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Al-Quds University

Removal of total phenols compounds from Olive Mill Wastewater by using Phillipsite natural Zeolite

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Thesis Approval

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Jerusalem – Palestine

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Dedication

To my Family, my father and mother

To my Brothers.

Declaration

I certify that this thesis submitted for the degree of Master is the result of my own research, except where otherwise acknowledged, and this thesis or any part of the same has not been submitted for a higher degree in any other university or institution.

Name: Mohanad Fayiz Yousef Njoum

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Date: 12/4/2014

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ABSTRACT

Several methods include chemical oxidation, coagulation, froth flotation and adsorption are used for pretreatment of Olive Mill Waste water (OMW). Adsorption of phenols offers the best prospects for OMW pretreatment in case of using the filtrate as a fertilizer for agricultural purpose; due to its efficiency in selective removal of undesired pollutants, using materials such as carbon, sand, ash, agricultural by-products. Disposal of OMW into environment cause adverse effect to soil, surface water, and groundwater due high content of COD and toxic compounds mainly phenols and tannins.

Natural Zeolites are abundant and low cost mineral compared to other adsorbent such like activated carbon. Removal of organic pollutants from polluted surface waters and wastewaters using natural Zeolite has been investigated by many researchers indicating good efficiency of phenols removal and regeneration for polluted water, but little authors investigated the Zeolite efficiency for phenols removal from OMW.

Zeolite (Phillipsite) is used for phenol removal from OMW, Columns of packed Zeolite used to investigate the natural tuff tendency for phenols compounds removal from OMW using different columns of 5 cm depth.

Column one was packed with Zeolite of calibrated sieve diameters between 90 and 1000 µm. Column two with homogenized Zeolite of particles diameter less than 2000 µm. Column three with calibrated particles of diameter equal to or less than 90 µm. Column four of with homogenized Zeolite of particles diameter less than 2000 µm applied to synthetic tannic acid solution of about 5435 mg/l initial concentration to simulate OMW content of total phenols.

Phenols concentration in the effluents show total phenol reductions as follows; column one an initial reduction of 56% with an average reduction of 37%, column two an initial reduction of 63% with an average reduction of 33.8 %, column three show an initial reduction of 22% with an average reduction of about 12%, and column four shows ability for synthetic tannic acid removal trends to exceed 6 mg/g, with an initial percent of reduction of 98% and average reduction of 81%.

Results show that natural phillipsite Zeolite has a tendency for removal of phenolic compounds exists in OMW. The significant increase in the tannic molecules removal efficiency and improvement of the removal kinetics from synthetic tannic solution in comparison to that applied for OMW indicate the adverse effect of the suspended particle (44 g/l) of OMW on total phenols removal efficiency as phenols removal is independent of ionic strength. The mechanism of interaction is adsorption to either the hydrophobic sites of the surface of the Zeolite or complexation with hydrophilic sites (metal ions) which is pH dependent; thus the adsorption of the phenols from the OMW could be enhanced by controlling the pH of the OMW through the column.

إزالة مركبات الفينول الكلية من مياه الصرف الناتجة عن معاصر الزيتون باستعمال فيليبسايت زيولايت.

إعداد: مهند فايز نجوم.

إشراف: د. عامر مرعي

الملخص:

الصرف العشوائي لمياه الصرف الناتجة من معاصر الزيتون (الزيبار) دون أي معالجة يسبب أضراراً للتربة إضافة إلى تلوث المياه السطحية والجوفية بسبب التراكيز العالية التي يحويها الزيبار من مركبات الفينول. تتم معالجة الزيبار باتباع العديد من الطرق وتشمل الأكسدة والتخثير بالأمواج فوق الصوتية والتعويم والادمصاص. ويتم إزالة مركبات الفينول بطريقة الادمصاص التي تعتبر من أفضل الخيارات للمعالجة الأولية للزيبار وذلك بإزالة مركبات الفينول من الزيبار في حال استعماله كسماد زراعي طبيعي وذلك يعود إلى إزالة المركبات المراد التخلص منها (الفينول) مع الحفاظ على المركبات الأخرى في الزيبار كالنيتروجين والفوسفات والبوتاسيوم باستعمال مواد مثل الكربون المحفّز, والرمل, والرماد, والمنتجات الثانوية من مخلفات النباتات. عينات الزيبار تم جمعها من منطقة رام الله (قرية بيت ريما) في موسم عصر الزيتون 2011.

تناولت العديد من الدراسات إزالة مركبات الكربون من المياه السطحية والمياه الجوفية باستعمال الزيولايت الطبيعي, والتي تشير إلى فعالية إزالة مركبات الفينول باستعمال الزيولات الطبيعي, ولكن القليل منها تناولت إزالة الفينول من الزيبار. ومن الجدير بالذكر أن الزيولايت الطبيعي هو معدن متوفر بتكلفة زهيدة مقارنة مع غيره من المواد المستعملة في معالجة المياه بالادمصاص كالكربون المحفّز. في هذة الدراسة تم إستعمال الزيولايت الأردني الطبيعي من (جبل عريتان) في الأردن لإزالة الفينول من الزيبار في عدة أعمدة زجاجية معبأة بالزيولايت بعمق خمسة سنتيمترات, لدراسة فعالية الزيولايت بأقطار متفاوتة لإزالة الفينول من الزيبار. وأظهرت النتائج أن فعالية إزالة مركبات الفينول تفاوتت تبعاً لأقطار الزيولايت المستعمل. في العمود الأول تمت إزالة أولية بنسبة 56 بالمائة, وبمعدل 37 بالمائة من القيمة الأصلية الموجودة في الزيبار. والثاني إزالة أولية 63 بالمائة بمعدل 34 بالمائة. والثالث إزالة أولية 22 بالمائة بمعدل 12 بالمائة. بينما أظهرت النتائج

إزالة أولية بنسبة 98 بالمائة بمعدل 81 بالمائة من قيمة مركبات الفينول المجهز بالمياه المقطّرة, وذلك لدراسة أثر المركبات المعلقة في الزيبار على فعالية الزيولايت لإزالة الفينول.

أظهرت النتائج أن الزيولايت له القدرة على إزالة مركبات الفينول الموجودة في الزيبار من دون معالجة. كما أظهرت أن الزيادة الملحوظة في فعالية إزالة الفينول من المياه مقارنة مع الزيبار تُظهر الأثر السلبي الكبير للمعلّقات الموجودة في الزيبار (44 غم\لتر) على فعالية الزيولايت في إزالة مركبات الفينول. إضافة الى ذلك يمكن الاستنتاج من نتائج دراسات سابقة أكدت أن ميكانيكا التفاعل بين مركبات الكربون والزيولايت الطبيعي المستخدم هي إما الإدمصاص بين حلقة البنزين في مركبات الفينول مع الجزء الغير مائي من الزيولايت, بشكل مستقل عن درجة الحموضة. أو تفاعل حلقة البنزين مع الأيونات المعدنية على الجزء المائي من الزيولايت والذي يحفّز بزيادة درجة الحموضة نتيجة لتحسين الكثافة الإلكترونية على حلقة البنزين مما يحسن التفاعل مع الزيولايت وبالتالي يحفّز إزالة مركبات الفينول.

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Abbreviation

OMW: Olive Mill Waste water.

COD: Chemical Oxygen Demand.

pH: degree of acidity.

Adsorption: transferring material from the fluid phase to a solid phase.

CEC: Cation exchange capacity.

g: gram.

l: liter.

σ: surface charge (C m^{-2}).

GAC: Granular Activated Carbon.

Chapter One

Introduction

1.1 Background

Olive Mill Wastewater (OMW) generated by the process olive oil extraction is considered to be the main waste product of this industry. The uncontrolled disposal and treatment of OMW is a serious environmental problem because it contains high concentration of organic Chemical Oxygen Demand (COD) and high content of inhibiting compound such as phenol compounds and tannins, which results with OMW resistant to biological degradation. In addition, OMW contains polysaccharides, lipids, protein and aromatic molecules that inhibits anaerobic micro organism population (Khatib, et al., 2009).

OMW, also has negative impacts on the regional environment, due to toxicity towards micro organisms in domestic wastewater treatment plants in addition to strong unpleasant odour after anaerobic digestion, potential threat of phenol compounds to surface and ground water sources, and leaching of mobile species such as Na^+ and NO_3^- which occurs below one meter depth leading to increase of the salinity and pollution of the groundwater. However; surface irrigation of the OMW increase the fertility of the soil in the first 50 cm layer of the soil promoting minor changes in the soil chemical properties below this layer (Mekki, et al., 2007).

The US Environmental Protection had classified phenol compounds as high priority pollutants; They are products and raw materials of the following industries: petrochemical, oil refinery, plastic, explosives, azo dyes, pigments, leather, paint, pharmaceutical, coking plant, steel and pesticides industries (Uberoi, et al., 1997; Srivastava, et al., 2006).

The improper discharge of these compounds in water bodies over a long period can cause the deterioration of water environments, while its intake by both human and animals causes liver and kidney damage, central nervous system impairment, diarrhea and excretion of dark urine (Sarkar and Acharya, 2006).

1.2 Chemical Properties of OMW

Different steps of olive oil production effluents contain oil components including phenols, fats, and organic compounds of large molecular size, these compounds present in both dissolved form and as micro droplets. It is believed that the improper disposal of OMW to the environment is a significant source of environmental pollution because its negatively impacts on the soil due to its high organic matter and nutrient concentrations. Direct reuse of this wastewater in agriculture is limited by the phytotoxicity and antimicrobial effects due in particular to its high contents of phenolic compounds which range near to (5 g l^{-1}). The low pH that ranges generally between 4 and 5, and the presence of toxic fatty acids (Achak, et al., 2009).

According to (Roncero, et al., 1974), the olive mill liquid wastes have the following characteristics: Dark brown to black color, strong odor of olive oil, high organic load (COD up to 220 g/l), pH between (3-6), high electrical conductance, high poly phenol concentration (0.5 - 24 g/l), large concentration of suspending particles.

Chemical content, OMW could be divided to major two groups; first of undesired phenols and tannins which lead to adverse negative impacts on both ground water and soil properties, second of desired components such as carbohydrates and nitrogenous compounds upon using of the OMW as fertilizer. Among the organic substances in the liquid wastes, sugars represent a significant percentage of about 60% of the dry weight of the OMW, comprising mainly of fructose, mannose, glucose, and traces of sucrose. Significant components are also the water soluble phenols representing a class of organic compounds that contain one or more aromatic rings with one or more substituted hydroxyl groups and a functional chain. Due to their hydrophilic nature, a significant amount of phenols are lost to the liquid wastes. The major phenol types that have been found in OMW are phenyl acids, phenyl alcohols. The strong antioxidant nature of phenols renders them particularly resilient and non-biodegradable, thus complicating any detoxification process for the OMW. (Baddi, et al., 2009) reported that main biophenols occurring in Olive Mill Wastewater are; Tyrosol, Hydroxytyrosol, Oleuropein, figure (1.1).

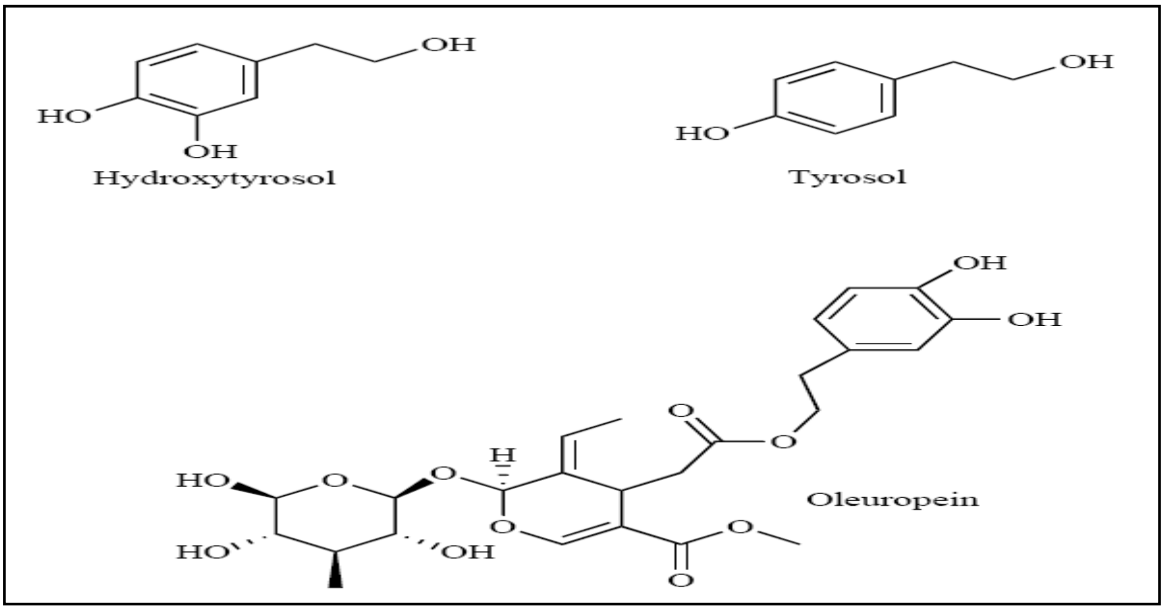

Figure (1.1): chemical structure of main phenol compounds founded in OMW.

(Hamdi, 1992) distinguished two phenol groups in the OMW. First group includes simple phenols which include non-auto-oxidizing tannins (small molecular weight) and flavonoids. The second group includes darker polymers, which occur from polymerization and auto oxidation of the compounds of the first group. Color of OMW depends on the ratio between these two groups and this fact explains why the wastewater gets darker when stored for a long period of time.

1.3 Environmental impact of olive mill waste water (OMW)

One of the most important characteristics of the olive mill liquid waste is its antimicrobial activity. This activity has been described and attributed mainly to its phenols content. However; there are opposing studies on the matter, since the antimicrobial activity of various concentrations of pure phenols does not always coincide with that of their corresponding concentrations in OMW, which seems to be induced by the presence of fatty acids (linoleic, oleic, linolenic, lauric and myristic), despite the fact that these acids are themselves not toxic (Lopez, et al., 1994).

From the basic poly phenols that have been detected in liquid wastes, methyl catechol has the highest antimicrobial activity, followed by catechol and hydroxytyrosol. For tyrosol there has been no detected antimicrobial activity. Furthermore, among the derivatives of the above phenols, o-cinone was particularly toxic, with acetylcatechol and guaiacol exhibiting only selective toxicity and polyphenols showing no antimicrobial activity (Capasso, et al., 1995).

