Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.846232

53 (2015) 627–636
January

Taylor & Francis
Taylor & Francis Group

Olive mills wastewater treatment using local natural Jordanian clay

Mohammed O.J. Azzam[a,]*, Samer I. Al-Gharabli[b], Mohammad S. Al-Harahsheh[c]

[a]*Department of Chemical Engineering, Jordan University of Science and Technology, P.O. Box 3030, Irbid 22110, Jordan*
Tel. +962 2 7201000, Ex.: 22380; Fax: +962 2 7201074; email: azzam@just.edu.jo
[b]*Department of Pharmaceutical Engineering, German-Jordanian University, P.O. Box 35247, Amman 11180, Jordan*
[c]*Department of Chemical Engineering, Jordan University of Science & Technology, P.O. Box 3030, Irbid 22110, Jordan*

Received 28 January 2013; Accepted 6 September 2013

ABSTRACT

In the Mediterranean area, olives are harvested and sent to mills where olive oil is extracted. These mills produce two types of wastes, namely olive kernel and olive mills wastewater (OMW). This OMW is considered an environmental problem because of its high organic content (COD over 80–200 g/l), high phenolics content (more than 400 mg/l), and low acidic pH (3–6). This study is about investigating the feasibility of using simple naturally occurring local Jordanian clay as a possible adsorbent to decrease the levels of the above negative characteristics of raw OMW as a step in developing a methodology to solve OMW problem without creating new problems to freshwater supply resources. Natural clay was calcined at several temperatures (350–550°C), some of which were further subjected to acid treatment using 1, 3, and 5 M-HCl solutions at 85°C. These treated clays were contacted with OMW in batch experiments to decide on optimum conditions to be used for a continuous packed bed treatment system. COD and phenolics contents of raw OMW were both reduced by about 10–20%. Packed bed of treated clay reduced COD of raw OMW by 50%. These results are promising and warrant further investigation.

Keywords: Olive mill wastewater; Clay; Phenols; COD; Adsorption

1. Introduction

Olive mills are small factories in which olive oil is produced. The waste products derived from olive oil extraction are aqueous effluent (olive mills wastewater, OMW) and solid residue; mainly containing the olive skin and stone (olive husk). According to a survey conducted for the year 2010 by the Department of Statistics, Jordan [1], there were more than 120 olive mills in Jordan which used more than 110,000 tonnes of olives to produce more than 21,000 tonnes of olive oil, 45,000 tonnes of solid residue and 96,000 m^3 of wastewater. The operation of olive oil extraction is mostly done during the oil-harvesting season (October–January). The above OMW is equivalent to about 0.9 m^3 wastewater per 1,000 kg of processed olives.

Jordanian regulations forbid dumping of generated OMW into city sewers or streams and rivers because

---

*Corresponding author.

OMW is considered highly polluted. It has many negative characteristics such as low acidic pH (pH values between 3 and 6). These low values of pH makes it difficult to treat samples of OMW by biological means in which bacteria favors growth in a pH range of 6.5–7.5. In addition, OMW has large phenolics content which makes OMW toxic. Phenolic compounds result in antimicrobial activities, which are an obstacle to biological processes that may be used for the treatment of OMW. Moreover, OMW has a high organic content with COD levels reaching 80–200 g/l [2].

Many investigations were done on this environmental problem. These investigations employed simple possible techniques, such as the use of OMW in irrigation and its effect on soil and plants [3,4], or the use of evaporation ponds and their effect on the properties of OMW [5,6], or even trying the co-treatment of OMW with other wastewater [7,8].

Other investigations employed biological methods, such as the use of anaerobic digestion of OMW [9,10]. Chemical techniques were also employed, such as the use of Fenton-like and photocatalytic reactions [11,12]. Adsorption was [2,13] and still being investigated [14,15] as a technique for improving the negative properties of OMW. Recently, the application of membranes in trying to treat OMW gained more attention [16–20].

Since it seems to be difficult to treat OMW completely by a single technique, the use of combined techniques was the natural way to proceed for some investigators. Such combined or hybrid techniques included, for example, physicochemical [21,22], electrochemical [23], electrochemical-biological [24], catalytic-biological [25,26], and physicochemical-biological [27,28] techniques.

This study goes along with the above reported studies. It employs adsorption as a method for improving the negative characteristics of raw undiluted OMW, such that the application of other techniques as a downstream treatment method; such as biotreatment; becomes more efficient or feasible. Specifically, naturally occurring Jordanian clay was used as adsorbent material to treat OMW. The effects on OMW were studied by monitoring COD and phenols levels.

2. Experimental

2.1. OMW characterization

Olive mill wastewater was collected from mills located in the northern part of Jordan. These mills operate using the continuous three-phase process. OMW was collected directly from the aqueous effluent of the three-phase separator (the last processing unit before the OMW is dumped into a collection tank). The characteristics of OMW are shown in Table 1.

2.2. Clay treatment

Jordanian natural clay was collected by the Jordanian Natural Resources Authority from a location called "Al-Qa'a". The collected clay was subjected to several treatment steps in order to prepare it to become a suitable adsorbent. The first step was to crush and mill this clay to several sizes (in the range of 2.00–0.063 mm). The second step was to classify this crushed and milled clay to different size fractions that were subjected to further treatment. The classification was done using sieving. The third step was to wash this clay to clean it from any soluble materials that may be present and also to eliminate any fine sizes that may be adhering to the surface of the milled and sieved clay. At this stage, it has been observed that the classified clay disintegrated to a fine size once contacted with water in the washing step. This indicated that the clay could not be used in its natural form. In other words, it needs some further treatment (i.e. calcination) to modify its structure and properties.

