

Characterization of spent bentonite recovered from winery waste to assess its recycling potential

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ABSTRACT

The Canadian wine industry is associated with the production of a significant amount of spent bentonite (clay added to the wine for clarification) as a solid waste byproduct. To improve the sustainability of wine production, we must understand the physiochemical and toxicological characteristics of these wastes and facilitate its reuse and recycling for more environmentally friendly applications. In this study, we evaluated the properties of a spent bentonite sample obtained from local winery in the Okanagan region of British Columbia, Canada. We initially collected the liquid red wine waste and filtered bentonite by removing the organic matter. Bentonite filtrate was dried, powdered and characterized for physiochemical and toxicological properties. The surface area, pH, and organic matter (OM) were determined. Fourier transform infrared spectroscopy (FTIRS) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) analysis were used to examine the chemical and morphological properties. The toxicity characteristic leachate test (TCLP) was conducted to measure the total heavy metal concentration. The results showed the spent bentonite has low pH (3.5 to 4), high OM (17 to 20 %), high K (373 to 557 mg/kg) and Mg (50 mg/kg), and lower Brunauer- Emmett-Teller (BET) surface area compared to the virgin. The TCLP results showed the concentration of heavy metals including Ba, Cu, As, Ti, Ni and Fe were relatively higher in the spent bentonite. Occurrence of new peaks/bands on the FTIR spectra of spent bentonite confirmed the existence of organic functional groups resulting from the organic components in the waste. According to SEM-EDS, the microstructure of the spent bentonite exhibited a flocculated arrangement and the ratio Al/Si decreased in the spent bentonite. Overall, the tests indicated that significant changes occurred in the physiochemical and toxicological characteristics of bentonite during the wining process. Identifying and quantifying these major property variations opens the ways to recycle this solid waste for more environmentally friendly purposes and creates a new platform for sustainable consumption and waste management in the future.

RÉSUMÉ

La propriété caractérisation de filtrer la bentonite d' vin industrielle de fixer son recyclage potentiel le total perdre significatif de la bentonite est produit annuellement en résidu d' vin fabrication en Canadien industrielle. Comprendre caractéristique physico-chimique et toxicologique de ces pertes, facilite de réutiliser et recyclage pour environnement amical application dans cette étude nous évaluer la propriété de différent perdre des échantillons bentonite obtenir de quelques facteurs d'extrait régional en Okanagan région de British Columbia, Canadien. Au départ nous rassemble des pertes et filtre la bentonite. De la bentonite filtrat ensuite elle ait séchée poudre pour caractérisation de physico-chimique et toxicologique propriété. La étendue surface, pH, matière organique (MO), ait déterminé. Fourier transform infra-rouge spectroscopy (FTIRS), scanning electron microscopy coupler avec énergie dispersive spectroscopy (SEM-EDS) usage pour comprendre changement de chimique et morphologique l' épreuve caractéristique filtrer toxicité (ECFT), nous e'te' conduire de mesurer la concentration de lourd metal element. Ces résultats montre que la perte de la bentonite avais bas pH (3.5 a 4), haut MO (17 a 20 %), haut K plus (373 a 557 mg/Kg), et Mg (50 mg/Kg) et plus bas Brunauer- Emmett-Teller (BET) la surface étendue comparer avec a virgin. De résultat de ECFT montre la concentration de lourd metal compris Ba, Cu, As, Ti, Ni et Fe relativement ait été plus élevée dans la bentonite, événement de nouveau pic/bande dans FTIR de perdre de spectre de la bentonite. Confirmer en existence d'organique avec groupes fonctionnels résultat dans organique composant dans la perte conforme a (SEM-EDS) en microstructure de perte bentonite un flocculer arrangement et de la proportion Al/Si diminuer en perdre bentonite. Combinaison, des essais indiqués ces significatif changement se produire en physico-chimique et toxicologique caractéristique de la bentonite en durée de proce'de' identité et qualitative ce majeur différence propriété ouvrir le chemin a recycler ce solid prdre pour plus environnement amical conseiller et cree's nouveau platform pour sustenable consummation et perdre administration a l'avonir.