It has been reported that the OMWs inhibit seed vegetation and plant growth (Greca, et al., 2001). This phytotoxicity has been attributed to their phenolic content as well as to some organic acids, such as acetic acids, produced during storage. It was observed that even after phenol removal, OMW's plant toxicity wasn't nullified, suggesting that it was not totally attributable to phenols (Capasso, et al., 1995).

The detrimental effect of olive mills waste waters on the various aquatic ecosystems, where are usually illegally disposed, is also very significant due to their proven toxicity. In several toxicity bioassays, this effect has been attributed mainly to the biodegradable tannins – and to a lesser extent to the non-degradable phenols compounds (Paixao, et al., 1999), as well as to catechol and hydroxytyrosol (Fiorentino, et al., 2003).

1.4 Impact of pretreatment of Olive mill wastewater (OMW)

Most researches indicate that spreading big amounts of OMW on the fields can cause damages to soils, groundwater and yields, due to their high content of phenolic substances (Limiroli, 1996; Perez, 1992), and their organic composition and the effects their organic matter can cause on the micro-biological dynamics of the soil (Proietti, 1995; Lopez, 1996). Furthermore, a moderate phytotoxic residual phenolic fraction from the superficial soil layer one year after the OMW application is of a phytotoxic potential comparable to that of 25-fold diluted OMW (Mekki, et al. , 2007).

Proposed methods for treating OMW, such as evaporation ponds, thermal treatment, physicochemical and biological treatments, and reuse of the OMW by distribution in agricultural soils as an organic fertilizer was studied. Physical-chemical pretreatment methods affect the reduction of the organic load in olive mill wastewater (OMW), in addition to removal of phenolic compounds present in OMW, achieving lower volatile and dissolved total phenol and less COD concentrations. Pretreatment of OMW enhance the anaerobic activity of the sludge in the batch systems significantly. Also; poly-phenols reduction by at least 50% concentration significantly alter and improve the OMW dynamics and interaction with soil permitting larger doses to be applied sufficiently enhancing the biological activity of degradation of organic load during land treatment with OMW. Thus; dilution and/or some type of pretreatment of the OMW in order to reduce the toxic effects on the environment are necessary to avoid toxicity of the phenols on the methanogen (Mekki, et. al., 2007).

1.5 Natural Zeolite

Depending on their geological setting, mineralogy and genesis, zeolites are formed either in closed system, open system, burial metamorphic, hydrothermal, deep marine or weathered zones (Sheppard, 1971; Mumpton, 1973).

Zeolites are crystalline hydrated alumino-silicates forming a three-dimensional framework of crystals. Tetrahedrons are the primary building blocks of zeolite crystals. Each tetrahedron is composed of a silicon or aluminium atom positioned in the middle and four oxygen atoms at the vertices (Ouki, et al., 1994). Each oxygen atom is shared between two tetrahedrons. Arrangement of these tetrahedrons in a crystal creates a framework with interconnecting channels of constant diameters range between 2 to 10 Å (Mumpton, et al., 1973).

The general chemical formula of zeolites is $Mx/n[AlxSiyO2(x+y)].pH2O$. Aluminium, silicon and oxygen atoms are referred to as structural atoms because they make up the rigid crystal framework. The cations denoted by M in the chemical formula (Na^+, K^+, Ca^{2+}, Mg^{2+}), can easily be exchanged by cations present in aqueous solutions with little effect on the alumino-silicate framework, M represents the cation of valence n, x is general equal, and p is the number of water molecules (Tsitsishvili, et al., 1992). The sum of (x+y) represent the total amount of tetrahedral while the portion with [ ] defines the framework composition. Based on the specific array of AlO_4 and SiO_4 tetrahedrons, zeolites are classified into: analcime, phillipsite and laumonite, erionite, synthetic zeolite A, chabazite and synthetic zeolite X, natrolite, mordenite and ferrierite, and clinoptilolite and heulandites (Breck, 1974).

1.5.1. Jordanian Zeolite:

Zeolites in Jordan were first discovered by Dwairi (Dwairi, 1987). The Jordanian phillipsitic tuff has a good efficiency in ammonium removal from wastewater, as good as Hungarian clinoptiololite, but phillipsite is more selective for ammonium ions (Dwairi, 1991). In addition, it was found that the Jordanian phillipsite is of good efficiency for cesium fixation and immobilization from nuclear waste in comparison with phillipsitic rich tuff from California and moderate rich tuffs from Arizona and Nevada (Dwairi, 1992). (Ed-Deen, 1998) evaluated zeolites from Tell Rimah for industrial wastewater treatment. The results have indicated that Tell Rimah Zeolitic tuff showed high selectivity for the removal of Cu, Cr, Ni and Zn from Electroplating Factory effluents and could be used for removing Pb and Fe from the wastewater of the Battery Factories. (Dwairi, 2007) studied the characterization of Jordanian zeolitic tuff and its potential use in wastewater treatment. He studied the mineralogy and geochemistry of all zeolitic tuff localities in Jordan and evaluated Jordanian natural zeolitic tuffs obtained from Hannoun (HNZ) and Mukawir (MNZ) volcanoes for removing selected heavy metals (Zn and Pb) and total organic carbon from domestic wastewater. The results showed that the main zeolite minerals are: phillipsite, chabazite, faujasite and analcime. The environmental experiments showed that HNZ and MNZ are suitable for domestic wastewater treatment.

(Yousef and Eswed, 2009) characterized the Natural Jordanian zeolitic tuff from Jabal Aritayn; the chemical composition of Jordanian zeolitic tuff obtained from XRF analysis is given in (table 1.1). He reported that channels diameter of phillipsite which is the major constituent of Jordanian zeolitic tuff ranges from 3.2 to 4.3Å. The Si/Al ratio calculated from these data was found as 2.6 (Yousef and Eswed, 2009).

Table (1.1): chemical composition of the natural Jordanian Zeolite.

Compound	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	TiO_2	K_2O	Na_2O	P_2O_5	L.O.I
Wt %	42.01	14.10	11.34	0.33	10.33	8.42	2.15	0.93	1.92	0.43	8.04

(Dwairi, 2009) evaluated the Jordanian phillipsitic tuff from Al-Ataita volcano for applications in wastewater treatment. He concluded that Al-Ataita phillipsitic tuff shows good removal percentages of ammonium from municipal wastewater. (Dwairi, 2010) used southern Jordanian zeolitic tuffs (Jabal Uniza) as pollutant control in removing heavy metals from industrial wastewater plants. He concluded that Jabal Uniza zeolitic tuff has a good removal percentage of heavy metals (Cd and Mn) from industrial wastewater.

Southern Jordan volcanic eruptions consist of many volcanic coins. Tall Juhira volcano is one of these coins. It lies about 175 km south of Amman, with a height of 1144 meters above the sea level. Lithologically, Tall Juhira volcanic rocks are 110 meters thick and comprise well bedded lapili and ash. The dominating zeolites in Tall Juhira zeolitic tuff are chabazite as the major mineral and phillipsite and fuajasite as minor minerals (Dwairi, 2007).

1.5.2. Structural properties of Zeolite:

Their deep and wide pore openings are just one of few characteristics which enable Jordanian Zeolite tuff to remove various contaminants. Another characteristic of Zeolite is their large surface area of 49 m^2/g with channel diameter range between 3.2 to 4.3 Å (Yousef, 2009).

1.5.3. Ion Exchange of Zeolite:

The structure of the natural Zeolite is suitable for ion exchange due to isomorphism: the replacement of Al^{3+} with Si^{4+} in the structure, giving rise to a deficiency of positive charge in the framework. This is balanced by mono and divalent exchangeable cations such as Na^+, Ca^{2+}, K^+ and Mg^{2+}. The main consequence of this structure type is represented by the reversibility of hydration and cation exchange processes that preserve the original network. Thus, they present specific properties (e.g., adsorption desorbtion capacity, ion exchange capacity, catalytic properties), which confer to this group of minerals important and diverse possibilities of usage. Ion exchange capacity and cation selectivity are the most important properties for zeolite as a natural molecular sieve material for wastewater treatment. Ion exchange is a process where insoluble substance removes ions of positive or negative charge from an electrolytic solution and releases other ions of similar charge into the solution in a chemically equivalent amount and Cation selectivity refers to the preference order of zeolite for cations based on the various factors which determine the selectivity. Ion size, valence and hydration energies are important factors in determining the selectivity of a given ion in a specific system. The zeolite prefers or is more selective for certain cations and less selective for others; (Liang Z and Ni J., 2009) have used natural zeolite to remove ammonium ions from wastewater and (Rahmani, A. et al., 2009) have demonstrated preferred method for removing traces of NH_4^+ from fresh hatchery water is a possible method to satisfy the standard for water reuse, the proposed design has used an ion exchange using natural clinoptiololite.

1.5.4. Chemical behavior of natural Zeolite in aqueous solutions:

The chemical behavior of the natural Zeolite is dependent on the chemical composition of the Zeolite, mainly the ratio of the silica to alumina as follows;

- Low silica Zeolite is more reactive in distilled water compared to high silica Zeolite.
- Low silica Zeolite shows a tendency to neutralize the solutions (1M NaCl) behaving either as a proton acceptor or as proton donor.

This is related to the H^+ uptake, as well as to the OH^- attack to surface reactions sites of the crystals. However, interaction of the hydrogen ions with the alumino-silicate framework of the Zeolites caused in a small extent, degradation-dissolution phenomena, resulting in surface eroded crystals. This physicochemical phenomena depends on

1. the structural characteristics and the chemical composition as well as,
2. the acidic/basic sites existing in the micro-pores structure of the Zeolite which are also responsible for the chemical behavior in aqueous solutions.

Low dissolution rates and adequately acid resistance of high silica Zeolites such as Clinoptilolite, heulandites, phillipsite were reported (Filippidis et. al., 1996). The chemical behavior of the natural Zeolite in aqueous solution depends on the nature of the solution as follows;

● The chemical behavior of the natural Zeolite in saline aqueous environments:

- Several natural Zeolitic species are formed or transformed under such conditions.
- pH is an important factor which controls the mineral in the saline, alkaline Zeolite deposits.

● The chemical behavior of the natural Zeolite in distilled water (basic range):

- Higher pH increase of distilled water for low silica Zeolite than high silica Zeolite. This attributed to more $Si-(O^-)-Al$ basic sites results in higher hydrogen ion uptake.
- The increase of pH in the acidic range mainly attributed to biding of protons to the basic sites $(> Al-OH+H^+)$= $(> AlOH_2^+)$. And lesser extent to the H^+ absorption through ion exchange reaction.

● The chemical behavior of the natural Zeolite in distilled water (acidic range):

The decrease of the pH in the basic pH range could be the result of:

- The removal of protons from the acidic surface sites;

$$(> Si-OH+OH^-) = (> SiO + H_2O).$$

- Detachment of protons from water molecules surrounding the exchangeable cations caused by OH^- attack on the zeolite.
- Acid treatment initially cause rapture of Al-O bonds, furthermore; Hydrolysis reactions and detachment of Si and Al species.

1.6 Problem Statement

Palestine is experiencing a severe water crisis caused mainly by the lack of control over the Palestinian water resources; due to the decreasing availability of fresh and suitable water resources to the Palestinians, in view of the increasing water demands, combined with the associated political complexity related to these limited, and mostly shared water resources (UNDP, 2013).

Approximately 1.8×10^6 tons of olive oil are produced annually worldwide where the majority of it is produced in the Mediterranean basin (Benitez et al., 1997). The average amount of olive mill wastewater produced during the milling process is 1.2–1.8 m^3 ton^{-1} of olives (Sabbah, et al., 2004). The total quantity of olives pressed in 2012 was 104,763 tons (figure 1.2). The ratio of produced OMW during milling of each ton of olive in West bank is 1.5 m^3 ton^{-1} as each ton of olive requires about 1.5 m^3 of water for washing, results with about 157144 m^3 of OMW in 2012 which are disposed with no control nor treatment (PCBS, 2013).

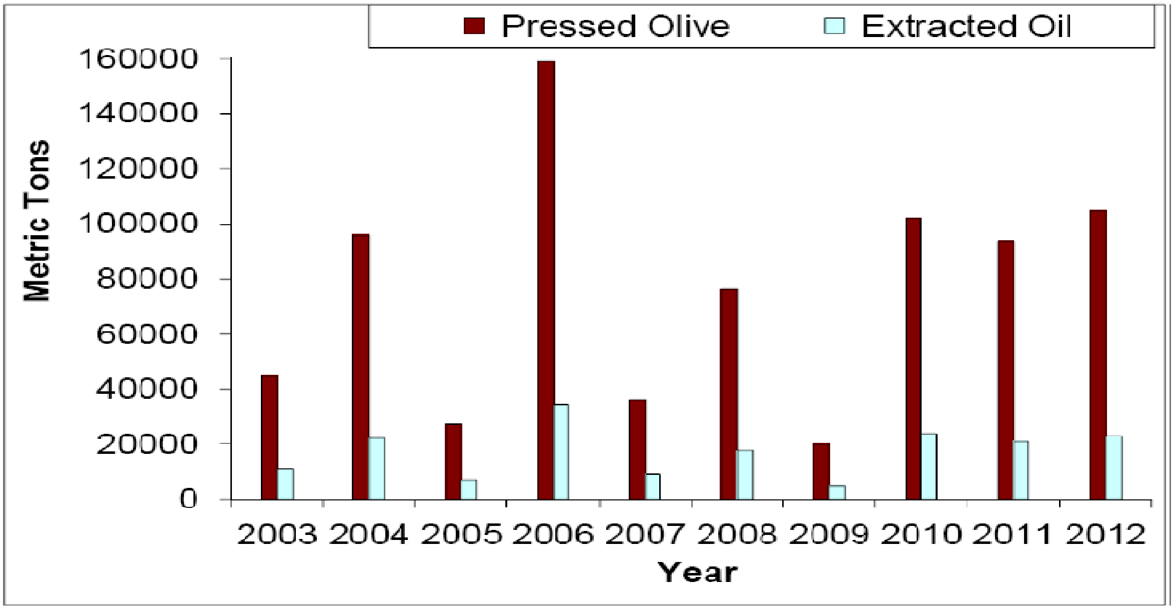

Figure (1.2): quantity of pressed olive and extracted oil in Palestine for the years 2003-2012.