Certain clay samples were then subjected to a heat treatment step. The heat treatment was done by placing the desired clay (one size) in a crucible and then inserting the crucible into an electric furnace to achieve two things. First, to dry the clay of any

Table 1
Characteristics of OMW

Property	Unit	Value
pH		4.6
Total suspended solids (TSS)	mg/l	20,700
Total dissolved solids (TDS)	mg/l	27,000
COD	mg/l	40,000
Phenols	mg/l	360
Ca	mg/l	2.11
Cu	mg/l	0.94
Fe	mg/l	Negligible
K	mg/l	25.18
Mg	mg/l	1.90
Na	mg/l	0.68
Pb	μg/l	Negligible
Zn	μg/l	33.43
Color		Dark brown to dark red
Conductivity	ms/cm	12.71

entrapped water (water smoking) which was done by heating the clay to a temperature slightly higher than 100°C. Second, to modify the clay chemical; and possibly physical; structure by driving out lattice water which was achieved by heating the clay to temperatures above 350°C. Five temperatures were applied, namely, 350, 400, 450, 500, and 550°C. Clay samples were kept at the specified temperature for 2 h. The heating rate between 100°C and the specified temperature was 7°C per minute.

The next step was to treat the calcined clay with hydrochloric acid (HCl). Three concentrations of the acid were used, namely, 1, 3, and 5 M. The treatment procedure was to place 10 g of calcined clay (0.212 mm < size < 0.710 mm) and 50 ml of the proper acid solution in a 250 ml Erlenmeyer flask. The flasks were sealed with polyethylene film and then placed in a heated reciprocating shaker with a controlled temperature at 85°C for a period of 2 h.

The acid treated clay samples were then washed with distilled water until constant pH was reached in the spent washing water (about 2 l of distilled water were needed per clay sample to reach a constant pH). After the washing step, the clays were dried (at 105°C) in preparation for the next step when they were to be contacted with OMW.

2.3. Clay–OMW interaction—batch experiments

The treatment of OMW using the above prepared clays was done at this stage. Unless otherwise stated, 2.00 g of the above treated clays were put in a 250 ml Erlenmeyer flask, and then 50 ml of raw (however filtered with a cloth) OMW was added to each flask. It is worth mentioning that the use of the cloth was to filter out any sludge or similar matter that sometimes appeared on the surface of OMW. This step did not affect the properties of OMW presented in Table 1. The flasks were sealed and then placed in a reciprocating shaker at a temperature of 32°C, and left to achieve equilibrium condition. The samples were left for 18 h in the shaker, which was more than enough time to approach equilibrium. After that, the OMW was separated from the clays and tested for COD and phenols content.

2.4. Clay–OMW interaction—continuous (packed bed) experiments

The next phase of this work was to conduct a continuous treatment of OMW instead of the above batch experiments. The bed was composed of a Plexiglas column, 30 cm high with an inside diameter of 2 cm. The bed was packed with treated clay particles having an average size of 1.50 mm (1.00 mm < size < 2.00 mm) to decrease the pressure drop in the bed and to mimic used sizes in commercial columns. The clay particles were subjected to the following treatment: calcination at 450°C for 2 h, then after cooling, clay particles were subjected to acid treatment. The acid treatment consisted of putting the calcined clay in 1 M-HCl solution for 2 h in a heated bath shaker. The temperature of the bath was controlled at 60°C. The clay concentration in the acid solution was 0.175 g-clay per 1 ml of 1 M-HCl solution. After that, the clay was washed with distilled water until a constant pH in the spent water was obtained. Then, this acid treated and washed clay was dried in an oven at 105°C for 24 h. After the clay has cooled, the bed was filled with this treated clay. About 106 grams of the above clay was needed to fill up the bed. A peristaltic pump with low flow rate capability was used. The flow rate through the packed bed was measured to be 0.10 ml of raw (however filtered with a cloth) OMW/s. The bed was not thermostated and was operated at room temperature. The empty bed contact time (EBCT) was 15.7 min (a typical value from practice). The feed to the bed was chosen to be from bottom to top to give a better wetting of the bed and to minimize any channeling effects. After about 9 min the first drop of OMW exited from the top of the bed. Samples of 10 ml were collected at discrete intervals.

2.5. Chemicals and instruments

Reagents that were used in this investigation included hydrochloric acid (assay quality acid, min. 35.4%) from Gainland Chemical Company (GCC), UK, sulfuric acid (assay quality, 95–98%) from Frutarom, UK, dipotassium hydrogen phosphate 3-hydrate from PRS Panreac, Spain, potassium dihydrogen phosphate (min. 98%) from BioChemica AppliChem, the Netherlands, potassium ferricyanide (min. 99%) from Pharmacos Ltd., England, 4-Aminoantipyrine (98%) from ACROS Organics, USA, silver sulfate (99%) from Riedel-de Haen, potassium dichromate (98%) from Vickers Laboratories Ltd., England, mercuric sulfate from Riedel-de Haen, and phenol (98.5%) from Panreac, Spain.

COD analyses were done using the closed reflux colorimetric method (method 5220D in Standard Methods for the Examination of Water and Wastewater [29]). A digester by Lovibond model ET 108 and a spectrometer model PC-Checkit COD Vario by Lovibond were used for COD measurements. Phenols analyses were done using the direct photometric method (method 5530D in the same above reference

[29]). A spectrophotometer model T70 UV/Vis spectrometer from PG Instruments Ltd., was used. FTIR-ATR analyses were done using Tensor 27 by Bruker.

