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An Integrated Process of Olive Mill Wastewater Treatment

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Abstract: Olive mill wastewater (OMWW) is considered as a challenge for environmental scientists. It is characterized by high values of total organics expressed by chemical oxygen demand (COD), biological oxygen demand (BOD_5), and phenols. In this paper, an integrated process of OMWW treatment, which includes lime precipitation, filtration using a novel technology of a membrane filter press (a pilot scale) and a post-treatment using activated carbon adsorption for the filtrate, was studied. Lime precipitation has removed ~71% of phenols, ~39% of COD, and ~88% of BOD_5 with a rise in the total suspended solids (TSS) from 31 kg/m^3 (before precipitation) to 69 kg/m^3 (after precipitation).

The filtration and dewatering operation cycle is approximately 125–150 min. Filtration was examined at different feed pressure (3–5 bar), different slurry concentrations (23–69 kg/m^3, dry weight), and filter aid pre-coat with different additions of diatomite body feed. Specific cake resistance, α, was found to increase with the increase in feed pressure and to decrease with diatomite pre-coating and slurry concentration increase. However, a further decrease in α values was obtained using diatomite body feed. Cake dewatering, via membrane squeezing, was applied using hot water (65°C) and cake moisture was dropped from ~64% before squeezing to 35% after squeezing. Twenty minutes were found enough for that stage to be accomplished. With vacuum application, for 30 min, over the hot cakes, cake moisture decreased to ~20% for cakes with an average thickness of 1 cm. The produced cakes lose more moisture by storing in open air (on the shelf), reaching an equilibrium value of 9% in 2–3 days. Calorific value of produced cake is 15.71 MJ/kg, suggesting strongly its use as an energy source. Activated carbon was used as an efficient sorbent for removing the remaining phenols

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and total organics from the filtrate as a post-treatment showing promising results. Maximum removal of phenols and total organics, by lime precipitation and filtrate post-treatment using activated carbon adsorption, reached ~99.7% and ~80%, respectively.

A process flowsheet and preliminary cost estimates are presented and compared with other processes. The thermal energy produced by the burning of the produced cakes would be enough for the thermal needs of both the olive mill plant and the proposed treatment process.

Keywords: Olive mill wastewater, lime, membrane filter press, cake, activated carbon

INTRODUCTION

OMWW generated by the olive oil extraction industry is a dangerous pollutant due to its high organic content with high levels of phytotoxic and antibacterial phenolic substances that resist biological degradation (1–3). Typical oil producing nations are Italy, Spain, Greece, Tunisia, Portugal, Marocco, Libya, and Algeria (4, 5). The olive oil wastewater, commonly called olive mill wastewater, vegetation water, or Alpechin is a dark liquid containing many dissolved and suspended substances (5), generally, produced during the extraction of oil from the olive fruits (6).

The chemical composition of OMWW is very variable depending on olive variety, cultivation system, degree of fruit maturity and the procedure of oil extraction with the latter being the most important (7). In general, OMWW contains 83–96% water, 3.5–15% organics, and 0.5–2% mineral salts (8). The organic matter is composed of oil (1–14%), polysaccharides (13–53%), proteins (8–16%) organic acids (3–10%), polyalcohols (3–10%) and polyphenols (2–15%) (9). Among these constituents, those of phenolic nature have antibacterial effect, phytotoxic effect, and dark color (10). The chemical oxygen demand (COD) of OMWW is extremely high, in the range of $10^5\,\mathrm{mg\,O_2/L}$ (8). Although the phenolic fraction accounts for a relatively minor contribution to COD (roughly 14%), it is generally acknowledged that the high toxicity of OMWW is entirely related to phenols (11).