Disposal of OMW with no control and treatment; causing a serious environmental problem due to high organic chemical oxygen demand (COD) concentration and a major problem of high content of microbial growth - inhibiting compound such as phenolic compound and tannins with concentration of 5500 mg/l, contaminating surface and groundwater. The improper disposal cause pollution of the soil, surface water, and groundwater (Comenzana, et al., 1995). (Mekki, et al., 2007) work aimed to characterize a soil after being amended with raw OMW demonstrating that the toxic effect of the OMW phenolic compounds, persist or change and keep their toxicity even long after the spreading period; in spite of microbiological activity of the soil to degrade and to attenuate these chemicals, as they infiltrate in soil and can pollute the groundwater. However, their results show that phenolic concentration decreased rapidly from 0 to 25 cm depth then continued to decrease weakly with depth but remained even detectable at 120 cm (Mekki, et. al., 2007).

“OMW amendment without pre-treatment seems to affect the structure and the composition of the soil.” (Mekki, et. al., 2007) concluded during spreading of OMW. The increased application of untreated OMW doses increased the total phenolic compounds content in all layers with the majority kept in the soil upper layer (0-25 cm) with decreasing of phenolic compounds of high molecular mass with depth while those of low molecular mass remained abundant. They also mentioned that polymers of low retention time were detected in the upper layer while phenolic compounds of high retention time infilterated in deeper layers of the soil (50-120 cm). they also proved that the extracted phenolic fraction from the treated soil to be phytotoxic to plant B. cernua. The study show that the dilution of OMW has an effect on the germaniation index test and the phytotoxicity of the phenolic compounds. Their study released that OMW amendment without pretreatment seems to affect the structure and the composition of the soil, due to the presence of phenolic compounds at different depths of all the OMW amended soils (4 months after OMW spreading), the germination index delay or even a total absence of the B. cernua germination (Mekki, et. al., 2007).

Physical treatment, chemical treatment, oxidation and vacuum evaporation processes were being applied to OMW taken from olive oil processing mill using one by one or all together of different treatment techniques. However, the rate of anaerobic biodegradation for OMW was found to be dependent on the physico-chemical pretreatment of OMW as it enhances the anaerobic biodegradation rate for OMW (Sabbah, et al., 2004). The physic-chemical pretreatment affected the removal efficiency of 40% increase relative to water diluted OMW for the same initial COD concentration and biomass concentrations of (20 g l^{-1} using PriGat biomass); a finding attributed to the high removal efficiency of polyphenols and other toxicants by the proposed pretreatment process for OMW (Khatib, et. al., 2009).

Several methods include chemical oxidation, coagulation, froth flotation and adsorption are major processes may be used for pretreatment of OMW (Singh and Rawat, 1994), adsorption seems to be most of all the methods offers the best prospects for overall treatment. But the use of some materials (e.g. carbon) as an adsorbent is of limited use because its high cost. Thus, it is necessary to look for using low cost materials (sand, ash, agricultural by-products). The use of these materials in the removal of organic pollutants from polluted surface waters and waste waters has been investigated by many researcher indicating good efficiency of treatment, but little was detailed for OMW poly-phenols treatment (Achak, et al., 2009).

Activated carbon is often the preferred adsorbent for the removal of organic compounds due to its high adsorption capacity (Stoeckli, et al., 2001; Haghseresht, et al., 2002). The non economical and the difficulty in regeneration of some high cost adsorbent such as granular activated carbon (GAC) are drawback faced when an adsorbent after adsorption are irreversible or not regenerated for another application. Hence, the disposal of an adsorbent as a waste after adsorption is not an economic option unless the adsorbent is of a very low cost. Thus, it is necessary to look for using low cost materials (e.g. agricultural by-products). The use of such low cost materials in the removal of organic pollutants from polluted surface waters and waste waters has been investigated by many researcher indicating good efficiency of treatment, but little was detailed for OMW poly-phenols treatment.

However; the use of activated carbon as an adsorbent is of limited use because its high cost, it suffers from its high cost and the irreversible nature of adsorption (Rengaraj et al., 2002). (Lin et al.; 2009) reported approximate cost comparison of some adsorbents which could be used for phenols adsorption; activated carbon (20-22 US$/Kg), natural zeolite (0.03-.12 US$/Kg), coal (0.19-0.15 US$/Kg), clay (0.04-0.12 US$/Kg)..

Most of these adsorbents need some specific condition to obtain the optimal adsorption performance, such as pH, temperature, initial pollutant concentration, density, and so on. The natural zeolitic tuff seem to be appropriate sorbent for its high flexible characteristics upon different treatment methods such as acid, thermal, salt modification, surfactant modification; altering its properties to meet the OMW requirements for specific content pollutant (poly-phenols) removal in addition to its relatively low cost (Singh and Rawat, 1994). Thus; the Zeolite seems to be a promising alternative adsorbent considering selective removal of specific pollutants from wastewaters. Although, the molecular diameter of the most simple phenol molecule (C_6H_5OH) is 4.3 Å, which still equal to the greatest pore diameter of the Jordanian structure (Yousef and Eswed, 2009).

1.7 Theory of Adsorption of Phenol Compounds Onto Natural Zeolite

In addition to the ability of the natural Jordanian Zeolite to selectively adsorb dissolved cation in a solution, it shows a tendency for adsorption of phenol compounds from aqueous solutions; this adsorption is significantly altered by the pH of the solution; since the solution pH affects both the phenols compounds of the solution and the net charge of the Zeolite (σ Cm^{-2}), figure 1.3 (Yousef and Eswed., 2009).

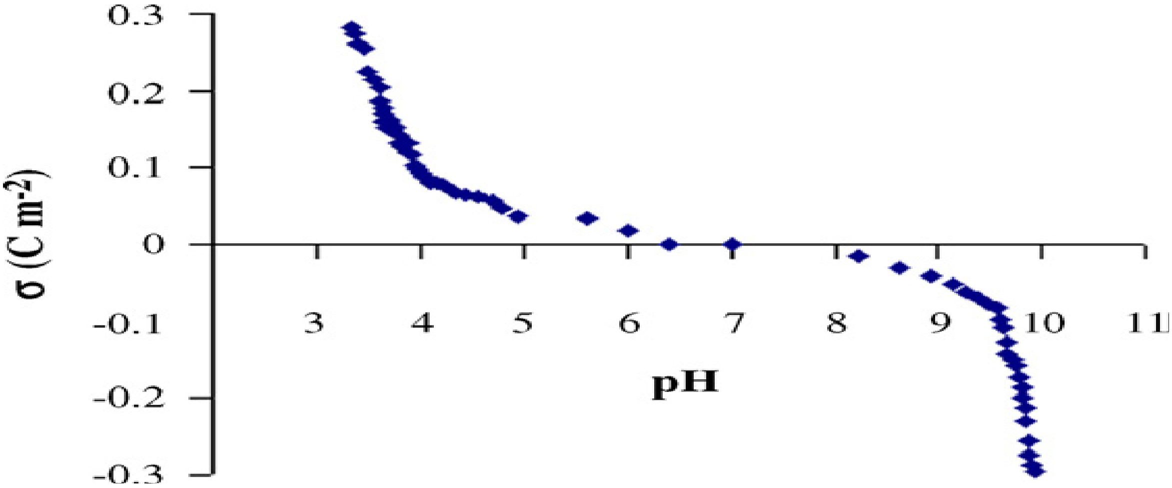

Figure (1.3): A plot of pH versus surface charge of zeolitic tuff (pHpzc = 6.9).

The point of zero charge of the natural Jordanian Zeolite is 6.9, solution pH also affect the phenol compounds as it controls the chemical formula converting it to phenolate by losing the hydrogen of the phenol hydroxyl groups when pH exceeds or equal the pKa values. where two types of interaction between phenols and the Zeolite were quantified (Yousef and Eswed, 2009);

1. pH independent interaction of phenols with hydrophobic sites of zeolite.

   This is the pH independent interaction of aromatic ring of phenols with the hydrophobic sites of zeolite.

2. the pH-dependent phenolate complexation with hydrophilic sites of zeolite (metal ions).

This is the pH-dependent phenolate complexation with metal ions on the hydrophilic sites of zeolite surface.

The adsorption of phenol, 2-chloropenol, 4-chlorophenol, 2,4-dichlorophenol, and 3,5-dichlorophenol enhanced with increasing pH values due to the increase of phenolates complexation with metal ions on zeolite surface. The number of hydrophobic sites of zeolite available for phenols was found to be greater than that of the hydrophilic sites. On the other hand, the affinity constants of the hydrophilic sites were found to be much greater than those of the hydrophobic sites (Yousef and Eswed, 2009).

The adsorption process of phenols onto zeolite was found to be independent on the ionic strength. The adsorption increases with increasing pH, due to the increase of phenolates complexation with metal ions on zeolite surface. The size of phenol determines their order of adsorption capacity onto the surface of zeolite, where phenol and monochlorophenols revealed higher adsorptivity than dichlorophenols (Yousef and Eswed, 2009).

1.8 Hypothesis

Natural Zeolite reduce total phenols compounds in OMW; mainly by reactions occurring on the external surface area of the mineral due to the size of the pores space of used phillipsite with maximum value of 4.3 Å which is the same for molecular diameter of the most simple phenol compounds (C_6H_5OH), using simple columns of packed Zeolite with appropriate depth without any chemical treatment of Zeolite.

1.9 Objective

To investigate the efficiency of the natural Jordanian Zeolite for the removal of the phenol compounds and tannins from OMW; through Zeolite columns dependent on the volume of the treated effluents and maximum column capacity of OMW.

Chapter Two

Literature Review

(Khatib et al., 2009) reported that The OMW is usually discharged in the open environment, thus producing pollution to the soil surface and underground water, their Approach was to reduce the chemical oxygen demand (COD) as a major OMW pollutant.

In the last decade, most of the research conducted on OMW treatment has been focused on the use and development of anaerobic methods and bioreactors that can remove efficiently the high organic load as well as reduce the toxicity of microorganisms-inhibiting materials present (Boari, et al., 1984; Benitez, et al., 1997; Paredes, et al., 2001).

(Benitez, et al., 1997; Martin, et al., 1991; Zemman, et al., 1997) reported that anaerobic bacteria decompose organic materials in a three-stage process In the first stage, anaerobic bacteria degrade complex organic materials into simpler compounds; namely, polysaccharides and polyphenols are converted to their monomers (monosaccharides and phenols, respectively).

During the second stage, acetogenic bacteria convert the phenols and the monosaccharide into organic acids, such as acetic, lactic and formic acids and alcohol. Finally, in the third stage, methanogenic bacteria, which are characterized by their sensitivity to pH, convert the organic acids into biogas (a mixture of 60–80% methane and other gases, mainly carbon dioxide).

Removal of organic pollutants and nutrients from olive mill wastewater by a sand filter was studied by (Achak, et al., 2009). OMW diluted with domestic waste water in one to one basis, the dilution is expected to enhance biological processes in the sand filter and ensures an important elimination of the organic load. The dilutions of OMW by 50% of domestic wastewater allowed a reduction of total suspended solids and organic matter, total suspended solids decrease by about 62%. Their enrichment by microorganisms of the domestic wastewater makes it possible to have a strong mineralization of the organic matter (Achak, et al., 2009).

Treatment of OMW using lime was investigated and was found to reduce the polluting effect of OMW by high percentages in an applicable method due to its low cost, and to enhance liquid evaporation in ponds after treatment more easily than raw OMW; due to the removal of the large quantity of fatty Components which forms an impermeable film on the surface of the waste water in the ponds, which do not permit the evaporation of water from the OMW. Total solids, volatile solids, poly phenols, volatile phenols, nitrogen, and oil grease removal range between 60% to 90%, and carbohydrate reduction up to 30% related to applied lime amounts (Aktas, et al., 2001).

As carbohydrates and nitrogenous compounds removal from OMW at high percentages(50–70%) after treatment with lime reduce the possible advantages of using the filtrate as a fertilizer for agricultural purpose (Aktas, et al., 2001). This disadvantage seems to be undesired potential effect upon land application of OMW.

Zeolite show considerable total phenol removal from OMW in comparison with clay and Bentonite with more possibility of Zeolite minerals regeneration and recovery for reuse in new total phenol removal (Santi, et al., 2008).

Chapter Three

Materials and Methods

3.1 Natural Jordanian Zeolitic tuff

Natural Jordanian Zeolite (from Jabal Aritayn) was crushed, homogenized, and sieved to different particle size portions. These sieve fractions were used for preparation of the four columns of different parameters dependent on the porosity as much as the surface area of the Zeolite. The sieve used are of the following diameters; 2000 µm, 1600, 1000, 710, 500, 250, 200, 160, 90, 75, 63, and less than 63 µm.

3.2 Preparation of the Zeolite Columns

Four columns of well packed crashed Zeolite were used for investigation of the phenols removal.

3.2.1. Column One:

The natural Zeolite of equal weight portions of sieve diameter between 90 µm and 1000 µm calibrated of equal weights and homogenized from sieve portions of 90, 160, 200, 250, 500, 710, and 1000 µm. They were well mixed and packed in glass cylindrical column of a diameter of 5 cm and 30 cm length. The Zeolite was packed until a bed depth of 5 cm was achieved. About 100 grams of the Zeolite needed for the column to obtain the desired depth of the Zeolite bed.

3.2.2. Column Two:

Natural Zeolite crashed and sieved through 2000 μm diameter sieve, sample of residual fractions (less than 63, 63, 75, 90, 160, 200, 250, 500, 710, 1000, and 1600 μm) well mixed and packed in glass cylindrical column of a diameter of 5 cm and 30 cm length. The Zeolite was packed until a bed depth of 5 cm was achieved. About 150 grams of the Zeolite needed for the column to obtain the desired depth of the Zeolite bed.

3.2.3. Column Three:

The natural Zeolite of equal weight portions of sieve diameter less than or equal to 90 μm calibrated of equal weights and homogenized from sieve portions of 90, 160, 200, 250, 500, 710, and 1000 μm. They were well packed in glass cylindrical column of a diameter of 5 cm and 30 cm length. The Zeolite was packed until a bed depth of 5 cm was achieved. About 100 grams of the Zeolite needed for the column to obtain the desired depth of the Zeolite bed.