The X-ray fluorescence (XRF) for the samples utilized a Philips PW1404 Wavelength Dispersive Sequential XRF Spectrometer controlled by Philip X40 software. The X-ray diffraction (XRD) used a Hiltonbrooks® generator with a Philips® X'Pert Pro PW 3040 60 diffractometer with an automatic divergence slit, and Cu anode producing X-rays of wavelength $\lambda = 1.54056$ Å. On the other hand, thermogravimetric analysis (TG/DTG) was performed using NETZSCH TG 209F1 Iris equipment, at a heating rate of 10°C/min.

The surface area analysis utilized a Quantachrome Autosorb Automated Gas Sorption System, which employed nitrogen as adsorbate, and the outgas temperature and time were 300°C and 5 h, respectively. The reported surface areas were calculated using a multipoint BET method, while both the micro-pore volumes and pore diameters were calculated using the SF method.

3. Results and discussion

3.1. Clay characterization and treatment results

3.1.1. Characterization of raw and treated samples of clay

Visual examination of the raw clay ore reveals that the bulk of the clay is of pale green color with veins of yellowish color. Table 2 shows the chemical composition of raw and treated samples of clay, in addition to the weight losses due to each treatment strategy.

XRD pattern of the bulk raw clay is shown in Fig. 1. Careful analysis of the pattern shows that the major minerals present in the investigated clay are montmorillonite ($(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2 \bullet n(H_2O)$), albite ($NaAlSi_3O_8$), jarosite (most probably hydronium-$H_3OFe_3(SO_4)_2(OH)_6$), gypsum ($CaSO_4{\cdot}2H_2O$), quartz (SiO_2), and possibly some illite ($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$). A further detailed examination showed that the yellowish veins intersecting the green matrix are composed mainly of jarosite and gypsum with traces of albite, while the green matrix is mainly composed of montmorillonite, quartz, and albite.

After calcination at 450°C, the XRD pattern analysis shows that albite and quartz did not lose their structure as evident in Fig. 1. As for other minerals containing structural water, they experienced phase transformation; for example, gypsum was transformed into anhydrite ($CaSO_4$) as evident from its major peak appearing at $2\theta = 25.39^\circ$, while the major peak of montomorillonite, at $2\theta = 6.39^\circ$, was collapsed due to thermal treatment and caused this to shift to $2\theta = 9.06^\circ$. Such observation was confirmed by the previous work of Zampori et al. [30] and Ferrage et al. [31]. The shift of the main montmorillonite peak can be ascribed to its dehydration [30,31] which is confirmed by the irreversible mass loss peak at about 135°C as evident from TG/DTG profile shown in Fig. 2. The other montmorillonite peaks ($2\theta = 19.6^\circ$, 21.6°, 35.6° and 61.7°) appeared in the same place as that of the raw sample [32]. Furthermore, it seems that montmorillonite

Table 2
Chemical (XRF) and physical analysis of raw and treated clay

Component	Content, wt.%					
		Calcined at 450°C followed by treatment with HCl				
	Raw clay	No HCl	0.5 M	1.0 M	1.5 M	3.0 M
Fe_2O_3	12.3	12.84	13.11	10.27	9.54	7.22
TiO_2	1.44	1.53	1.83	1.88	1.91	2.03
CaO	3.29	3.63	1.07	0.81	0.71	0.72
K_2O	1.31	1.44	1.06	1.03	1.07	0.85
SiO_2	45.44	49.22	57.95	59.86	61.19	65.8
Al_2O_3	13.18	14.25	15.4	15	15.13	13.95
MgO	2.4	2.7	2.04	1.76	1.54	0.88
L.O.I	16.6	8.34	5.49	5.6	5.36	6.56
Wt. loss%	–	11.3	11.7	21.7	25.0	30.0
Surface area (m^2/g)	61.68	47.25		132.7		185.2
Pore volume (cm^3/g)	0.0259	0.0209		0.0569		0.0793
Pore width (nm)	1.892	3.040		1.882		1.892

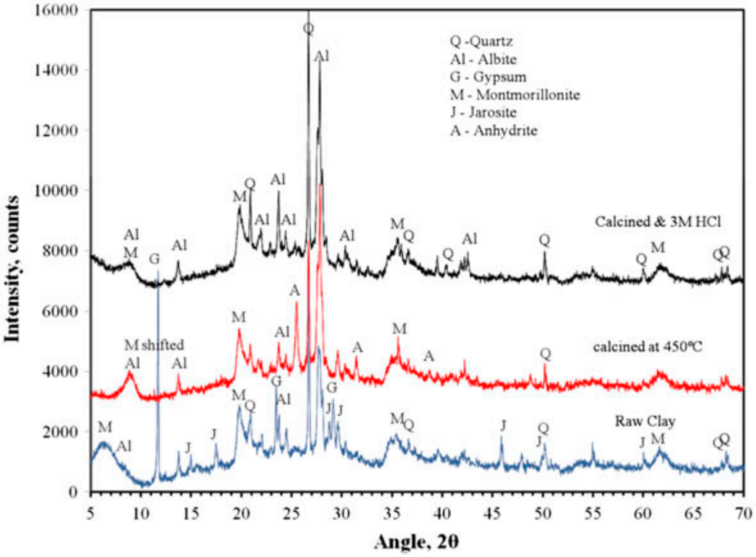

Fig. 1. XRD pattern of raw, clacined, and acid treated clay samples.

remained stable after acid treatment, even 3 M-HCl solution was not enough to destroy its structure [33] although considerable amount of Mg was removed by acid treatment (see Table 2). Grim [34] proved that montmorillonite can preserve its main structural features up to 75% loss of its mass.

The anhydrite was dissolved after acid treatment as evident from the XRD pattern (Fig. 1) of acid treated clay (the peak at $2\theta = 25.39^\circ$ disappeared). The content of CaO in the acid treated clay was also reduced sharply (Table 2). Of course, the source of Ca is not only the gypsum, but also from montmorillonite and possibly some substitution in the structure of albite.

