2020). Physical methods of stabilization of wines against crystalline haze. *Magarach. Viticulture and Winemaking*, 22(3), 277-282.

Khwaja, S., Hussain, S. I., Zahid, M., Aziz, Z., Akram, A., Jabeen, U., Rasheed, A., Rasheed, S., Baqa, K., & Basit, A. (2023). Persistent organic pollutants distribution in plasma lipoprotein fractions. *Brazilian Journal of Biology*, 83, e248910. http://dx.doi.org/10.1590/1519-6984.248910. PMid:34550288.

Kishkovsky, Z. N., & Skurikhin, I. M. (1988). *Chemistry of wine*. Moscow: Agropromizdat.

Lopes, V. G., & Nascimento, G. N. L. (2021). Food safety: relation between pesticides and poisoning. *Food Science and Technology*, 41(1), 174-179. http://dx.doi.org/10.1590/fst.39519.

Mammadova, S. M., Fataliyev, H. K., Gadimova, N. S., Aliyeva, G. R., Tagiyev, A. T., & Baloglanova, K. V. (2020). Production of functional products using grape processing residuals. *Food Science and Technology*, 40(suppl. 2), 422-428. http://dx.doi.org/10.1590/fst.30419.

Mikhaylovna, A. N., Grigorievich, M. M., & Viktorovich, A. M. (2020). Thermoxid-3a for stabilization of wines to crystal turbid. *Fruit Growing and Viticulture of the South of Russia*, 63(3), 206-216.

Shimoga, G., & Kim, S. Y. (2022). Makgeolli - the traditional choice of Korean fermented beverage from cereal: an overview on its composition and health benefits. *Food Science and Technology*, 42, e43920. http://dx.doi.org/10.1590/fst.43920.

Taran, N. G., Ponomareva, I. N., Soldatenko, E. V., & Taran, M. N. (2015). Improving the technological methods of stabilizing white sparkling wines against crystalline and colloidal turbidity. *Winemaking and Viticulture*, 6, 18-20.

Vinogradov, V. A., Zagoruiko, V. A., Kulev, S. V., Chaplygina, N. B., & Mikheeva, L. A. (2013). Study of the technological process of complex stabilization of wine materials against colloidal and crystalline turbidity. *Magarach. Viticulture and Winemaking*, 43, 83-88.

Wong, J.W., Webster, M.G., Halverson, C.A., Hengel, M.J., Ngim, K.K., & Ebeler, S.E. (2003). Multiresidue Pesticide

Analysis in Wines by Solid-Phase Extraction and Capillary Gas Chromatography-Mass Spectrometric Detection with Selective Ion Monitoring. *Journal of Agricultural and Food Chemistry*, 51(5), 1148-1161.

Xing, L., Wang, Y., Luo, R., Li, X., & Zou, L. (2022). Determination of 31 pesticide residues in wolfberry by LC-MS/MS and dietary risk assessment of wolfberry consumption. *Food Science and Technology*, 42, e61921. http://dx.doi.org/10.1590/fst.61921.

Zagoruiko, V. A., & Chursina, O. A. (2016). Creation of new auxiliary materials for the stabilization of wines against colloidal turbidity. *Scientific Works of The North Caucasian Zonal Research Institute of Horticulture and Viticulture*, 11, 176-180.