3.2.4. Column Four:

Natural Zeolite crashed and sieved through 2000 μm diameter sieve, sample of residual fractions (less than 63, 63, 75, 90, 160, 200, 250, 500, 710, 1000, and 1600μm) well mixed and packed in glass cylindrical column of a diameter of 5 cm and 30 cm length. The Zeolite was packed until a bed depth of 5 cm was achieved. About 150 grams of the Zeolite needed for the column to obtain the desired depth of the Zeolite bed. This column was used for synthetic tannic acid solution application instead of OMW.

Table (3.1): Zeolite properties versus applied solution of each column.

column	**particles size (μm)**	**Zeolite (g)**	**solution type**	**effluent (ml)**
1	90 ≤ Particles ≤1000	100	OMW	150
2	particles < 2000	150	OMW	90
3	particles ≤ 90	100	OMW	150
4	particle < 2000	150	tannic acid	250

3.3 Olive Mill Wastewater

Olive Mill Wastewater (OMW) samples from West bank olive trees were collected directly from two phases olive mill in Rama allah region (Bait Reema village), then stored in poly ethylene containers underground in darkness. OMW samples were well shaken before experimental application to natural Zeolite and were filtered to reduce the effect of the high total suspended solids in the OMW using natural sand columns. Sand was washed with distilled water and oven dried over night at 60 ºC before being used for OMW filtration to remove any impurities may be contaminated within the sand particles. Total phenol content was measured before and after each experimental application of OMW to Zeolite.

3.4 Sampling of Olive Mill Wastewater

Samples of olive mill wastewater (OMW) were collected from Ramallah region which is intensively cultivated with olive trees from Bait Reema Village locates (x= 159910, y= 159931) at elevation of about 500 meters above sea level. These samples were collected from the season 2011 (figure 3.1). OMW samples stored in dark underground were used for the column experiments hold for the examination of the natural Zeolite ability for the removal of the poly phenols compounds from OMW.

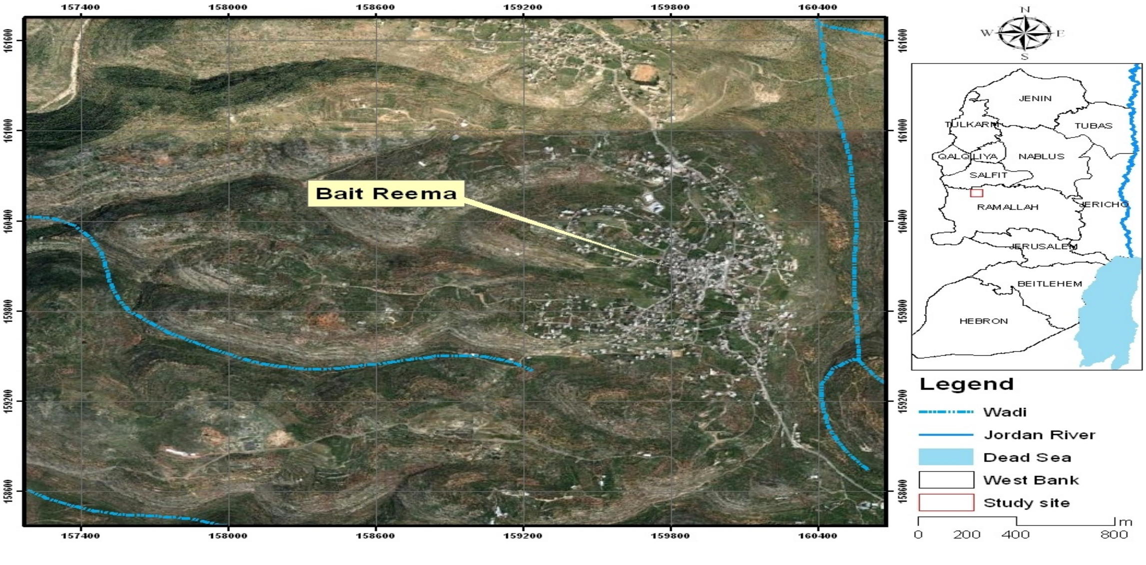

Figure (3.1): location of the sampling region.

3.5 Tannic acid solution

Solution of synthetic tannic acid prepared by dissolving of about 5500 mg of pure tannic acid in one liter distilled water

3.6 Application of OMW into Zeolite Columns

Column experiments were applied to investigate the tendency of the Natural Zeolite tuff for removal of the total phenols from OMW. Column experiments enhance the efficiency of the adsorption process of the total phenols from OMW by managing the exposure of the adsorbent to the OMW ensuring most possible infiltration and sorption of pollutant gradually to the exchange sites of the tuff. Moreover; columns experiments are much more simulated to the actual wastewater treatment plants of the wastewater than batch experiments. The removal depends on the adsorbent properties (e.g. pore volume, particles diameter, CEC), sorbent properties (e.g. molecular diameter, polarity, hydrophilicity, suspended solids).

The ability of the natural Zeolite for the removal of the phenolic compounds from the OMW samples was tested by using this Zeolite for the removal of tannins compounds from a synthetic solution of concentrations simulating those exist in the OMW. Synthetic solution of tannins concentration of about 5370 mg/l tannic acid dissolved in distilled water was applied for a column of natural Zeolite of particles diameter of less than 2000 μm of bed depth of five cm. The application of the synthetic tannic acid solution of concentration simulates those of total phenols in the OMW provide a comparison between the different phenol compounds exists in the OMW and the most complicated form of phenols considering the tannic acid solution. Application of tannic solution indicate the effect of different components rather than phenols of OMW on the removal efficiency (effect of OMW components on interaction between phenol compounds and Zeolite surface). Nutrients in OMW, sugars, carbohydrates, fatty acids and nitrogenous compounds may affect the phenol compounds removal physically and/ or chemically due to high total suspended solids of the OMW, as much as the behavior and interaction of phenols compounds with these components within the OMW upon the possible changes of the OMW chemical and physical properties during application on to the Zeolite. The filtered OMW was applied into the natural Zeolite columns immediately after filtering through the sand columns.

3.6.1. Zeolite of particles size between 90 µm and 1000 µm:

Filtered OMW was applied to the column in order to reduce the effect of the total suspended solids content in the OMW. About 150 ml of OMW were able to percolate through the column successfully before the clogging of the column with OMW percolated through.

3.6.2. Zeolite of particles size less than 2000 µm:

Filtered OMW applied for column of Zeolite of particles diameter less than 2000 µm. From the 225 ml applied to the column in portion of 100, 100, and 25 ml, only about 90 ml of OMW was able to percolate through the column successfully, then clogging state was reached

3.6.3. Zeolite of particles equal or less than 90 µm:

Only 150 ml of OMW of the 200 ml applied were percolated through the column before clogging state.

3.6.4. Zeolite of particles size less than 2000 µm (Tannic acid solution):

Tannic acid solution of 5506 mg/l applied for column of Zeolite of particles diameter less than 2000 µm. All the 300 ml applied to the column in portion of 100, 100, and 100 ml percolated through the column successfully.

3.7 Characterization of OMW

3.7.1. Total Phenol Concentration:

Total phenols concentration in OMW before and after application into Zeolite columns were measured. Application of OMW was continued until clogging of the column was reached. This amount of treated effluent was analyzed for total phenol concentration in sequence samples of several portion in order to describe the behavior of the total phenol concentration in the OMW through the column with respect to the volume treated, where finally the Zeolite: OMW treated ratio can be concluded.

Total phenol were determined by following the Folin- Ciocalteau method according to the standard method for the examination of water and wastewater. 20th edition. By addition of one ml of Folin- Ciocalteau reagent into 50 ml of diluted sample to a suitable dilution factor, normally (1:500) dilution factor. Then, 10 ml of carbonate tartrate reagent prepared by dissolving 200 g (Na_2CO_3)and 12 g sodium tartrate in 1 liter distilled water. Then absorbance was measured at 700 nm wavelength after 20 minutes using uv-spectrophotometer. The values of the absorbance were related to a standard solution calibration curve of tannic acid solutions of concentrations 1, 2, 4, 8, 16, 32 mg/l to calculate value of total phenols concentration (mg/l).

3.7.2. Total Suspended Solids:

Total suspended solids in the OMW samples was measured for different samples of OMW; samples of OMW were well mixed to ensure homogenous content of all the suspended particles that exists in OMW. Known volumes of well mixed OMW were weighted and filtered though cellulose filter paper of micro pores of 2.5 micrometer in diameter, these filter paper were dried at 60 ºC over night then weighted using sensitive balance, the filtering was repeated using different filter papers till no suspension were noticed on the filter paper. Then, weighing of the filter papers after the filtering and drying at 60 ºC overnight.

The differences in the weights of the filter papers before and after filtering of the OMW sample was divided over the volume of the OMW sample to obtain the value of the total suspended solids in the OMW.

Total suspended solids of the OMW samples calculated following the weight differences illustrated in the following equation;

$$TSS\left(\frac{g}{l}\right) = \frac{W_2 - W_1}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.2)$$

Where; TSS = total suspended solids (g/l).

W_2 = weight of the filter paper and the filtered solids (g).

W_1 = weight of the filter paper (g).

V = volume of the OMW sample (liters).

3.7.3. Column Maximum Capacity for Phenols Removal:

To evaluate the ability of the natural Zeolite for the removal of phenolic compounds; the capacity of the Zeolite for reduction of the phenolic compounds (mg) in the OMW was computed for each column of the natural tuff by following the following equation;

$$\text{Phenol adsorbed (mg/g)} = (C_0 - C) * V/W \quad \ldots\ldots\ldots\ldots\ldots(2.3)$$

Where; C_0 = initial phenol concentration in the influent.

C = phenol concentration at specific time.

V = volume of the effluent OMW sample of concentration of ‘C’.

W = weight of used Zeolite in the column (grams).

3.7.4. Physical properties of the OMW samples:

The OMW samples used were measured by pH electrode, EC electrode to determine the acidity and electrical conductivity of the samples using pH and EC meters.

Chapter Four

Results and Discussion

Total phenol content in OMW samples measured before and after application to Zeolite columns, these values were measured in the treated effluents of the OMW samples. Sampling was conducted in portions of known sampling time intervals with an appropriate samples volumes.

4.1 Total Phenol Concentration

Total phenols concentration measured for each influent sample used in each column, besides the phenols concentration in the collected portions of the effluent samples. Each column influent and effluents samples were measured together with regards to one standard curve. Total phenol concentration of 5985, 6227, 5890 mg/l measured for OMW influents applied to columns 1, 2,3, and 4; respectively. The following figure illustrates the standard curve of the standard tannic acid concentrations 1, 2, 4, 8, and 16 mg/l and their absorbance at 700 nm; the linear fitting of the relation between the absorbance of the standards versus the tannic acid concentration with a correlation coefficient $R^2 = 0.99$ is:

$$Y = 0.06\,X \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.1)$$

Where; Y = Absorbance at 700 nm.

X = concentration of tannic acid in mg/l.

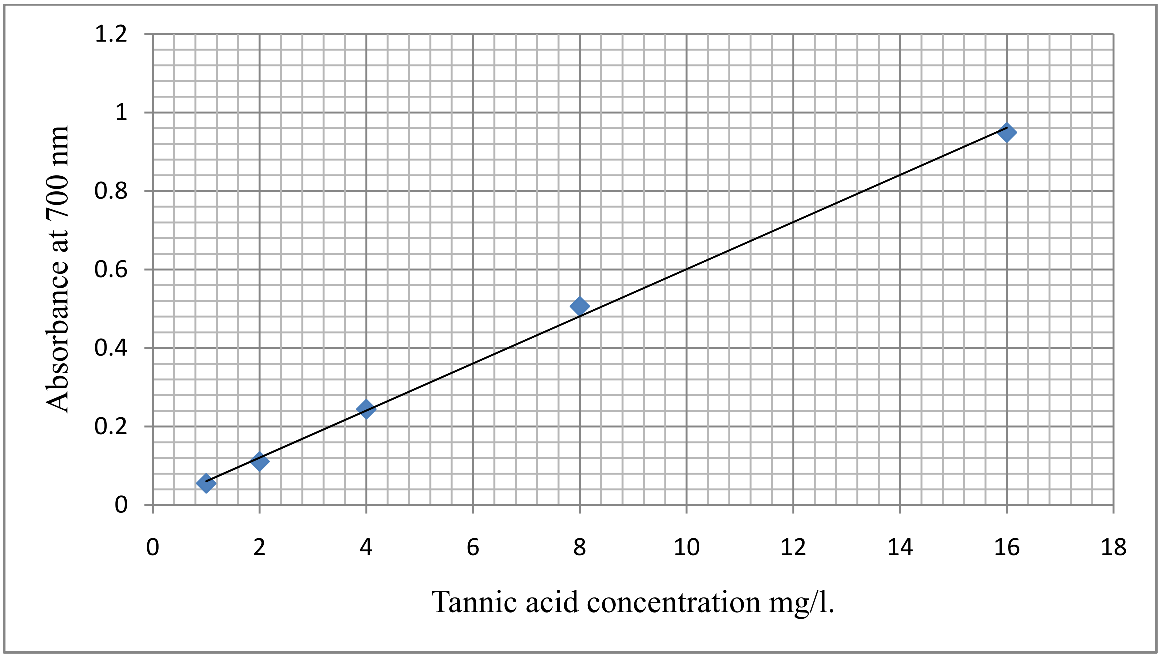

Figure (4.1): absorbance of the standards at 700 nm versus the tannic acid concentration (mg/l).

The physical properties of the OMW are: Electric conductivity [at 25°C] of 10.8 mS/cm, pH of 4.6, water content of 94.70 %, density of 1.01, carbon content of 33.9 %, and total organic carbon of 40.3 g/l. The tannic acid concentration of 5506 mg/l of the tannic acid in the synthetic tannic solution measured using Folin- Ciocalteau method.

Column One: Zeolite of particles size between 90 µm and 1000 µm

Natural Zeolite of sieve diameter between 90, 160, 200, 250, 500, 710, and 1000 µm. The porosity of the packed Zeolite measured using OMW is of about 49%.

4.1.1. Total phenol concentration of the effluent samples:

About 150 ml percolated through the column during two hours. The total phenol concentration in the effluent sample reached a steady state value after 90 minutes of effluent sampling, with total phenol concentration of about 5089 mg/l, figure 4.2.