Jarosite lost its main structural features after thermal treatment, as evident from the XRD pattern of the calcined clay when compared with that of the raw clay, due to the loss of structural water [35]. The mass loss peak at about 370°C is due to the loss of water from hydronium jarosite. Furthermore, it seems that appreciable part of calcined jarosite was dissolved in HCl as evident from the reduction of Fe_2O_3 content in the acid treated clay samples (Table 2).

3.1.2. Thermogravimetric analysis

Fig. 2 shows the TG/DTG curves of raw and calcined clay samples. The first mass loss of the raw clay can be ascribed to moisture removal from the sample. The second derivative mass loss peak appears at a temperature of about 130–140°C. Its shape suggests that several events occur within this temperature region. The literature suggests that in this temperature region both gypsum [36] and montmorillonite [30,31] dehydrate. The later mass loss at around 465°C is due to the release of structural water from montomorillonite. However, the mass loss at 800°C, which appears only in the raw and calcined clays could be related to some carbonates or some structural water of the clay minerals that had been removed by acid treatment.

3.2. Batch experimental results

The initial characteristics of OMW are shown in Table 1. These properties are consistent with so many reported characteristics of OMW in the literature.

Fig. 3 presents the equilibrium COD results of the batch interaction between OMW and treated clay. The initial COD was around 40,000 mg/l. These results indicate that clay that has been calcined at 450°C and then treated with 1 M-HCl solution resulted in a better COD reduction than all other tested conditions (~19% COD reduction, with COD uptake of 165 mg/g). The standard deviation of experiments was 3.2% (based on five replicates), which suggests that the observed reductions in COD values are experimentally significant (Note: one error bar is shown on Fig. 3 to simplify the drawing). To confirm the results of the above observation (when using clacined clay at 450°C and 1 M-HCl treatment), two more experimental conditions were tested using calcined clay at 450°C and then acid treated at, once with 0.5 M-HCl and the other with 1.5 M-HCl. The results of these two extra tests are shown on the same figure (Fig. 3) and they were consistent with the above observation of optimum reduction in COD values when using calcined clay at 450°C and then acid treated with 1 M-HCl.

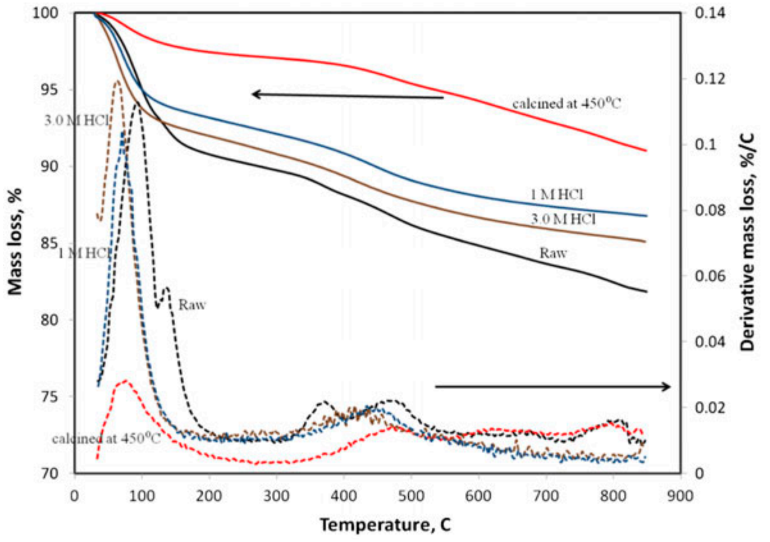

Fig. 2. TG/DTG curves for raw, calcined, and acid treated clay samples.

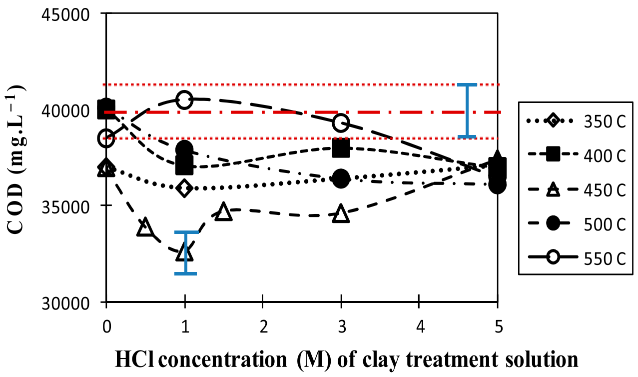

Fig. 3. Effect of HCl concentration (M) of clay treatment solution on COD level in OMW. The dashed horizontal line at COD ~ 40,000 mg/l represents the initial COD, while the other two dotted horizontal lines (above and below it) represent the ±3.2% accuracy.

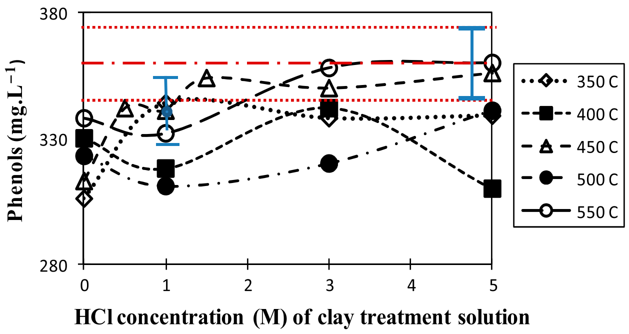

Fig. 4. Effect of HCl concentration (M) of clay treatment solution on phenols concentration in OMW. The dashed horizontal line at phenols ~360 mg/l represents the initial phenols, while the other two dotted horizontal lines (above and below it) represent the ±4.0% accuracy.