1. INTRODUCTION

The winemaking industry is a major contributor to the global economy worldwide. The Canadian wine industry has seen major growth in the past decades, from being concentrated in three main wine-growing regions, namely Ontario, British Columbia, and Quebec (Doloreux & Lord-Tarte, 2012) to generating about \$9 billion Canadian Dollars in the year 2015 (Hewer & Gough, 2021). The different stages in the winemaking process (i.e., crushing, destemming, and pressing of grapes, sedimentation, fermentation, decanting, clarification, filtration, stabilization, maturation, bottling, and ultimately, commercialization) generate numerous organic and inorganic wastes (Ahmad et al., 2020; Arvanitoyannis et al., 2006; Devesa-rey et al., 2011; Portilla Rivera et al., 2021). Wine clarification, also known as wine fining, in particular, generates large amounts of inorganic clays, namely bentonite and/or perlite. Solid grape remnants (grape marc, stalks, etc.) are filtered using perlite, an aluminum-silicate of volcanic origin before the start of fermentation (Nóvoa-Muñoz et al., 2008), while haze-causing wine proteins are removed by bentonite clays before the wine is bottled (Pocock et al., 2011).

1.1 Bentonite Clay as a Wine Clarifying Agent

Bentonite is primarily composed of montmorillonite, a 2:1 dioctahedral smectite whose structure consists of two tetrahedral silicon oxide sheets and one octahedral aluminum hydroxide sheet, combined as a crystalline structural layer unit. In addition to montmorillonite, bentonite could contain quartz, chalcedony, feldspars, calcite, dolomite, analcime, and pyrite, among others (Catarino et al., 2008). Bentonite clarification of wine consists of three distinct physical reactions - dispersion of the agent, adsorption of the solutes, and the settling of the complex. The adsorption of proteins and other soluble cationic components in wine is dependent primarily on the cation exchange capacity (CEC) of the bentonite added, i.e., the displacement of aluminum ions by sodium, calcium, or magnesium ions. The isoelectric (or iso-ionic) point (pI) of wine proteins has a net positive charge for ready adsorption onto the negative bentonite surface (Blade & Boulton, 1988).

Globally, approximately 16 million tons per year clay was produced for industrial purposes (specifically bentonite), mostly in the USA and China (Ugolini et al., 2020). Spent bentonite output of Spanish wineries is about 4000 tons a year, and their annual bentonite sludge production is much more considering the weight of adsorbed proteins and other impurities (Arias-Estévez et al., 2007). The staggering amount of waste will ultimately end up in the landfill and thus, highlights the need for the industry to consider taking appropriate measures to deal with the growing waste. Unlimited direct disposal of these waste in soil endangers the environment by polluting the soil, emission of greenhouse gasses (Loh et al. 2013) and pollution of surface and groundwater sources (Muralikrishna and Manickam 2017; Heard 2016). Due to stringent environmental regulations and scarce land

resources, disposal of spent bentonite in landfills is not feasible and possible alternative methods for using spent bentonite must be investigated.

1.2 Potential Environmental Applications of Spent Bentonite

Spent bentonite differs significantly from virgin bentonite as wine clarification alters the bentonite's structural, physical, and chemical properties. Due to its higher organic matter content, spent bentonite may be used in various soil management practices like soil fertility enhancement, pollution alleviation, and soil disinfection. Bentonite acquires adsorbates and high amounts of nutrients like carbon (C), nitrogen (N), potassium (K), phosphorus (P) during wine fining; hence, soil application at moderate dosage levels would enhance soil nutritional abilities without being environmentally detrimental (Arias-Estévez et al., 2007; Fernández-Calviño et al., 2015; Rodríguez-Salgado et al., 2017). It is especially desirable because of the slow release of nitrogen, through successive processes of ammonification and nitrification (Bustamante et al., 2007; Rodríguez-salgado et al., 2017). For higher dosages and due to the phytotoxic nature of waste bentonite (Da Ros et al., 2018; Moldes et al., 2008), it may be composted with other virgin or waste materials before direct unamended soil application (Bertran et al., 2004; Bustamante et al., 2009; Diaz et al., 2002).