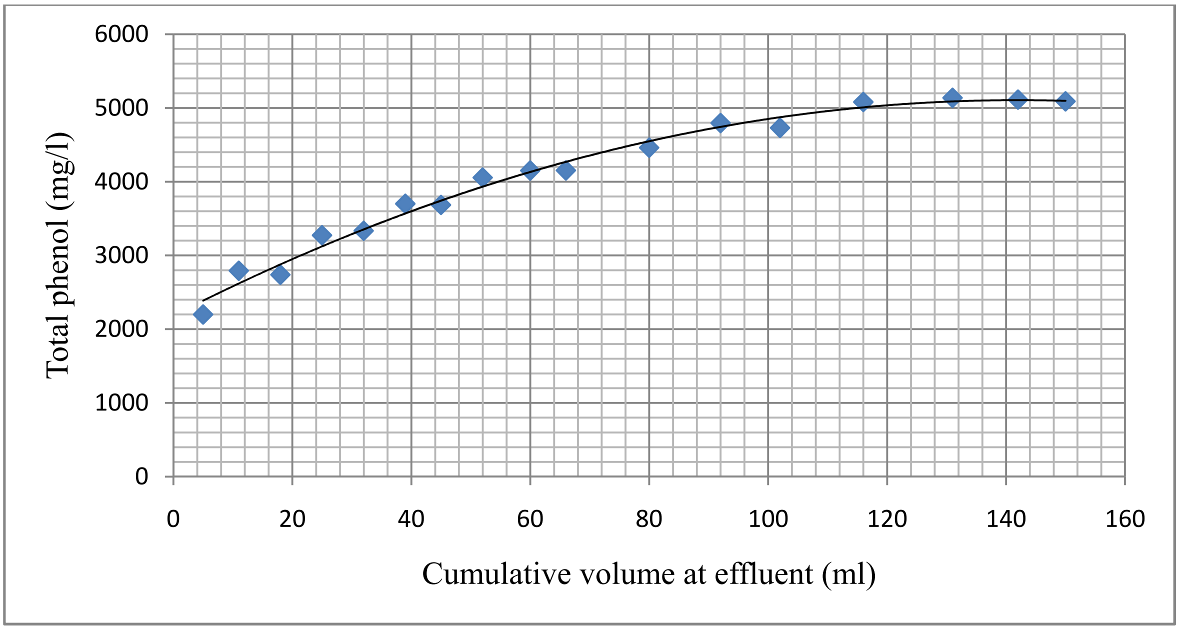

Figure (4.2) total phenol concentration of effluent samples (C_i = 5985 mg/l).

The initial phenol concentration was 5985 mg/l. The average percentage of total phenol removal from the OMW was about 33.8% of the initial total phenol concentration in the influent sample of 5985 mg/l. The first reduction percentage of the total phenol content in the first effluent sample was found to be of about 63% of the initial phenols content in the influent OMW.

4.1.2. Column maximum capacity for phenols removal:

The natural Zeolite showed ability for removal of the total phenols compounds from the influent OMW gradually, this capacity for removal started at 0.20 mg/g computed for the first sample of the effluent and decreased gradually to 0.07 mg/g for the last sample of effluent, with an average of about 0.15 mg/g. The cumulative values of the removed total phenols from the whole amount of the treated olive mill wastewater percolated through the column (150 ml) was about 2.57 mg/g. However; the average value of the removal capacity of the total phenols from each percolated sample was altered between (0.07~ 0.28 mg/g) during the percolation of the OMW through the 5 cm Zeolite column. Cumulative amount of the total phenols (mg) removed by each gram of natural Zeolite related to percolated cumulative effluent volume illustrated in figure 4.3.

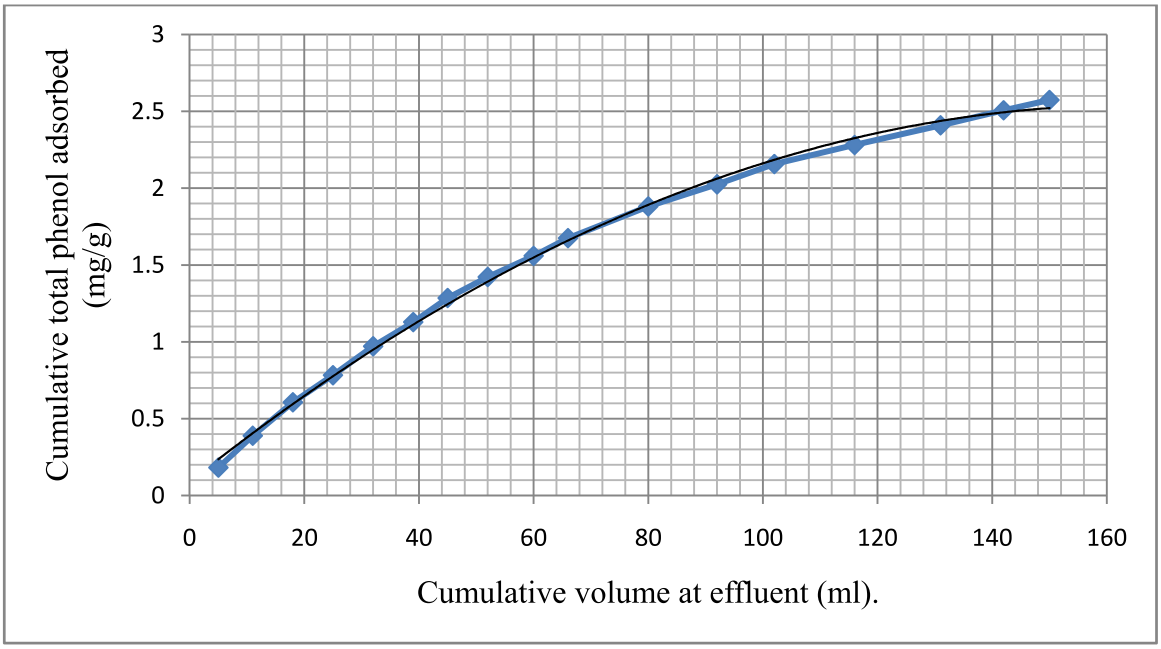

Figure (4.3): cumulative amount of total phenol removed versus cumulative volume (ml).

The cumulative removal total phenols compounds from the OMW was increased up to about 2.57 mg/g, the following equation (3.2) represent the behavior of cumulative phenols removal per each gram Zeolite which could be fitted with a correlation coefficient of R^2= 0.99.

$$y = -9 \times 10^{-05} x^2 + 0.0297x + 0.0891 \ldots\ldots\ldots\ldots\ldots\ldots..(4.2).$$

where; y= weight of total phenols removed by each gram Zeolite (mg).

x= volume of OMW effluent percolated through the column (ml).

There is a significance effect on the physical properties of the OMW after treatment with the natural Zeolite, results in electrical conductivity reduction from 3170 µS/cm to values between (587~1912 µS/cm). These physical properties enhancement may be related to the removal of nutrients and other components rather than phenols exist in the OMW by exchange with cations on the Zeolite mineral results in salinity alteration (appendix 4.1).

No significance relation between the removal of the phenols from the OMW and the values of the electrical conductivity could be observed, figure 4.4. Significant effect of the Zeolite on the electrical conductivity could be observed which percentage reduction range between (40~80 %) of the initial value of the influent. Thus; the removal of dissolved nutrient from OMW is independent of the phenols removal. This significant nutrients removal may refer to the availability of internal surface of the Zeolite pores for nutrients through the Zeolite micropores channels which is unreachable for the phenols compounds due to hindrance effects of the pores diameter. The electrical conductivity of the effluent samples never reach the initial value of the influent of 3170 µS/cm.

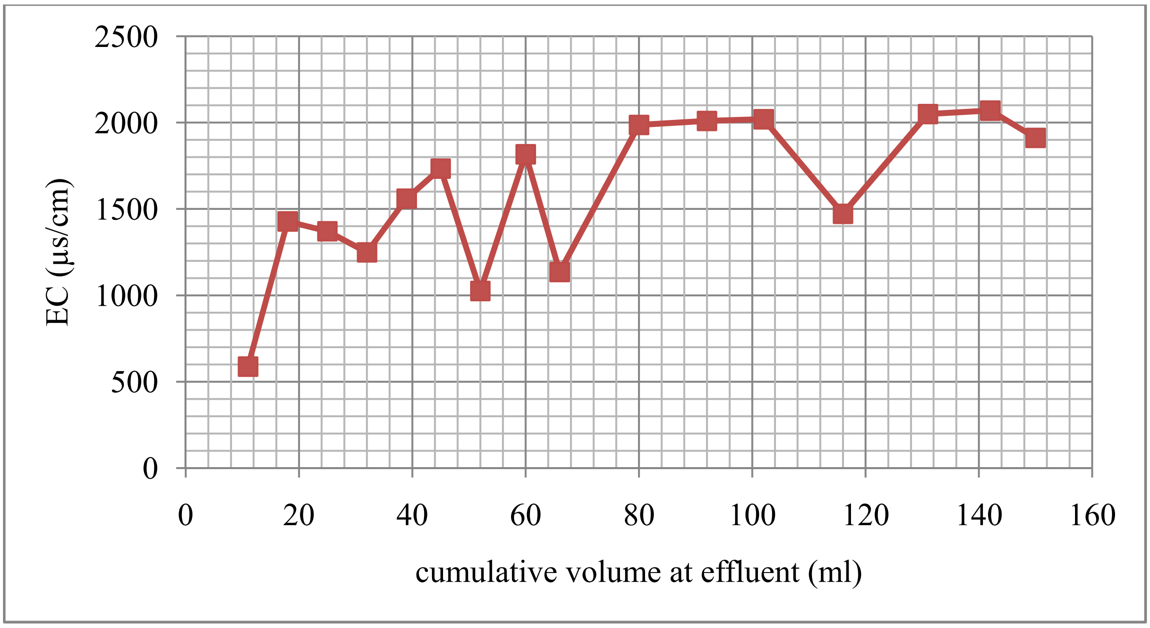

Figure (4.4): electrical conductivity of the effluent samples versus cumulative volume percolated.

Also, pH values of the effluents were with no significance relation to neither the total dissolved solid or the total phenols content of the OMW effluents, this may be indicator for a separated interaction between Zeolite surface and the other nutrients exists in the OMW samples rather than phenols, although that the phenols molecules may corresponds to pH values figure 4.5.

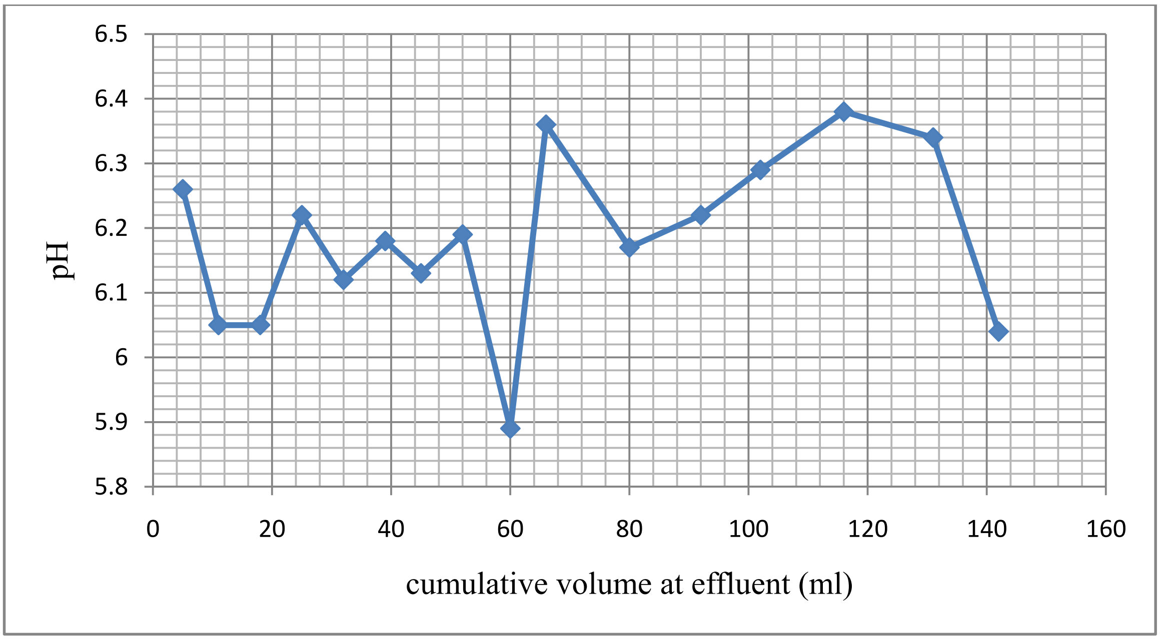

Figure (4.5): pH values of OMW effluent samples versus cumulative amount of effluent percolated through the column.

Column Two: Zeolite of particle size less than 2000 µm

Column of bed depth of five cm contains natural Zeolite of equal sieve fraction portions of diameter less than 63, 63, 75, 90, 160, 200, 250, 500, 710, 1000, and 1600 µm. The porosity of the packed Zeolite measured using OMW is of about 48%.

4.2.1 Total phenol content in the effluent sample:

Maximum first phenol removal percentage measured in the first effluent sample was 56 % of the initial influent concentration with maximum percolated volume of OMW (90 ml) is less than that measured of column one of 63% . However; column one could treat larger amount of OMW of about 150 ml compared to 90 ml maximum volume percolated through column two (appendix 4.3).