Another observation from Fig. 3 is that COD values of OMW treated with 5 M-HCl solution were converging (around a value of 37,000 mg/l) for all tested calcination temperatures of investigated clay, resulting in an average percentage reduction of COD value of about 8% with COD uptake of 33 mg/g.

On the other hand, Fig. 4 presents phenols concentrations in OMW under the same conditions of Fig. 3. The initial phenols concentration was around 360 mg/l. The standard deviation of these experiments was 4% and is shown in Fig. 4. Unfortunately, the data is not conclusive in providing optimum conditions for the reduction of phenols in OMW. However, despite the fluctuating results, one can say that both clay that has only been calcined and clay that has been calcined and acid treated with 1 M-HCl produced relatively better reduction in phenols content of OMW, than the other cases.

Figs. 5 and 6 show the effect of concentration of clay, interacted with OMW, on COD and phenols concentrations, respectively. These experiments were done using clays that have been calcined at 450 and 500˚C and then acid treated using 1 M-HCl (or 3 M-HCl) solution. It is observed from Fig. 5(a) and (b) that COD values were leveling at concentration of 2.00 g of 450˚C-calcined clay per 50 ml of OMW, whereas, COD values leveled at 1.00 g of 500˚C-calcined clay per 50 ml of OMW. The leveling of COD values indicates that some COD constituents (possibly low molecular weight molecules) have been removed by clay

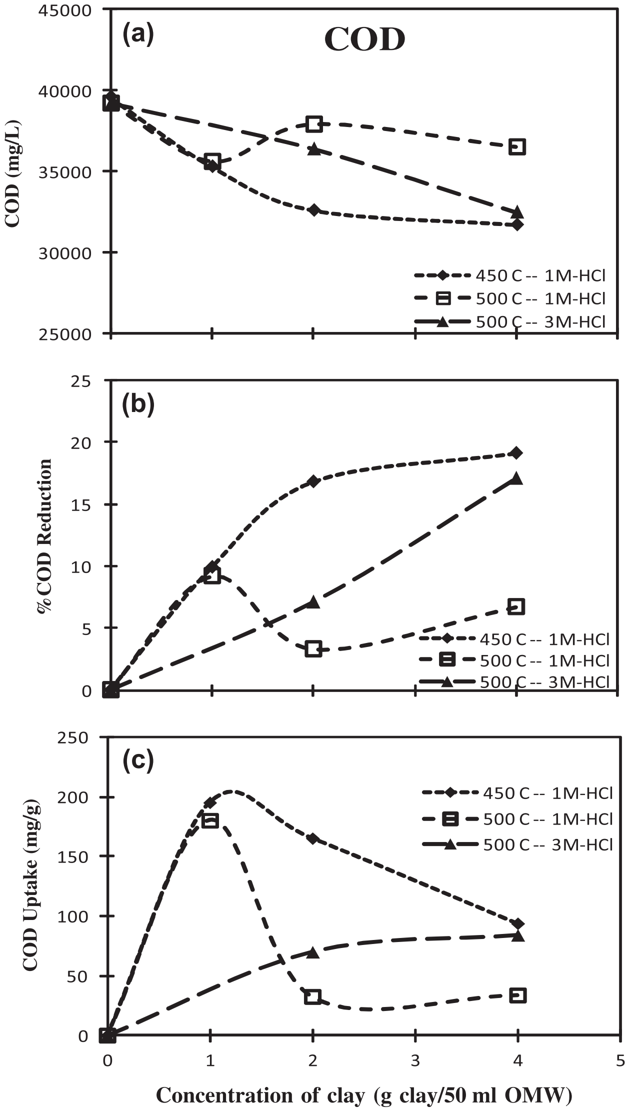

Fig. 5. Effect of concentration of clay in OMW on: (a) residual COD in OMW, (b) percentage COD reduction in OMW, and (c) clay's COD uptake.

resulting in no more reduction in COD by increasing the concentration of clay. This suggests that the used clay is selective to certain organics [15]. On the other hand, comparing the higher COD values of OMW (i.e. lower percentage reduction in COD, Fig. 5(b) for the case of 500˚C (1 M-HCl) relative to the case of 450˚C (1 M-HCl) may indicate that the pores (or possibly active sites) of used clay have been blocked by certain clay constituents during the higher calcination temperature, hence, resulting in higher COD values. This explanation is supported by the results of 500˚C (3 M-HCl) where COD values were lower than the case of 500˚C (1 M-HCl), which suggests that the 3 M-HCl acid treatment of clay has further cleaned up the pores of clay or may have cleaned up possible active sites.