Apart from reducing the mass and volumes of agricultural wastes, composting also diminishes its pathogen content (González-Marcos et al., 2015). Economically, it would provide wineries incentives to commercialize the composts as a high-quality, nutrient-rich agricultural product and when such a compost is applied to nutrient-deficient vineyard soils (Payen et al., 2021), and it provides added benefits of nutrient cycling within a circular economy framework. Spent bentonite is often composted with commonly found agricultural wastes like rice husk or chicken litter (Soda et al., 2006) or even municipal soil waste sludge (Hungria et al., 2017). Contaminated lands with diverse organic and inorganic pollutants from agrochemicals- herbicides (Pateiro-Moure et al., 2009) or fungicides (Rodríguez-salgado et al., 2014) for example may be treated and hence, alleviated in concentration by bentonite-amended soils. Organic soil amendments are increasingly being paired with traditional solarization (i.e., inducing passive solar heating in soil by mechanical methods to combat microbe or pest infestation) methods to enhance microbial activity (Shea et al., 2021). Winery waste could be a potential agent in promoting soil biosolarization (Achmon et al., 2016).

To develop potential innovative and environmentally friendly applications of spent bentonite, there is a need for a comprehensive study of the characterization of spent bentonite. Such a study would be impossible without a thorough assessment of the properties of the spent bentonite. However, there exists a lack of comprehensive study on the properties of spent bentonite from the wine industry. To contribute to the dearth of literature on the properties of winery waste-bentonite, the motivation behind this study is to supplement existing literature and to

establish a method to match its properties to potential applications for recycling and reuse. We examined the spent bentonite obtained from local wineries in the Okanagan valley, British Columbia, Canada to evaluate its properties. The virgin bentonite was also obtained from the winery to compare and illustrate the post-clarification changes brought about by winemaking process. Physicochemical properties of spent bentonite such as natural moisture content (NMC), specific gravity, pH, electrical Conductivity (EC), organic matter (OM) and cation exchange capacity (CEC) were determined using standard laboratory methods. Surface area of spent bentonite was investigated via Brunauer- Emmett-Teller (BET) nitrogen adsorption test. Microscopic techniques (scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Fourier-transform infra-red spectroscopy (FTIR) were utilised to confirm the microstructural and morphological properties. Spent bentonite was also evaluated for its toxicological properties, especially for agronomic application, using toxicity characteristic leachate procedure (TCLP).

2. MATERIAL AND METHODS

2.1 Sample Preparation

Virgin bentonite and winery waste were procured from a local winery in Okanagan. Virgin bentonite (denoted as VB) was pulverized using a ball mill and then passed through the sieve #200 (75- μ m mesh opening). The liquid waste samples contained grape stalk, grape pomace and spent bentonite. From this effluent, we first collected the entire solids including spent bentonite and other organic matter (denoted as SB) by oven-drying at 50 °C for 40 hours. The oven dried sample was pulverized and passed through #200 sieve and stored in the refrigerator for further studies.

Separately, we also washed the liquid waste using the ASTM D1140-17 wet sieving method to separate the bentonite particles (less than 75- μ m) from the organic matter. Then the remaining liquid portion was transferred into 50 ml centrifuge tubes and centrifuged at 4000 rpm for 20 minutes using Sorvall X Pro ST plus centrifuge. The supernatant was separated and vacuum filtered and mixed with precipitates in centrifuge tubes and air dried. The air-dried material (denoted as SB_W) was pulverized and stored at 4°C temperature for further studies.

2.2 Characterization of Virgin and Spent Bentonite

Table 1 presents the physiochemical properties of the virgin bentonite (VB), spent bentonite (SB) and washed bentonite (SB_W) determined by laboratory tests based on American Society for Testing and Materials (ASTM) standards. The electrical conductivity (EC) and pH of the residues were determined in a 1:10 (w/v) water extract; the total organic matter content (OM) was determined by loss on ignition (LOI) at 450 °C for 2 h. Dry matter of the samples was determined after 24 h at 105 °C to express all data on a dry weight.

CEC was measured as per ASTM method (ASTM D7503–18) for measuring the exchange complex and CEC of inorganic fine-grained soils. For measuring soluble

cations, 40 ml RO water was added to 2 g of oven-dried soil samples, shaken for 24 hours and centrifuged at 3000 for 10 minutes. For measuring bound cations, 40 ml of 1M sodium acetate was added to 2 g of oven-dried soil samples and shaken for 24 hours and centrifuged at 3000 for 10 min. This washing procedure was repeated 5 times. After removing the supernatant in previous step, 40 ml isopropanol was added to the soil, shaken, and centrifuged at 3000 rpm for 10 minutes for 3 times to remove any excess Na ions. For measuring CEC, 50 ml of 1M KCl was added to the cleaned soil and the samples were shaken for 1 hour and centrifuged at 3000 for 10 minutes. The supernatant solution was further diluted and tested using inductively coupled plasma- mass spectroscopy (ICP-MS) to measure the major cation concentrations (such as Na, K, Ca, Mg and Fe) and determine the CEC.