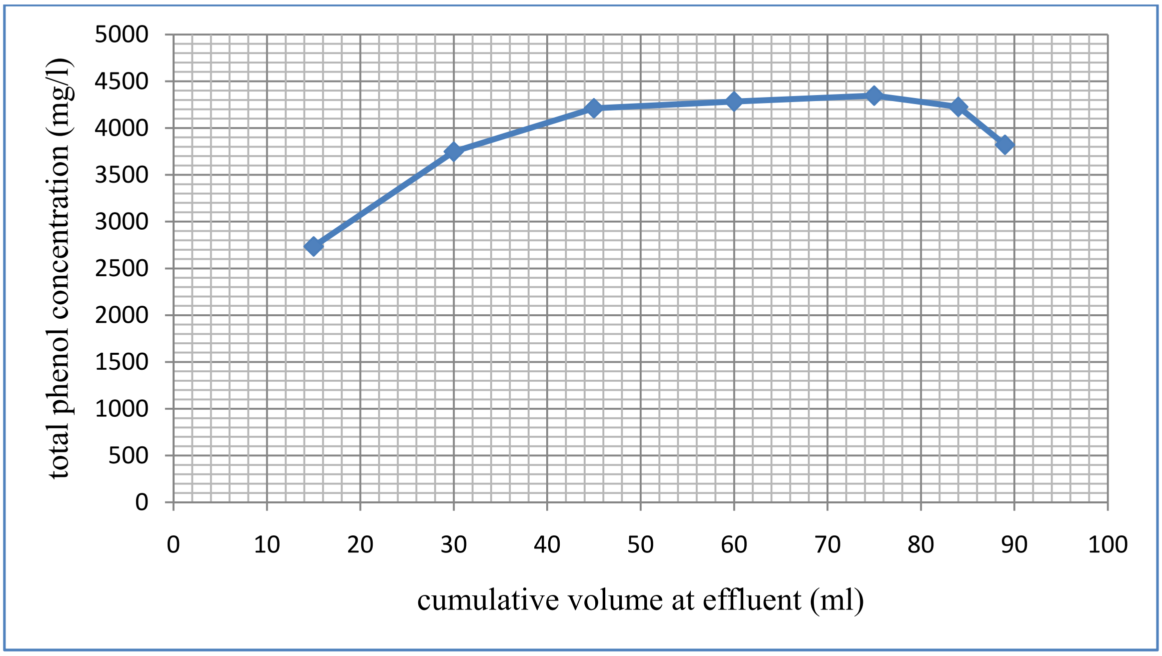

Figure (4.6): total phenol concentration of effluent samples (C_i = 6227 mg/l).

The concentration of the total phenol content in the first effluent sample was of 2735 mg/l, this value of concentration increased gradually to 3821 mg/l in the last effluent sample figure 3.6. The average concentration of the total phenol in the effluent samples was about 3911 mg/l corresponds to total phenols content removal from OMW Effluent samples of 37% of the initial value of the total phenol concentration exists in the influent sample of 6227 mg/l.

4.2.2. Column maximum capacity for phenols removal:

Total phenol content removal measured as a amount of removed phenols compounds with respect to each gram of Zeolite in the bed depth of 5 cm.

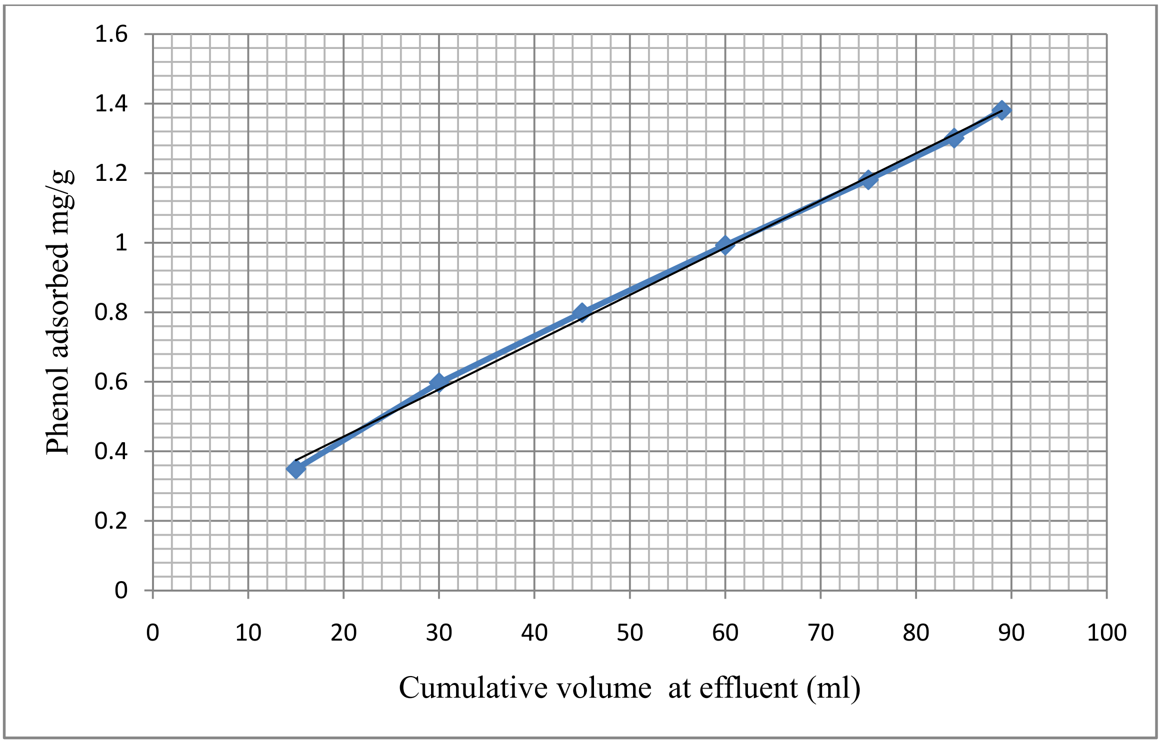

Figure (4.7): cumulative amount of total phenol removed versus cumulative volume (ml).

The amount of the removed phenol compounds from 90 ml OMW reached an amount of about 1.4 mg/g after percolating of about 90 ml of the OMW figure 4.7. The following equation illustrates best fitting of the above curve of the amount of total phenol removal is with a correlation coefficient of $R^2 = 0.99$;

$$y = 0.0136\,x + 0.1711 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4.3)$$

where; y = total phenol adsorbed per each gram of Zeolite (mg/g).

x = volume of OMW effluent that passed through the column (ml).

Even though the existence of the particles of diameter less than 90 µm in this column, which means more surface area available for phenol compounds in OMW. Maximum amount of phenols per each g Zeolite of 1.4 mg/g is less than column one of 2.57 mg/g.

Column three: Particles equal or less than 90 µm.

Glass column of 5 cm bed depth of Zeolite sieve diameter less or equal 90 µm, were calibrated for unique weights fractions. . The porosity of the packed Zeolite measured using OMW is of about 67%.

4.3.1. Total phenol content in the effluent sample:

The initial concentration of total phenol in the influent samples was of about 5890 mg/l, Clogging occurred after about 200 minutes percolating about 200 ml. Figure 4.8.

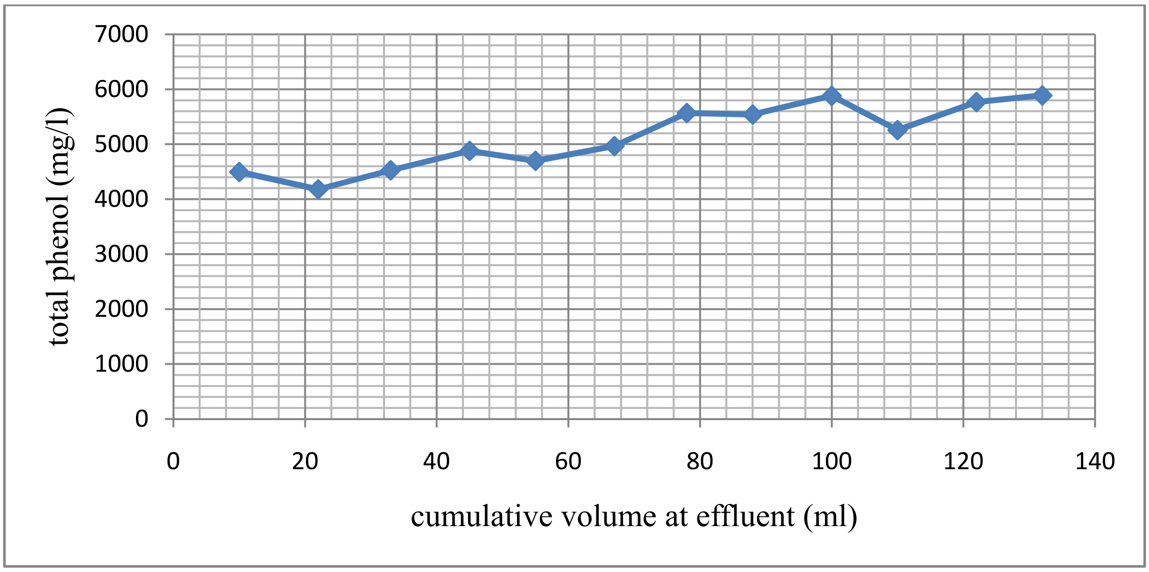

Figure (4.8): total phenol concentration of effluent samples ($C_i = 5890$ mg/l).

The previous figure shows the behavior of the total phenol concentrations of the influent OMW sample for only the first 132 ml of the effluent which were percolated through five centimeter Zeolite depth during 105 minutes. Then the percolated OMW showed an increase in the phenols content during the following 195 minutes, where about another 168 ml of the OMW sample were successfully percolated through the column.

4.3.2. Column maximum capacity for phenols removal:

Amount of removed phenols from the OMW of values 2.26 mg/g is of significant increase in comparison to that of 1.4 mg/g of capacity of removal achieved in the column two of particles diameters less than 2000 µm. However; this difference is of less significance in comparison to the column one which contains Zeolite of particles diameter between 90 µm and 1000 µm with a maximum capacity of about 2.57 mg/g. This could be considered as an indicator for the role of the Zeolite tuff of particles of lower diameters on the removal of the phenols from OMW. The following figure illustrate the first stage of interaction between the phenols and Zeolite.

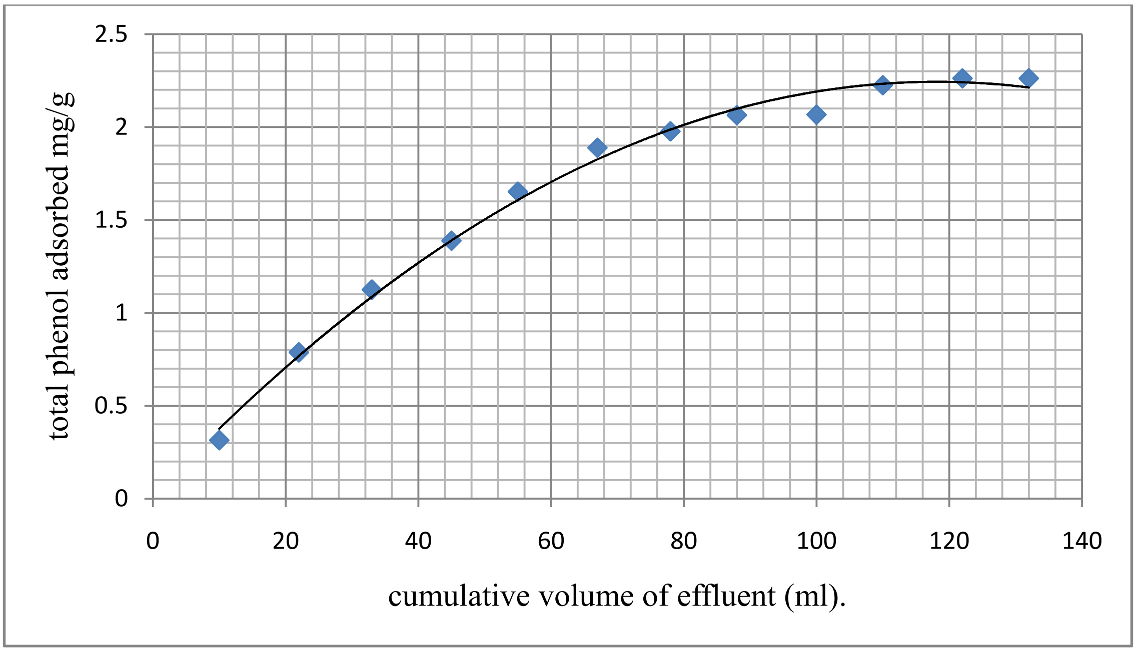

Figure (4.9) cumulative amount of total phenol removed versus cumulative volume (ml).

The following equation (4.4) illustrates the best fitting for the removal of total phenols from the OMW per each gram Zolite versus the cumulative volume percolated through the column with a correlation coefficient R^2= 0.99:

$$y = -0.0002\, x^2 + 0.038\, x + 0.015 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.4)$$

where; y = total phenols removed per each gram Zeolite in mg/g.

x = cumulative volume of OMW effluents (ml).

However; there is a significant difference in the phenols behavior through the column compared to that of the first column of particles diameter between 90 and 1 µm and second column of particles diameter of less than 2000 µm. Initial percentage of the phenols removal from the OMW was about 22 % of the initial concentration of influent sample, and an average removal percentage of about 11.8 % of the initial influent value.

Column four; Particles diameter of less than 2000 µm (Tannins solution)

Column of bed depth of five cm contains natural Zeolite of equal sieve fraction portions of diameter less than 63, 63, 75, 90, 160, 200, 250, 500, 710, 1000 , and 1600 µm. Total tannic acid concentration in the effluent samples were measured before and after percolation through the column.

4.4.1. Tannic acid Concentration in the effluent samples:

Behavior of tannic acid concentration in the effluent samples percolated through the column versus effluent volume is described in figure (4.10), which illustrate the interaction between tannic acid and Zeolite.

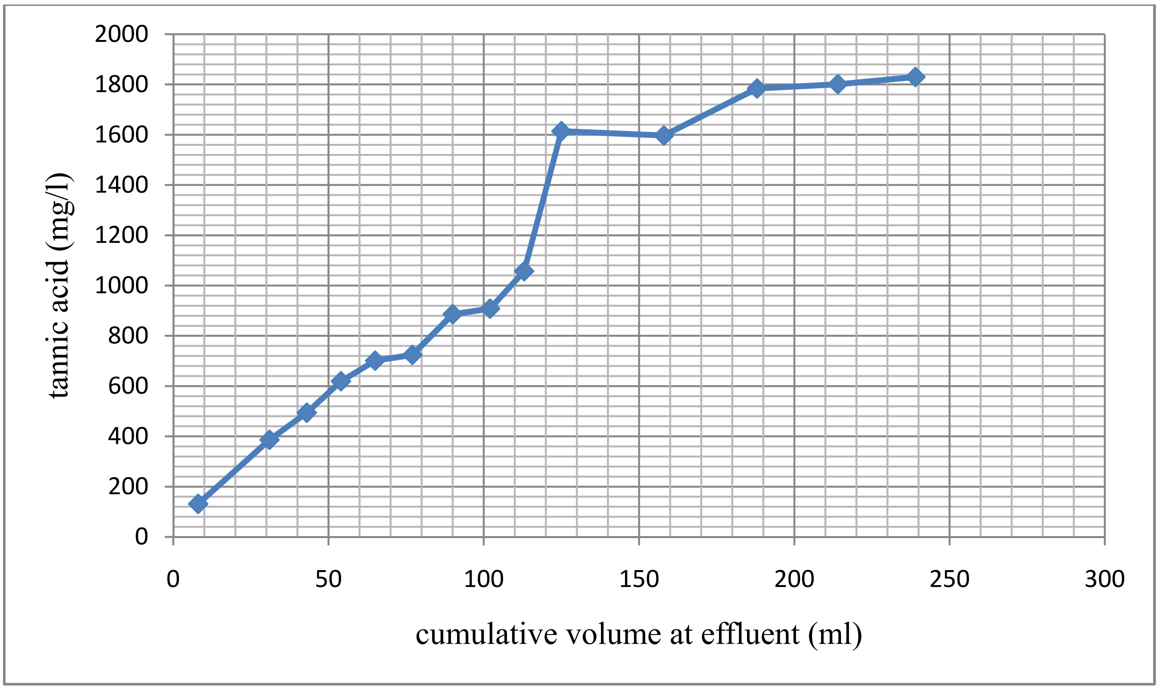

Figure (4.10): tannic acid concentration in the effluent sample versus cumulative volume percolated column four.