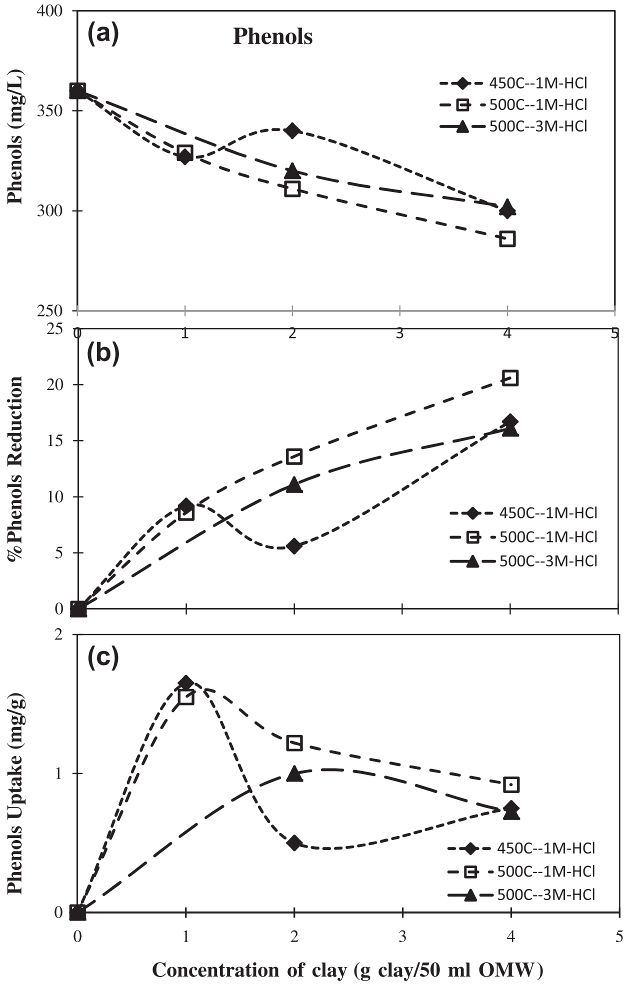

Fig. 6. Effect of concentration of clay in OMW on: (a) residual phenols concentration in OMW, (b) percentage phenols reduction in OMW, and (c) clay's phenols uptake.

On the other hand, Fig. 6(a) and (b) indicate that all investigated clays continued to produce lower phenols concentrations in OMW at higher clay concentrations. This indicates that phenolic materials present in OMW were still adsorbable on the investigated clay, however, the level of decrease in their concentrations was relatively low (a maximum was around 20% reduction).

The above results are not surprising. Natural clay is known to be hydrophilic (and organophobic) [37], and therefore, its adsorption to phenols and other organics would be expected to be low as suggested and observed by several investigators [38–40]. Even though, the surface area of clay, calcined at 450˚C and acid treated with 1 M-HCl solution, was almost tripled (Table 2), and almost quadrupled for the 3 M-HCl case, the reduction of COD and phenolics values of OMW was relatively low (at best less than 20% reduction in COD, and almost not significant for phenols).

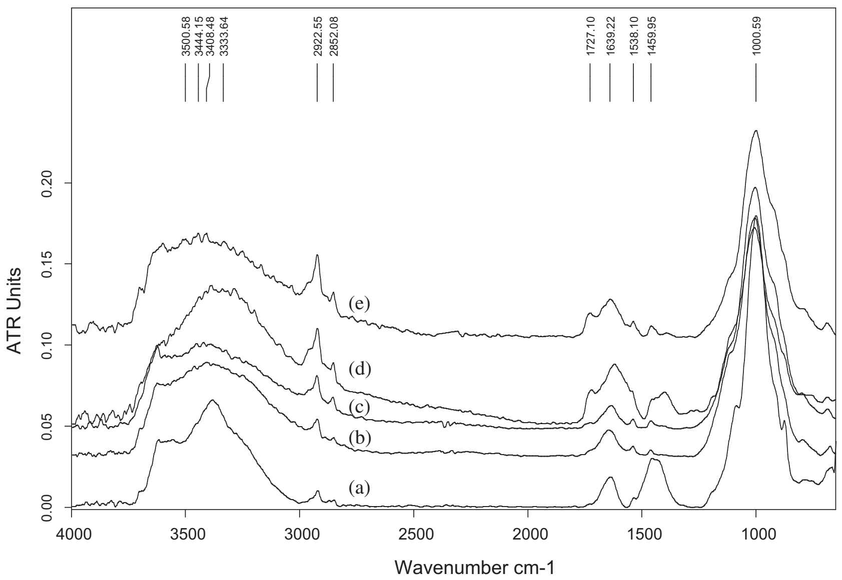

Fig. 7. FTIR-ATR spectra of (a) raw clay, (b) calcined clay at 450˚C, (c) calcined at 450˚C and acid treated clay at 1 M-HCl, (d) calcined clay after contact with OMW, and (e) calcined and acid treated clay after contact with OMW.

It may be a good idea to try to modify the investigated natural clays to make them organophilic as suggested by some investigators [38–40].

Fig. 7 shows the FTIR-ATR analysis of five systems namely: raw clay, calcined clay (450˚C), calcined and acid treated clay (1 M-HCl), calcined clay after contact with OMW, and calcined and acid treated clay after contact with OMW. Infrared spectra were recorded for the surfaces of clay (before and after contact with OMW) using FTIR-ATR technique. As representative examples, five spectra were depicted in Fig. 7. The general features for all spectra were broadband centered at about 3,400 cm^{-1}. The asymmetric shape of the OH stretching band reflects the diversity of O–H groups on the surface of clay. The C–H stretching peaks clearly appear at 2,922 and 2,852 cm^{-1} correlated to symmetric and asymmetric modes of vibration, respectively. Noteworthy, the intensity of the peaks increased significantly in spectra (d) and (e) due to the exposure of clay to OMW. Broad peaks that can be assigned for Si–O bonds in the silicate were also recorded in the range of 950–1,100 cm^{-1}. The features at about 1,459 cm^{-1} which represent carbonates stretching bands nearly vanished after calcination (spectra b, c, and e). A new peak appeared at around 1,400 cm^{-1} in spectrum (d) when only calcined clay was exposed to OMW which could be assigned to phenol, O–H in-plane bending. This peak did not appear in spectrum (e) when clay was treated with HCl solution in addition to calcination before exposure to OMW. This result is in accordance with the data shown in Fig. 4, where acid treated clay did not uptake much phenols compared to the only calcined (no acid treatment) case.