Table 1- Physiochemical properties of Virgin bentonite (VB), Spent Bentonite (SB) and washed SB (SB-W)

Properties	VB	SB	SB_W
Specific gravity, G ^a	2.67	2.61	2.63
Natural moisture content, NMC (%) ^b	11.15	20	17
specific surface area, SSA (m ² /g) ^c	70	6.86	NA
pH @ 20 °C ^d	9.27	3.93	4.5
EC (ds/m)	1.68	0.8	0.64
Organic matter (%) ^b	4.63	29.2	5.3
CEC (cmol/kg)	155	41	72
Particle size distribution (%) ^e			
Silt and clay fractions (<75 μ m)	100	100	100
Sand fraction (75 μ m - 4.75 mm)	0	0	0
Gravel fraction (>4.75 mm)	0	0	0

^a ASTM D854-14, ^b ASTM D2974-20 e1, ^c Arnepalli et al., (2008). ^d ASTM D4972-19, ^e ASTM D6913M-17.

The Brunauer–Emmett–Teller-specific surface area (SBET), pore volume and average pore size of the samples were measured using nitrogen physisorption at 77 K within the vapour pressure range (P/P0) of 0.01–0.99 on a micromeritics TRISTAR II plus surface area & porosity analyzer. Prior to measurement, the samples were degassed at 150°C for 24 h. The IR spectra of the samples in the 500–4000 cm⁻¹ were obtained with a PerkinElmer Spectrum Two FTIR using an ATR (attenuated total reflectance) module. The surface morphology and bulk elemental composition of PFA were explored using a TESCAN Mira 3 XMU SEM coupled with an Oxford Instruments X-Max EDS detector. The characteristic leaching procedure (TCLP) was conducted as per the United States Environmental Protection Agency (U.S. EPA, 1986). The toxicological analysis was carried by acid digestion in aqua-regia (concentrated HNO₃ and HCl in 1:3 ratio) at high temperature. An aliquot of cooled and filtered solution was diluted and analyzed using Agilent 8900 Triple Quadrupole ICP-MS (inductively coupled plasma-mass spectrometry) equipped with a CETAC ASX520 autosampler to measure the total extractable concentrations of major, minor, and trace elements.

3. RESULTS AND DISCUSSION

3.1. Physiochemical properties

3.1.1 Chemical properties

Table 1 shows that The VB has 4.6 % organic matter content. Organic matter highly increased to 29.2 % in spent bentonite (SB). According to Table 1, VB has the basic pH of 9.27 and the pH changed to 3.93 for SB. The basic pH of the VB could be the result of high exchangeable sodium ions in it. The pH changes to acidic, after the bentonite is used for clarification. Results of decrease in the pH of the spent is compatible with the results from Bustamante et al. (2008a) who reported acidic pH of the winery spent bentonites. The decrease of pH can be related to adsorption of alcohols to clay surface. Aliphatic alcohols form single layer complexes on clay surfaces. In this case the alcohols alkyl chain will lie parallel to the surface of the clay. Alcohols will lose their OH proton and act as acid, changing the pH of the pore fluid to an acidic pH. The change in pH values after washing shows an increase. The VB has an EC of 1.68 ds/m and the EC value reduces to 0.8 for SB and 0.64 in SB_W. The EC values of the spent decrease in compare with the VB and it decrease again after washing. The results of EC are not compatible with Bustamante et al. (2008a) who reported a range of 2.99-13.47 ds/m with mean value of 6.15 ds/m for winery sludge EC which are higher than the measured EC values.

The CEC of VB changes from 155 cmol/kg to 41 cmol/kg in SB, and after washing it slightly increase to 72 cmol/kg for SB_W. According to Table 1 CEC reduction in the spent bentonite confirms the results of reduction in SSA of spent bentonite from 70 to 6.8 (m²/g).

Table 2 shows that the concentration of phosphorus (P) and Potassium (K) increases in the spent samples but the concentrations of Magnesium (Mg) and Calcium (Ca) decreases in the spent comparing with the VB.