The acidity of the solution at the effluent samples, versus volume of the treated effluents are illustrated in the (appendix 5). There is a significant effect of the treatment with the natural Zeolite on the total tannins content as much as the pH of the solution.

4.4.2. Effect of the Zeolite on the solution physical properties:

The significant effect of the removal of the tannic acid molecules from the solution influent on the pH values of the effluent samples indicates strong relation between the tannins and pH values; thus removing these compounds from the OMW would reduce the negative impact of the OMW acidity which is considered harmful for the biodegradation process associated with any further treatment plants or land application on soil for fertilizing purposes figure 4.11.

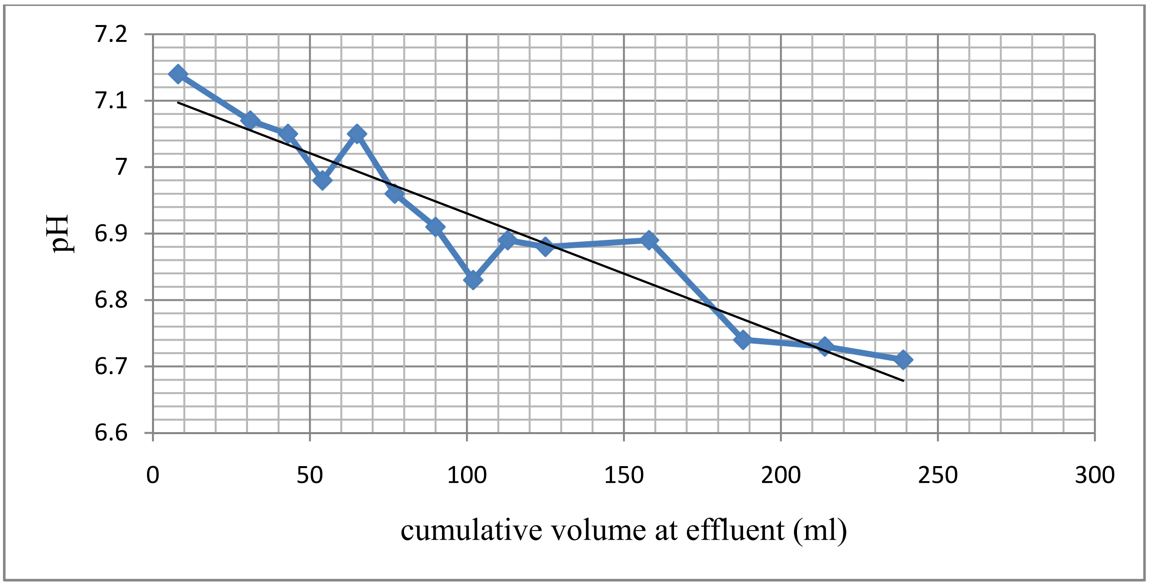

Figure (4.11): pH dependent of the effluent sample on the time of contact through the column.

The previous figure show the high ability of the natural Zeolite to reduce the acidity of the tannins solutions (initial value of 3.01); which mainly refers to the removal of these tannins from the solution.

The following equation describes the pH behavior of the effluent samples related to volume percolated through the column with a correlation coefficient $R^2 = 0.90$ as follows;

$$y = -0.0018x + 7.1116 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.7).$$

Where; y = pH value of the effluent samples.

x = Cumulative volume of the percolated tannic acid at the column effluent (ml).

The values of OMW pH increased after percolating through the column with less tendency in comparison to the synthesized tannic acid solution. It increases from 5.15 to 6.18, this is much lower than the tannic solution with pH increment from 3.01 to 6.9 for the same column properties (column 2).

Tannins compounds have a significant role on the pH value of the synthesized tannic solution, an average pH value of the effluent sample of all effluent samples of the tannic solution was of 6.9, compared to initial pH value of 3.01 for the influent sample. Since low dissolution rates and adequately acid resistance of high silica Zeolites such as Clinoptilolite, heulandites, phillipsite were reported, as much as the high ratio of the silica to alumina of the Jordanian Zeolite with about 42% weight percent for silica compared to 14 % for alumina; probability of buffering effect of Zeolite on the solution is not applicable, resulting in less tendency for tannins precipitation due to the increase in the solution pH; thus it is more reasonable that pH decrease was achieved due to the tannins removal.

The mechanism of the removal of the phenols compounds from the OMW through the Zeolite column is expected to follow the pH independent interaction, where the aromatic rings of the phenols compounds interact with the hydrophobic sites of the Zeolite; as pH of the OMW through the column stay less than the Zeolite zero point of charge and the pKa of the phenols.

Significant increase in the average removal efficiency of the tannins from the synthesized tannic acid solution may refers to the higher increase in the pH values of the solution inside the column. pH increment increases the phenolates complexation with metal ions on zeolite surface following the pH dependent interaction between the Zeolite surface and the tannins. This is noticed in the sudden spontaneously decrease in the removal efficiency of tannic acid (column 4) from 81 % to 71 % of the initial value at effluent sample number 10 which was around the pH value of 6.9 which affects the Zeolite charge; thus the percentage of the removal dropped again to values of about 66% which is close to that achieved in the column two applied for OMW with percentages of 56% of the initial concentration. Thus;

interaction between Zeolite and the phenol compounds alter depending on the pH of the solution.

4.4.3. Column maximum capacity for tannic molecules removal:

The following figure shows the total amount of removed phenols from the OMW influent sample per each gram of the Zeolite;

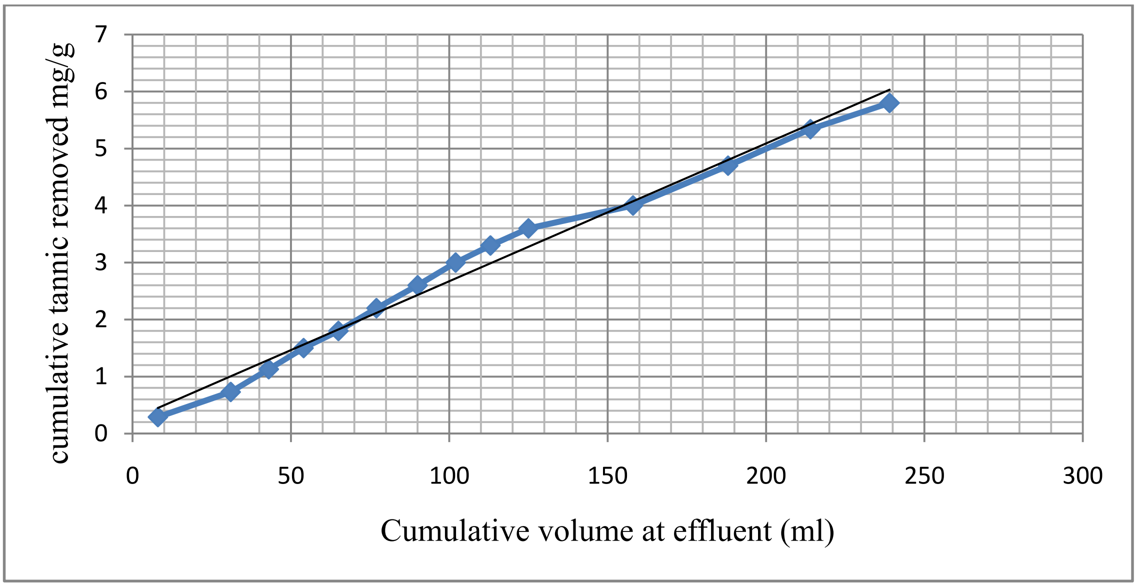

Figure (4.12): weight of tannic acid removed per each gram of the influent sample.

The previous figure shows the capacity of the natural Zeolite for the removal of the tannic acid from the synthetic tannic acid solution which has an initial tannic concentration of about 5435 mg/l. The following equation illustrates fitting of the cumulative tannic acid removed per each gram versus the cumulative effluent volume with a correlation coefficient $R^2 = 0.98$;

$$y = 0.0242x + 0.2538 \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4.5)$$

Where; y = weight of tannins removed per each gram of the Zeolite (mg).

x = Cumulative volume of the effluent samples (ml).

The previous figure shows that the natural Jordanian Zeolite has ability for the removal of the tannins from aqueous solutions, in concentration similar to those in the OMW samples in a greater tendency for higher removal capacity that could reach about 4 mg/g as much as a higher capacity for more amounts of the influents to be treated within shorter time. The amount of the synthetic solution of about 300 ml that percolated through the column is significantly greater than OMW of about 225 ml volume percolated through the column of the same parameters column 2. These amount of percolated solutions were achieved within 100, and 120 minutes for 300 and 225 ml; respectively. This shows the effect of other components exist in the OMW on the removal efficiency of the phenol compounds from OMW, which is seen in the effect of the Zeolite on the total dissolved solids (TDS) of the OMW after percolating through the column one, as much as the electrical conductivity of the effluent samples of column one which were significantly reduced, while slight changes observed in the pH values. However; the significance effect of the Zeolite on the tannic acid solution acidity which raised pH from about 3 in the influent sample to an average value about 6.9 in the effluent samples, indicates the huge effect of the tannins and phenolic compounds on the acidity of the OMW, this refers to the high percentage of tannins removed from the solution, figure 4.9.

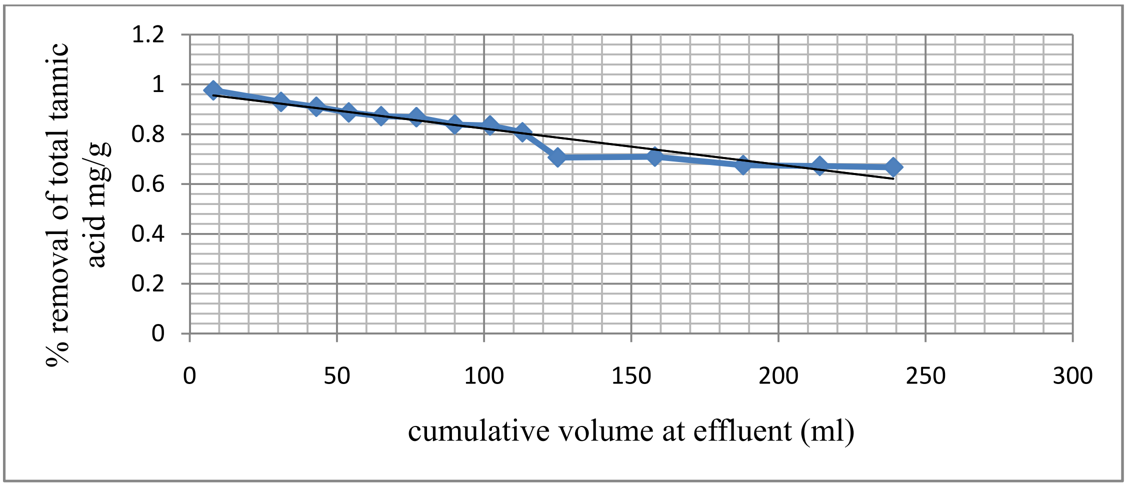

Figure (4.13): percentage reduction of the tannins from the tannic acid solution.

The previous figure illustrates the high ability of the natural Jordanian Zeolite for removal of the tannins from the tannic acid solutions; this reduction is described by the following equation with a correlation coefficient $R^2 = 0.92$;

$$y = -0.0014x + 0.9673 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.6)$$

where; y = percentage reduction of the total tannic acid in the effluent samples.

x = Cumulative volume of effluent samples of tannic acid solution.

The ability of the natural Zeolite to remove the phenol compounds from the OMW is significantly affected by presence of the other nutrients in the OMW; this may refers to hindrance effect due to the competitive adsorption of the dissolved nutrients in the OMW resulting in the habitation of the interaction between the Zeolite surface and the phenols of the OMW.

4.5 Total Suspended Solids of OMW

Total suspended solids (TSS) of the different eight samples of the OMW were measured, five samples were of volume of 20 ml, and the other three samples were of volume of 25 ml. The average concentration of the total suspended solids in the eight samples was of about 44.3 g/l.

4.6 Summary

The percentage removal of total phenols from the OMW and the initial removal are plotted for the four columns in comparison to the volume of effluent for which the percentages of removal were calculated, figure (4.14).

In order to compare the amount of removed total phenols from the OMW, per each gram of Zeolite in spite of the difference in the treated volumes . Figure 4.14 shows removal kinetics and the maximum amount of cumulative removal of total phenols per each gram of Zeolite versus cumulative volume of percolated OMW.