3.3. Packed bed experimental results

Fig. 8 shows the results of COD of the packed bed experiment as a break-through curve. As described in the experimental section above, the flow rate of OMW was 0.10 ml/s and the EBCT was 15.7 min. The initial OMW output of the bed showed about 50% reduction in COD, which kept decreasing to about 20% reduction in COD level after 22 min. After more than 1 h, the reduction in COD reached about 10%. These results further confirm the above batch experimental results in that the amount of COD percentage reduction is moderately significant, and a large quantity of

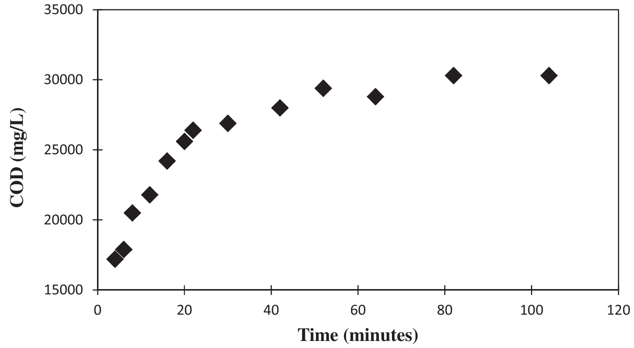

Fig. 8. Break through curve for COD of OMW flow through a packed bed of clay. COD of raw OMW fed to the packed bed is 32,400 mg/L.

clay was needed to reduce the COD level by 50% as seen in the packed bed experiment.

4. Conclusions

In this investigation, both COD and phenols of raw OMW were reduced by 10–20% in batch experiments, while the reduction in COD in the continuous packed bed experiment was 50%. These reductions are relatively significant quantities considering the large amounts of organic matter involved (COD $\sim$40,000 mg/l). Even though, the results did not achieve COD levels that may allow treated OMW to be used for irrigation purposes, however, they warrant further investigation of this approach like attempting to modify the investigated clays to become more organophilic. In addition, such large amounts of reduction in COD values would be expected to greatly improve the application of classical biological treatment of OMW as a downstream treatment method. One should not forget that the treatment of OMW is not expected to be possible using only one treatment methodology.

References

[1] Department of Statistics, Jordan. Agricultural Statistics Bulletin, National Strategy for Agricultural Development Surveys: 2010, August 2011.

[2] M.O.J. Azzam, K.I. Al-Malah, N.I. Abu-Lail, Dynamic post-treatment response of olive mill effluent wastewater using activated carbon, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. A39 (2004) 269–280.

[3] K. Chartzoulakis, G. Psarras, M. Moutsopoulou, E. Stefanoudaki, Application of olive mill wastewater to a cretan olive orchard: Effects on soil properties, plant performance and the environment, Agric. Ecosyst. Environ. 138 (2010) 293–298.

[4] C. Rousidou, K. Papadopoulou, G. Zervakis, B.K. Singh, C. Ehaliotis, D.G. Karpouzas, Repeated application of diluted olive mill wastewater induces changes in the structure of the soil microbial community, Eur. J. Soil Biol. 46 (2010) 34–40.

[5] R. Jarboui, F. Sellami, C. Azri, N. Gharsallah, E. Ammar, Olive mill wastewater evaporation management using PCA method: Case study of natural degradation in stabilization ponds (Sfax, Tunisia), J. Hazard. Mater. 176 (2010) 992–1005.

[6] R. Jarboui, M. Chtourou, C. Azri, N. Gharsallah, E. Ammar, Time-dependent evolution of olive mill wastewater sludge organic and inorganic components and resident microbiota in multi-pond evaporation system, Bioresour. Technol. 101 (2010) 5749–5758.

[7] A. Jail, F. Boukhoubza, A. Nejmeddine, S. Sayadi, L. Hassani, Co-treatment of olive-mill and urban wastewaters by experimental stabilization ponds, J. Hazard. Mater. 176 (2010) 893–900.

[8] M.A. Dareioti, S.N. Dokianakis, K. Stamatelatou, C. Zafiri, M. Kornaros, Exploitation of olive mill wastewater and liquid cow manure for biogas production, Waste Manage. 30 (2010) 1841–1848.

[9] L. Bertin, S. Lampis, D. Todaro, A. Scoma, G. Vallini, L. Marchetti, M. Majone, F. Fava, Anaerobic acidogenic digestion of olive mill wastewaters in biofilm reactors packed with ceramic filters or granular activated carbon, Water Res. 44 (2010) 4537–4549.

[10] M.R. Gonçalves, J.C. Costa, I.P. Marques, M.M. Alves, Strategies for lipids and phenolics degradation in the anaerobic treatment of olive mill wastewater, Water Res. 46 (2012) 1684–1692.

[11] L.M. Nieto, G. Hodaifa, S. Rodríguez, J.A. Giménez, J. Ochando, Degradation of organic matter in olive-oil mill wastewater through homogeneous Fenton-like reaction, Chem. Eng. J. 173 (2011) 503–510.

[12] M.I. Badawy, M.Y. Ghaly, M.E.M. Ali, Photocatalytic hydrogen production over nanostructured mesoporous titania from olive mill wastewater, Desalination 267 (2011) 250–255.

[13] K. Curi, S.G. Velioglu, V. Diyamandoglu, Treatment of olive oil production wastes, In: K. Curi (Ed.), Treatment and Disposal of Liquid and Solid Industrial Wastes, Proceedings of the 3rd Turkish–German Environmental Engineering Symposium, Istanbul, Pergamon Press, Oxford, pp. 189–205, 1979.

[14] M. Jeguirim, A. Chouchène, A.F. Réguillon, G. Trouvé, G. Le Buzit, A new valorisation strategy of olive mill wastewater: Impregnation on sawdust and combustion, Resour. Conserv. Recy. 59 (2012) 4–8.