Table 2 – Concentration of macro nutrients (mg/kg) for spent bentonite (SB), washed SB (SB-W) and virgin bentonite (VB)

Elements	SB	SB_W	VB
phosphorus (P)	3.93	13.87	0.24
potassium (K)	143.99	557.87	16.43
Magnesium (Mg)	13.26	50.65	27.80
Calcium (Ca)	8.06	33.00	43.46

3.1.2 physical properties

3.1.2.1 Gradation and specific gravity

According to Table 1 both VB and spent bentonite samples consisted of 100% fines (clay), 0 % sand, and 0% gravel. The virgin bentonite used in the process is only consisted of bentonite. This will increase the adsorption properties of the bentonite, and according to Table 1 while fermentation no changes occurred to the gradation. The specific gravity of VB was 2.67, it reduces to 2.61 for SB and it increases again to 2.63 after washing process. The decrease of the specific gravity of SB can be due to the fact that mixture of bentonite and organic matter have less specific gravity

since specific gravity of organic matters is lower than clay. The increase of specific gravity of bentonite after washing in SB-W samples can be justified accordingly, that is washing will remove a percentage of organic matters but not the total organic matters and the specific gravity will increase but not to the specific gravity of virgin samples.

3.1.2.2 BET Analysis

Figure 1 displays the nitrogen adsorption-desorption isotherms of VB and spent bentonites. According to Figure 1, nitrogen intake, slowly increases in the first half of the isotherm and it sharply increase in the second half of the isotherm. The samples exhibit a type II Brunauer-De-ming-Telleradsorption isotherm, and H₃ type based isotherm according to International Union of Pure and Applied Chemistry (IUPAC) guidelines. The H₃ type curve shows the slit shape pores in the samples. According to Table 1, the surface area in VB and SB was 23.43 m²/g, 6.86 m²/g respectively. This results show a decrease in SSA of VB bentonite (VB) after fining process. The reduction of SSA in the SB sample can be attributed to reduction of active sites in clay due to adsorption of organic materials in the solution. Organic molecules positively charged by protonation, surface acidity of the bentonite after addition to the wine, facile the adsorption of these ionizable molecules. As these molecules are adsorbed in active sites in clay the available sites for adsorption of nitrogen will decrease. The results of reduction in SSA in

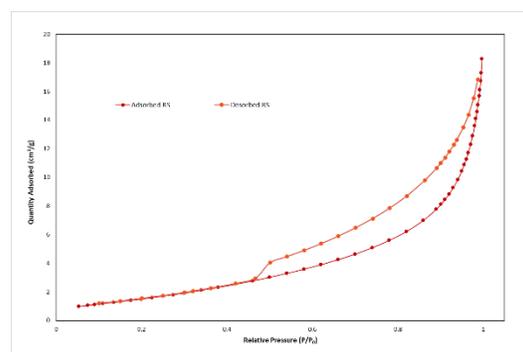


Figure 1- Nitrogen adsorption- desorption isotherms of Spent Bentonite

spent samples are in agreement with the results reported by (Wang et al. 2015), in which the surface area of an oil refining clay was reduced after storage. The reduction of CEC in the spent bentonite are in line with the results of reduction in SSA. The results of CEC in this research are not in agreement with the results of Pateiro-Moure et al. (2009) who reported an increase of 80 (cmol₍₊₎ kg⁻¹) units in bentonite CEC after fining of the wine which is removal of proteins which cause haze in the wine by adding bentonite.

3.2 Microstructural properties

3.2.1 SEM-EDS

Figure 2 shows the surface morphology and bulk elemental composition of VB, SB and SB_W samples. As shown in Figure 2, VB displays large particles with smooth surfaces and irregular flakes. In contrast, the spent bentonite morphology, Figure 2 (SB_W, SB) show a curly porous texture with rough small pores microstructure and smaller particles. The morphology changes to a more porous flaky anhedronal structure after washing (Figure 2 (SB_W)). The morphology of the washed samples is flocculated with increase in interlayer spacing and face to face and face to edge aggregation of particles. The flocculation of bentonite structure in SB and SB_W according to SEM images (Figure 2) can be justified using the double diffusion layer (DDL) proposed by (Gouy 1910; Chapman 1913). According to this theory the thickness of clay DDL is a function of ionic strength of the clay pore fluid. As the ionic strength of the pore fluid increases in acidic environment it causes a compression in thickness of DDL and flocculation of the bentonite structure.