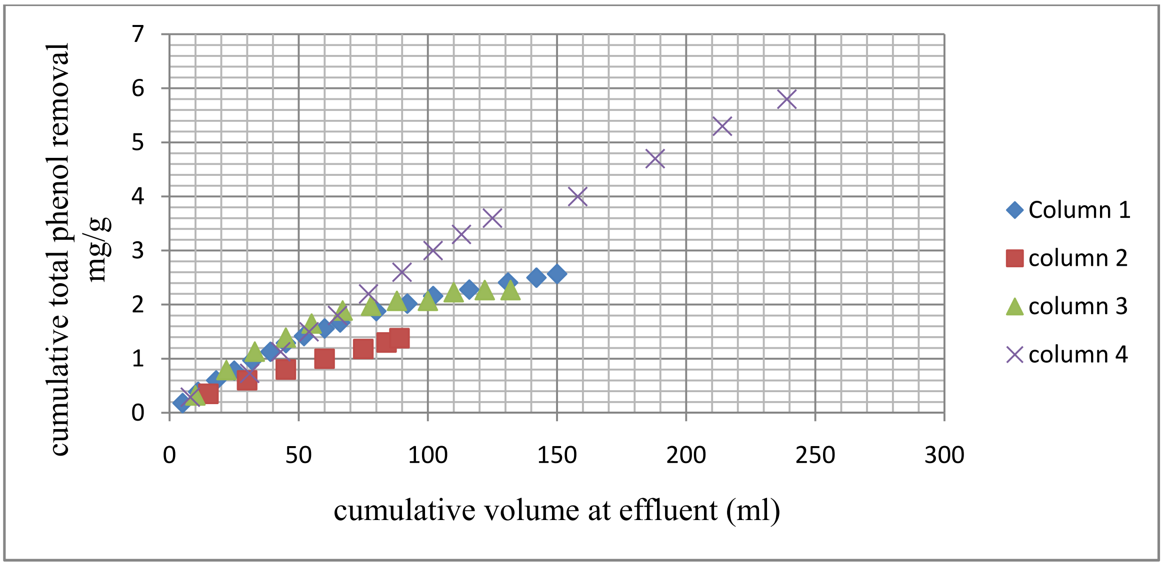

Figure (4.14): cumulative removal of total phenol versus cumulate effluent.

The volume of the treated effluents that percolated successfully through each column depend on the particles diameters of sieve fractions used and is influenced by the high total suspended solids of OMW. Thus; in order to compare this effect on the removal efficiency of phenols from OMW, the values of the average removal percentage and the amount of total phenol adsorbed from 90 ml (determinant effluent volume of column 2) of OMW in each column are computed (appendix 8) per one gram of Zeolite to overcome the weights of Zeolite differences in each column figure 4.14. As much as the initial percentage of phenols removal from the first effluent sample from each column per each gram Zeolite is computed per one ml of effluent to overcome differences in the first sample volumes of 5. 15. 10, 8 ml for columns 1, 2, 3, 4 respectively. Considering the cumulative volume of the effluent samples as the determinant factor with the minimum effluent volume of 89 ml obtained in column two in comparison to effluents volumes of 150, 300, 280ml obtained for columns one, three, four; respectively.

It is clear that the suspended solids of OMW reduce the removal efficiency of phenols, this effect can be noticed in the significant difference in the cumulative removed tannins from the tannic solution in column four. Moreover; the particle diameter effect appear in column two where more removal achieved by columns one and three where more portions of particles diameter less than or equal to 90 μm are used results in more surface area of Zeolite subjected to the phenols molecules. In spite of the particle diameter effects on the less phenols removal from OMW in column two, this column shows significant increase in the removal of tannic molecules from the tannic solution in column four where both column (2 and 4) have the same properties of Zeolite.

However; the effect of the significant increase of the initial removal percentage and the cumulative removed tannic compounds by column four could be noticed in the significant increase of the total removed tannic compounds for the total effluent volume with 5.8 mg/g removed tannic compounds and average removal of 81% compared to column two with values of 1.4 mg/g and 37%, respectively. Due to the difference in the amount of Influent which can percolate through the column, these differences trend to be more significant for the whole amounts of the percolated effluents.

Removal efficiency calculated for each column for determined volume of the effluent (90 ml) differs with regard the sieve fractions of the Zeolite particles diameter used in each column. Also; in the previous figure the cumulative adsorbed phenols from the first 90 ml of the effluent samples in each column calculated for each gram of Zeolite (appendix 8). The compared values for the given parameters and the calculated values for the comparisons are in table 4.1 and (appendix 8).

Table (4.1): calculated values for Zeolite columns for the first 90 ml of percolated effluent.

Column	1	2	3	4
average removal percent from 90 ml OMW per gram zeolite %	0.4	0.25	0.4	0.6
cumulative adsorbed phenols from 90 ml OMW per gram Zeolite (mg/g)	2.02	1.38	2.06	2.60
initial removal per 1 ml effluent per gram zeolite	0.126	0.025	0.055	0.650
volume of the first sample (ml)	5	15	10	8
Zeolite weight (g)	100	150	40	150
total column removal (mg/g)	2.57	1.38	2.26	5.80

CHAPTER FIVE

CONCLUSION

The natural Jordanian Zeolite used without any treatment show ability for the reduction of the total phenols compounds exist in the OMW samples, as much as the reduction of the tannins compounds. The filtering of the OMW before application to Zeolite column is of high priority due to high suspended solids loads of about 44.3 g/l; which affect the infiltration of the OMW sample through the column bed causing early clogging.

Interaction between the phenol compounds in OMW and the natural Jordanian Zeolite takes place only on the Zeolite external surface due to phenols physical parameters of molecular diameter exceeds the maximum pores diameter of the Zeolite structure. External surface area effect could be noticed clearly by using different particles diameters of crashed tuff. More portions of smaller particles diameter were used, more total phenols removal efficiency of the phenols from OMW could be achieved. Besides the amount of the removed phenols from the OMW samples, maximum volume of OMW could percolate through the column altered between (90~300 ml) of OMW depending on the diameter of used particles.

Particles of diameter less than 2000 μm in diameter (column 2) shows the highest average removal percentages of an average value of 37 % of the initial concentration of the OMW influent and average percentage removal of 81% of the initial tannic acid influent of concentration of 5506 mg/l, followed by the Zeolite of particles diameter between 90 micrometers and 1000 µm (column 1) with an average removal percentage of 33.8 %, finally, Zeolite particle of diameter less than or equal to 90 micrometer (column 3) shows the lowest average removal efficiency of about 11.8 %. However; the initial values of the removal percentages followed a different trend with an order of 63%, 56%, , 22 %, 98 % for columns 1, 2, 3, 4; respectively.

The removed phenol compounds per each gram of the Zeolite from the first 90 ml in each column proportional to the Zeolite particles diameter with 1.38, 2.02, and 2.06, and 2.6 mg/g for particles less than 2000 µm, between 90 and 1000 µm, less or equal to 90 µm, and column four with tannic solution, respectively.

The natural Zeolite trend to has much higher capacity for the removal of the phenols compounds from the OMW, as the behavior of the Zeolite in removing the tannic acid molecules from the synthetic tannic solution of a concentrations simulate those values of the OMW tend to exceed 5.8 mg/g in a linear behavior (figure 3.11). The average reduction of the total phenols from OMW of about 37% of the initial influent value (column 2), in comparison to an average tannins reduction percentage ranging about 81 % of the influent initial values of tannic acid concentration; indicate that suspended solids in OMW have a competitive effect on the availability of the phenol compounds for interaction with Zeolite surface; as adsorption of phenols compounds from aqueous solutions were reported to be independent on the ionic strength of the solution.

Moreover; the adsorption of the phenols from the OMW could be enhanced by controlling the pH of the OMW through the column increasing concentration of phenolate in OMW, causing their complexation with hydrophilic sites on Zeolite surface of metal ions, (which is pH dependent adsorption) rather than phenols adsorption to the hydrophobic sites of the Zeolite surface.

Recommendations

Further studies on the natural Zeolite for the removal of the phenols compounds from OMW are needed to evaluate the adsorption kinetics of these compounds to the Zeolite rather than adsorption kinetics for specific compounds; as much as to evaluate the effect of these compounds competition to the adsorption sites on the Zeolite surface. Also; more columns experiments in sequence ranking are needed to investigate the suspended solids of OMW effects on the removal as much as the pH of the solution. These columns needed to subjected to OMW by pumps of controlled flow rate, in order to investigate the time of contact effect on the removal efficiency at large scale.

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Appendix

Appendix (1): physical properties of OMW used in columns: anions, and metals content analysis.

Physical properties of OMW		
Measurement	Average	STEDV
Electric conductivity [mS/cm at 25°C]	10.8	0.0
pH	4.6	0
Water content [%]	94.7	0.0
Density	1.01	0.00
Total Phenol content [g/l]	0.225	0.02
Carbon content of OPWW [%]	33.9	1.6
Nitrogen content of OPWW [%]	0.9	0.1
Hydrogen content of OPWW [%]	4.5	0.4
Sulphur content of OPWW [%]	<0,1	*
Total organic carbon [g/l]	40.3	3.8
Fluoride [mg/l]	0.3	0.2
Chloride [mg/l]	1028.3	125.2
Nitrate [mg/l]	1.3	0.9
Phosphate [mg/l]	465.8	14.8
Fe [mg/l]	82.7	7.7
Zn [mg/l]	2.2	0.2
Mn [mg/l]	1.0	0.1
Cu [µg/l]	166.6	9.0
As [µg/l]	4.4	0.5
Sb [µg/l]	12.8	3.2
Pb [µg/l]	47.7	0.5
Sn [µg/l]	5.2	0.0
Cr [µg/l]	56.9	1.5

Note: Results in appendix (1) was conducted through DFG collaboration project between Water and Environmental Research Laboratory at Al Quds University and University of Landau-Koblenz in Germany.

Appendix (2): characteristics of OMW effluent samples collected from column 1.

Sample	time (minutes)	volume (ml)	total phenol (mg/l)	% reduction	Removed phenol (mg/g)
1	5	5	2200	63.24	0.18
2	5	6	2793	53.33	0.36
3	5	7	2739	54.23	0.58
4	5	7	3274	45.29	0.66
5	5	7	3335	44.27	0.84
6	5	7	3701	38.16	0.88
7	5	6	3685	38.43	1.04
8	5	7	4056	32.23	1.01
9	5	8	4151	30.64	1.10
10	5	6	4153	30.60	1.21
11	10	14	4461	25.46	1.21
12	10	12	4795	19.88	1.09
13	10	10	4730	20.96	1.28
14	10	14	5080	15.12	1.05
15	10	15	5137	14.16	1.11
16	10	11	5112	14.58	1.24
17	10	8	5089	14.97	1.34

Appendix (3): physical properties of OMW effluent samples collected from column 1.

Sample	EC (µS/cm)	pH	TDS (mg/l)	Salinity
1	587	6.26	548	0
2	1428	6.05	1310	0.5
3	1371	6.05	1256	0.5
4	1249	6.22	1165	0.4
5	1560	6.12	1464	0.6
6	1734	6.18	1605	0.7
7	1025	6.13	960	0.3
8	1817	6.19	1700	0.7
9	1135	5.89	1067	0.3
10	1987	6.36	1863	0.8
11	2010	6.17	1891	0.8
12	2020	6.22	1896	0.8
13	1472	6.29	1417	0.5
14	2050	6.38	1915	0.8
15	2070	6.34	1933	0.8
16	1912	6.04	1822	0.8
Influent	3170	5.15	OFF	1.6

Appendix (4): characteristics of OMW effluent samples collected from column 2.

Sample	Time	Volume	Phenol (ppm)	%Reduction	Removed phenol (mg/g)
OMW	*	170 mL	6227.1	*	0.35
1	6	15 mL	2734.3	56	0.25
2	6	15 mL	3748.8	40	0.2
3	7	15 mL	4212.6	32	0.2
4	9	15 mL	4285	31	0.18
5	13	15 mL	4347.8	30	0.12
6	17	9 mL	4227.1	32	0.08
7	14	5 mL	3821.3	39	0.35

Note: sampling start after 60 minutes of OMW application (duration of OMW percolating through the column).

Appendix (5): characteristics of OMW effluent samples collected from column 3

Sample	time (minutes)	volume (ml)	total phenols (mg/l)	percent of reduction	removed phenol (mg/g)
1	2	10	4495.3	22.0	0.32
2	15	12	4179.1	27.0	0.47
3	8	11	4525.8	21.0	0.34
4	8	12	4878.0	15.0	0.26
5	9	10	4697.7	18.0	0.26
6	8	12	4966.7	14.0	0.24
7	10	11	5567.5	5.5	0.09
8	10	10	5540.6	6.0	0.09

9	10	12	5881.0	0.2	0.00
10	10	10	5256.9	10.7	0.16
11	10	12	5767.6	2.1	0.04
12	5	10	5889.0	0.0	0

Appendix (6): characteristics of OMW effluent samples collected from column 4.

Sample	time (minutes)	volume (ml)	tannic acid (mg/l)	% reduction	pH	removed tannic mg/g
1	3	8	131	98	7.14	8
2	9	23	386	93	7.07	23
3	5	12	494	91	7.05	12
4	5	11	619	87	6.98	11
5	5	12	701	87	7.05	11
6	5	12	724	87	6.96	12
7	5	13	886	84	6.91	13
8	5	12	908	84	6.83	12
9	5	11	1057	81	6.89	11
10	5	12	1614	71	6.88	12
11	8	33	1597	71	6.89	33
12	20	56	1784	66	6.73	30
13	10	25	1801	67	6.71	26
14	10	19	1830	66	6.71	25
Influent	*		5506	*	3.01	

Appendix (7): total suspended solids measured in OMW samples.

Sample	weight of filter (g)	weight of filter and solids (g)	volume Zebar (mL)	TSS (g/l)
1	1.26	2.23	25	38.8
2	1.27	2.3	25	41.2
3	1.28	2.33	25	42
4	1.273	2.15	20	43.9
5	1.25	2.24	20	49.5
6	1.25	2.26	20	50.5
7	1.27	2.15	20	44
8	1.27	2.15	20	44

Appendix (8): compared parameters of four columns, the description 90 ml illustrate that the corresponding values were calculated for the first 90 ml of the effluents.

Description	*Column*	*1*	*2*	*3*	*4*
First sample parameters	initial removal per 1 ml effluent %	12.6	3.7	2.2	12.3
	initial removal percent %	63	56	22	98
	initial volume of first sample(ml)	5	15	10	8
	initial sample time (minutes)	5	6	2	3
First 90 ml of the effluent sample	average removal %	40	37	16	89
	total sample volume (ml)	92	89	88	90
	sampling time (minutes)	70	72	70	42
	adsorbed phenols (mg/g)	2.02	1.38	2.06	2.6
	cumulative adsorbed phenols (mg/40g)	80.8	55.2	82.4	104
Column parameters	total column effluent volume (ml)	150	90	300	280
	total column removal (mg/g)	2.57	1.38	2.26	5.8
	total column weight (g)	100	150	40	150
	Total applied influent (ml)	180	225	400	300