[15] M.O.J. Azzam, K. Al-Malah, Z. Al-Gazzawi, S.A. Al-Omari, Dynamic treatment response of olive mills wastewater (OMW) using series of adsorption steps, Clean Soil Air Water 38 (2010) 822–830.

[16] A. Cassano, C. Conidi, E. Drioli, Comparison of the performance of UF membranes in olive mill wastewaters treatment, Water Res. 45 (2011) 3197–3204.

[17] M. Stoller, Effective fouling inhibition by critical flux based optimization methods on a NF membrane module for olive mill wastewater treatment, Chem. Eng. J. 168 (2011) 1140–1148.

[18] A. El-Abbassi, M. Khayet, A. Hafidi, Micellar enhanced ultrafiltration process for the treatment of olive mill wastewater, Water Res. 45 (2011) 4522–4530.

[19] T. Coskun, E. Debik, N.M. Demir, Treatment of olive mill wastewaters by nanofiltration and reverse osmosis membranes, Desalination 259 (2010) 65–70.

[20] E. Garcia-Castello, A. Cassano, A. Criscuoli, C. Conidi, E. Drioli, Recovery and concentration of polyphenols from olive mill wastewaters by integrated membrane system, Water Res. 44 (2010) 3883–3892.

[21] B.K. Mert, T. Yonar, M.Y. Kilic, K. Kestioglu, Pre-treatment studies on olive oil mill effluent using physicochemical, Fenton and Fenton-like oxidations processes, J. Hazard. Mater. 174 (2010) 122–128.

[22] O. Yahiaoui, H. Lounici, N. Abdi, N. Drouiche, N. Ghaffour, A. Pauss, N. Mameri, Treatment of olive mill wastewater by the combination of ultrafiltration and bipolar electrochemical reactor processes, Chem. Eng. Process 50 (2011) 37–41.

[23] F. Hanafi, O. Assobhei, M. Mountadar, Detoxification and discoloration of Moroccan olive mill wastewater by electrocoagulation, J. Hazard. Mater. 174 (2010) 807–812.

[24] F. Hanafi, A. Belaoufi, M. Mountadar, O. Assobhei, Augmentation of biodegradability of olive mill wastewater by electrochemical pre-treatment: Effect on phytotoxicity and operating cost, J. Hazard. Mater. 190 (2011) 94–99.

[25] S. Azabou, W. Najjar, M. Bouaziz, A. Ghorbel, S. Sayadi, A compact process for the treatment of olive mill wastewater by combining wet hydrogen peroxide catalytic oxidation and biological techniques, J. Hazard. Mater. 183 (2010) 62–69.

[26] M.A. Sampaio, M.R. Gonçalves, I.P. Marques, Anaerobic digestion challenge of raw olive mill wastewater, Bioresour. Technol. 102 (2011) 10810–10818.

[27] A. Scoma, L. Bertin, G. Zanaroli, S. Fraraccio, F. Fava, A physicochemical–biotechnological approach for an integrated valorization of olive mill wastewater, Bioresour. Technol. 102 (2011) 10273–10279.

[28] K. Baransi, Y. Dubowski, I. Sabbah, Synergetic effect between photocatalytic degradation and adsorption processes on the removal of phenolic compounds from olive mill wastewater, Water Res. 46 (2012) 789–798.

[29] Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Work, Water Environment Federation, Washington, DC, 1992.

[30] L. Zampori, G. Dotelli, P. Gallo Stampino, C. Cristiani, F. Zorzi, E. Finocchio, Thermal characterization of a montmorillonite, modified with polyethylene-glycols (PEG1500 and PEG4000), by *in situ* HT-XRD and FTIR: Formation of a high-temperature phase, Appl. Clay Sci. 59–60 (2012) 140–147.

[31] E. Ferrage, C.A. Kirk, G. Cressey, J. Cuadros, Dehydration of Ca-montmorillonite at the crystal scale, Part I: Structure evolution, American Mineralogist 92 (2007) 994–1006.

[32] K. Emmerich, F.T. Madsen, G. Kahr, Dehydroxylation behavior of heat-treated and steam-treated homoionic cis-vacant montmorillonites, Clays Clay Miner. 47(5) (1999) 591–604.

[33] D. Carroll, H.C. Starkey, Reactivity of clay minerals with acids and alkalies, Clays Clay Miner. 19 (1971) 321–333.

[34] R.E. Grim, Clay Mineralogy, McGraw-Hill, New York, NY, 1953.

[35] H. Spratt, L. Rintoul, M. Avdeev, W. Martens, The thermal decomposition of hydronium jarosite and ammoniojarosite, J. Therm. Anal. Calorim. (2013), doi: 10.1007/s10973-013-3213-1.

[36] D.L. Hudson-Lamb, C.A. Strydom, J.H. Potgieter, The thermal dehydration of natural gypsum and pure calcium sulphate dihydrate (gypsum), Thermochim. Acta 282–283 (1996) 483–492.

[37] S.H. Lin, R.S. Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review, J. Environ. Manage. 90 (2009) 1336–1349.

[38] H.B. Senturk, D. Ozdes, A. Gundogdu, C. Duran, M. Soylak, Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: Equilibrium, kinetic and thermodynamic study, J. Hazard. Mater. 172 (2009) 353–362.

[39] U.F. Alkaram, A.A. Mukhlis, A.H. Al-Dujaili, The removal of phenol from aqueous solutions by adsorption using surfactant-modified bentonite and kaolinite, J. Hazard. Mater. 169 (2009) 324–332.

[40] V.N. Nguyen, T.D.C. Nguyen, T.P. Dao, H.T. Tran, D.B. Nguyen, D.H. Ahn, Synthesis of organoclays and their application for the adsorption of phenolic compounds from aqueous solution, J. Ind. Eng. Chem. 19 (2013) 640–644.