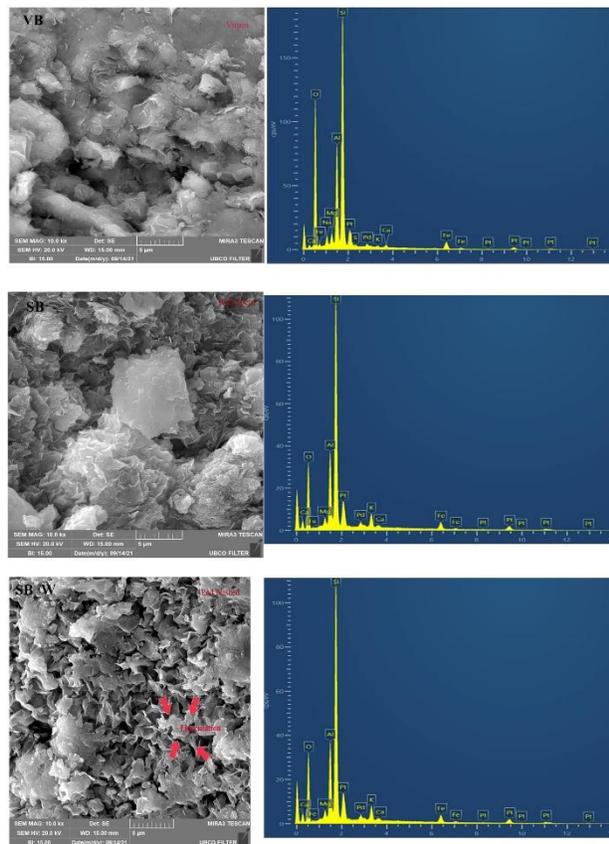


Fig 2. Surface morphology and bulk elemental composition of virgin bentonite (VB) , spent bentonite (SB) and washed SB_W

The ratios of Al/Si, Ca/Si, Ca/Al are presented in Table 3 according to EDS test. According to Table 3, the ratio of Al/Si in VB was 0.42 and decreased to 0.31 and 0.34, in the SB and SB_W respectively. Decrease in Al/Si ratios can be the result of solution of aluminum ions in acidic pore liquid of the soil (Sivapullaiah et al. 2009). The trend of changes in Al/Si ratios are compatible with the pH results. The Ca/Si and Ca/Al ratios increased in the spent and

washed samples in compare with the VB. The results of the EDS in Figure 2 also show a decrease of O and Na in the scanned faces in spent and washed samples in comparison with the VB bentonite.

Table 3 – EDS data for Virgin (VB), spent (SB) and washed bentonite (SB-W)

Elemental ratio	VB	SB	RB
Al/Si	0.42	0.31	0.34
Ca/Si	0.013	0.016	0.042
Ca/Al	0.030	0.055	0.125

3.2.2. Fourier transform infrared spectroscopy

The FTIR spectra of VB, SB_W, and SB (Figure 3) illustrates characteristic absorption bands of montmorillonite recorded in the 500 to 4000 cm^{-1} region. The spectra display Si-O-Si symmetric stretching vibration absorption bands at 779 and 795 cm^{-1} , Si-O-Si asymmetric stretching vibration at 1097 cm^{-1} and Si-O-Al bending vibrations at 521 cm^{-1} . These results are in agreement with (Mana et al. 2008). The band at 3696 cm^{-1} presents O-H stretching of inner and surface hydroxyl groups and the bands at 3454 cm^{-1} present O-H stretching of adsorbed water (Mullassery et al. 2015, Zhou et al. 2019). The adsorption bands at 1629 cm^{-1} show C=O carboxylate group of organic matters (Nuzzo et al. 2020) and bands at 1730 cm^{-1} represent ester carbonyl vibrations. The spectra of VB, SB and SB-W are not similar. The SB exhibited stronger intensity bands at 1730 cm^{-1} and 1629 cm^{-1} . In addition, new bands which appear at 2870 and 2926 cm^{-1} emerge in SB spectrum, are related to asymmetric and symmetric stretching vibrations of CH_2 (Liang et al. 2020) and band emerging at 1320 are attributed to the C-N stretching vibration of the aromatic primary and secondary amines and 1420 cm^{-1} shows the symmetric COO-stretching of carboxylates and 1436 cm^{-1} indicates $-\text{CH}_2$ or $-\text{CH}_3$ bending vibration assigned to organic matter. These weak bands indicate existence of organic matter in SB. The other difference between VB, SB and SB-W is the decrease in intensity of inner and surface hydroxyl groups and O-H stretching of adsorbed water in compare with VB.