There are several processes described in the literature for the treatment of OMWW; however, until now, there is not an economic and profitable process, commonly accepted, for the OMWW treatment. The most simple and frequently applied method is the disposal in ponds and lagoons. However, this is a temporary solution because evaporation depends on weather changes. In addition, the ponds cause serious negative environmental impacts on nearby areas due to the bad odors, insect proliferation, leakages, and infiltrations to the surroundings (11, 12). Nevertheless, the main problem with evaporation ponds is their insufficient capacity because of the progressive change from the classic system, that produces 0.5–1 L/kg of OMWW per kg of olive, to the modern continuous centrifugation system, which produces more than double the volume of OMWW (1.3–2 L/kg) (13).

Another alternative for OMWW treatment is land utilization by direct irrigation using doses lower than 800 m^3/ha. Limitations to its use are due mainly to the phytotoxicity of OMWW caused by its polyphenols and salt (13).

Biodegradation, with aerobic and anaerobic microorganisms, has been used to treat OMWW, but it has not yet a significant application (14, 15). The presence of phenolic compounds makes the microbiologic degradation of OMWW very inefficient. In fact, the phenolic compounds have a chemical structure with benzene rings that is very stable and difficult to degrade (16). Other techniques are advanced processes such as ultrafiltration, reverse osmosis, wet air oxidation, etc., which have a high cost (12).

Treatment of OMWW for the removal of organic matter from the liquid phase can also be achieved by means of lime ($Ca(OH)_2$) coagulation (17). OMWW treatment using $Ca(OH)_2$ was carried out by Tsonis et al. (18) and COD dropped 20–30% with calcium hydroxide treatment, when it was added until the pH of the waste reached 11. In further studies by Aktas et al. (6), the impact of lime pretreatment on total solids, COD, and polyphenols removal for 17 different OMWW was evaluated. OMWW treatment resulted in about 41.5–46.2% COD removal. Although lime is an inexpensive and readily available material, lime coagulation generally has several drawbacks, namely (i) increase of solution pH and hardness, (ii) need for large dosages leading to the generation of excessive volumes of sludge, and (iii) need for coupling with flocculation to improve efficiency (19–21). In order to overcome some of these limitations, the filtrate obtained from the slurry filtration can pass through a cation resin column.

Oxidation of the organic content of OMWW was also studied using hydrogen peroxide (22), manganese dioxide (23), and monopersulfuric acid (24), but high operating costs have been pointed out as the major drawbacks of the process.

Adsorption treatment methods were also applied for OMWW treatment. Al-Malah et al. (25) used two consecutive treatments: settling, centrifugation, and filtration followed by a post-treatment for the filtrate using activated clay (bentonite). According to their study, maximum removal of phenols and organic matter was about 81 and 71%, respectively. Activated carbons from agricultural by-products were also tested for OMWW treatment (26).

In this paper, two main subsequent treatments were used to remove the phenols and other organics from OMWW. First treatment includes precipitation of phenols and other organics using calcium hydroxide followed by solid separation and cake formation using a pilot membrane filter press. The press allows filtration, cake squeezing, and cake drying via vacuum application over warm cakes. A post-treatment for residual phenols and total organics in the filtrate using activated carbon adsorption was accomplished in a bench level.

EXPERIMENTAL

Lime Precipitation

Fresh OMWW usually has a smell reminiscent of olive oil, but, when fermented, it assumed a fetid smell (13). Fresh OMWW, delivered from Cooperativa dos Produtores de Azeite do Torrão (Alentejo, Portugal) to our treatment unit, was acidified to pH 2 using sulfuric acid to prevent bacterial and fungal activities. Few experiments were carried out to optimize the time required for maximum precipitation and the amount of lime, $Ca(OH)_2$, required for maximum removal of phenols and other organics. From preliminary studies, almost 2 h were found enough for maximum precipitation. Accordingly, different amounts of solid $Ca(OH)_2$, 1–13 g, were added to 100 mL of OMWW (previously acidified to pH 2) under continuous agitation for 5 h. At the end of the experiments, the supernatant was filtered and several testes were carried out including total suspended solids (TSS), the concentrations of phenols and total organics (expressed as COD), turbidity and BOD_5.