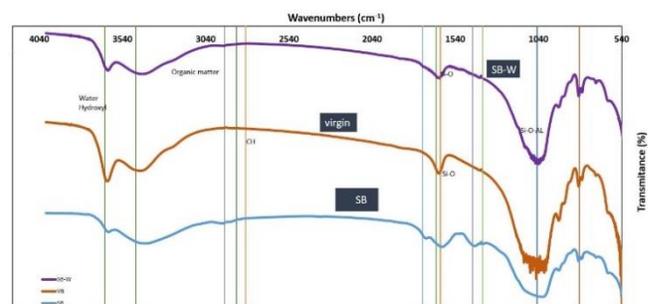


Figure 3 – FTIR spectra of the virgin bentonite (VB), spent bentonite (SB) and washed bentonite (SB_W)

3.3. Toxicological properties and ICP data

Table 4 shows the heavy metal concentration of VB and SB samples existing as bound cations. Sodium acetate is used to wash the bound cations. The results in Table 4 shows that there was no concentration of tin (Sn), mercury (Hg), thallium (Tl) and thorium (Th) as bound cations in virgin bentonite (VB) and spent (SB) samples. The concentration of lead (Pb), copper (Cu), arsenic (As), nickel (Ni), antimony (Sb) and iron (Fe) increased in the spent bentonite samples. These concentrations can be increased as result of additional ingredients before, during or after the fermentation process. The concentration of barium (Ba), uranium (U) and molybdenum (Mo) decreased after washing process. Also, the concentration of bound cations doesn't exceed the maximum permissible concentration of heavy metals.

Table 4- Concentration of heavy metals in virgin (VB), spent bentonite (SB) and washed bentonite (SB-W)

Heavy metal	Unit weight (g/cm ³)	SB_W (mg/kg)	SB (mg/kg)	VB (mg/kg)
Lead (Pb)	11.34	-	0.195	-
Barium (Ba)	3.59	-	0.63	1.197
Tin (Sn)	7.28	-	-	-
Copper (Cu)	8.94	0.187	0.61	0.035
Arsenic (As)	5.77	0.003	0.03	0.006
Mercury (Hg)	13.53	-	-	-
Cadmium (Cd)	8.69	-	0.002	0.001
Thallium (Tl)	11.85	-	-	-
Nickel (Ni)	8.91	0.007	0.038	0.001
Thorium (Th)	11.72	-	-	-
Uranium (U)	18.95	-	0.006	0.001
Antimony (Sb)	6.68	-	0.003	0.005
Iron (Fe)	7.87	6.41	28.38	0.424
Molybdenum (Mo)	10.22	-	0.01	0.006

4. CONCLUSION

The wine industry in Canada produces vast amounts of spent bentonite annually. Spent bentonite depends significantly on virgin bentonite, source of products and fermentation procedure as all of these alter the bentonite's structural, physical, and chemical properties. Finding the post-clarification changes in spent bentonite and its characterization is crucial for its further efficient and effective environment friendly applications.

In this study a set of laboratory experiments were designed to characterize the physical, chemical and toxicological characteristics of winery spent bentonite.

-The spent residues were characterized by low EC, acidic pH, high phosphorous and potassium, and low concentration of magnesium and calcium. Furthermore, organic matter contents of the spent bentonite increased 24.5 % in compare with the Virgin bentonite.

-Heavy metal analysis showed increase in the lead (Pb), copper (Cu), arsenic (As), nickel (Ni), antimony (Sb) and iron (Fe) of the spent.

- According to BET test, nitrogen adsorption trend shows a decrease in surface area of the spent bentonite in compare with the virgin bentonite. The decrease in the surface area of the spent bentonite can be due to the occupation of available sites on the surface of the clay by organic matters.

- Washing was effective in decreasing the concentration of the lead (Pb), barium (Ba), tin (Sn), arsenic (AS), iron (Fe) and molybdenum (Mo).

-The presence of the organic matter in the spent bentonite is proven by FTIR results. Organic matter adsorption leads to a decrease in specific surface area and cation exchange capacity of the spent material.

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