Solid Separation by Filtration Using a Membrane Filter Press

Filtration Equipment Description

The membrane filter press (US Filter J-VAP, model no. 470V30-7-1MYLW, serial number JV0044, manufactured in 2000) is a seven-chamber, plate and frame style filter press. Total volume of the seven chambers is 28 L with total filtration area of 1.9 m^2. A thorough description of the equipment, membrane plates, tubing, and filter cloth was published earlier in our previous study (27). In this study, the filter plates were rearranged to use three chambers only with 0.8143 m^2 filtration area and 12 L chambers volume, using four plates producing three cakes in each filtration cycle.

The filter operation steps are manually controlled through valves and switches for each motor in a control panel. The slurry feed pump is a pressure-regulated, air-operated, double diaphragm pump (All-Flo pump company, model: BK-15, serial no. 105647). The pumping cycle continued to operate until the filter chambers were filled with solid and the pump almost stalled. The feed pump was used at pressure range of 3–5 bar.

In the squeezing stage, the membrane plates were inflated with water. A centrifugal pump (MTH pump, model T51G BF) and a heater (Ogden, model: KS-0591-M7) were used to fill the membranes at squeezing pressure 6–7 bar and the water was returned to the squeeze water supply tank at 65°C (27).

Vacuum drying was applied over the hot cakes at 0.0481 bar, via a liquid ring vacuum pump (Squire Cogswell Company, number C00-2240/1, Type: PM124-M30A) through the filtrate outlet ports and the central core (27).

Water vapor departs the hot cakes through the eyelets series on the top and bottom of each membrane plate and also through the central core and condensing in a tank, knock-out tank (28), before reaching the vacuum pump.

The 12-steps dewatering cycle is listed in Table 1. Three dewatering cycles are processed per day producing about 3.5 kg and 3 kg of solids after lime treatment (on dry basis) per batch (three cakes) for filtration with and without filter aid pre-coat, respectively.

System Limitations

The feed pressure was measured through a manometer installed between the feed pump and the press, however, cycling of the feed pump (double diaphragm pump) caused the pressure to fluctuate through the feed stroke of about the pressure value ±0.1 bar and an average pressure value between the maximum and minimum for the manometer for each stroke was recorded. The viscosity of the slurry was assumed to be the same as water.

Filtration Cycles

Phenols and other organics were precipitated by lime addition prior to solid separation using the novel membrane filter press technology. Based on the previous bench studies, 40 kg of $Ca(OH)_2$ were mixed with the acidified OMWW slurry (1 m^3) in the feed tank under continuous mechanical and air agitation for 24 h.

A mechanical and air agitators were used to keep the slurry homogeneously suspended in the feed tank 30 min prior to the filtration start and during the filtration process. A slurry of diatomite filter aid (Celite Hyflo Supercel, Celite Co.) with an average particle size 30.1 μm was prepared by mixing 170 g diatomite with 90 L of tap water (1.89 g/L) in a 100 L tank. Pre-coating of filter aid was carried out by feeding the well-agitated

Table 1. Dewatering steps of lime treated OMWW

Step	Time required, (min)	Step	Time required, (min)
1. Press close	2	7. Squeezing	20–30
2. Membrane drain	1	8. Air drying	5
3. Diatomite pre-coat	10	9. Hot squeezing with vacuum drying	30–60
4. Fill press	1–2	10. Vent press	1
5. Filtration	20–30	11. Open press	1
6. Core blow	2	12. Retract plates and discharge cakes	3

diatomite slurry into the filter press at a rate of 35 L/min and the filtrate was returned to the pre-coat tank for recirculation. Pre-coating process was continued for 10 min.

Filtration and Drying Operations

Prior to diatomite pre-coating and dewatering cycle starting, the membranes should be drained. This is accomplished through deflating the membranes by applying air at pressure of 2 bar with certain valves arrangement (27). The water in the membrane plates from a previous squeezing step (in a previous dewatering cycle) is forced back to the squeeze water tank. This step ensures that there is no water in the membranes before the filtration cycle is started. The filtrate progress was monitored by the volume of filtrate produced. Volume was recorded to the nearest cubic centimeter using a calibrated 20 L filtrate vessel. Time was also recorded to the nearest seconds. The filtration process was continued until the feed pump almost stalled.

Core blow was carried out by applying air at low pressure, 1–2 bar, for 2 min to empty the central core prior to washing and drying steps (27). Cake washing was not applied to avoid any dissolution for precipitated organics. Cake drying was accomplished via membrane squeezing followed by vacuum drying. Membrane squeezing was carried out by circulating 65°C water through J-VAP membrane filter plates at pressures (6–7 bar) following the squeezing filtrate volume with time until it was far-dropping. This stage was continued for 20–30 min and a sample of the squeezed filtrate was collected to be analyzed.

Air drying was applied straight after the squeezing was accomplished using compressed air at 5 bar for about 5 min (27). Hot squeezing was applied again at the same pressure for about 5 min to restore the cake temperature prior to vacuum application.

Vacuum was then applied at pressure of 0.0481 bar on the cake chamber simultaneously with continued cake squeezing for 30 min. The vacuum in the cake chamber caused the boiling point of the water to drop to 45°C (28). Straight after the dewatering cycle was completed and cakes were separated, moisture content was measured by drying ~50 g of a representative sample of each cake at 120°C until constant weight in a moisture analyzer oven (Mettler LJ16). The dried sample was allowed to cool in a desiccator and then weighed. The final moisture content was calculated from the difference in the weight of the cake sample before and after drying.

Filtrate Post-Treatment

Residual non-precipitated phenols and other organics in the filtrate, after solid separation, were treated by adsorption using granular activated carbon

(Cal, Chemviron carbon) with the following properties: surface area (N_2 BET method): 1050 m^2/g; mesh size: 12 × 40 (US sieve series); mean particle diameter: 0.9–1.1 mm; apparent density: 0.44–0.55.

From preliminary experiments, the equilibrium was achieved in almost 48 h. A total of 50 mL of filtrate were mixed with different doses of activated carbon and left under continuous shaking (100 rpm), using an orbital shaker (AGITORB 160E), at 25°C, until equilibrium was reached.

Cake Characterization

Cake elemental analysis, ash content, and calorific value were measured by INETI (Instituto Nacional de Engenharia, Tecnologia e Inovação, Lisboa, Portugal).

Analytical Methods

TSS was measured for OMWW after acid treatment and after lime precipitation using method 2540 D described in Standard Methods (29). Several tests were conducted to characterize OMWW after removal of suspended solids by filtration, before and after lime precipitation and also after filtrate post-treatment by activated carbon adsorption. Total phenols were determined according to the method 5550B proposed in Standard Methods (29), which is based on the Folin-Ciocalteau reagent using a UV spectrophotometer Hitachi U2000 at maximum absorbance in the range of 600–700 nm. Turbidity was measured in a LP2000 turbidity meter, from HANNA instruments, and calibrated against formazin standards using method 2130 described in Standard Methods (29). COD was measured using method 5220D described in Standard Methods (29) via an Aqualytic PC Compact photometer and BOD_5 was measured using a BOD_5 sensor and an Aqualytic inductive stirring system, according to method 5210B described in Standard Methods (29) for 5-day test. Fat and grease were analyzed using method 5520D of Soxhlet extraction described in Standard Methods (29).

Experiments of lime precipitation and activated carbon post-treatment, and analytical tests were carried out at least three times and maximum analytical error was found to be less than 5%. Experiments including filtration, squeezing, and vacuum drying were also carried out three times and maximum analytical error was found to be less than 5%, conditioned that the filter cloth is clean before use. Filter cloth was cleaned first by passing pressurized water over the cloth surface to remove big particles adhered to the cloth surface and then by impregnation in 10% commercial alkaline hypochlorite solution overnight to remove the fine unfiltered particles followed by successive water rinsing to remove any residuals of the alkaline hypochlorite solution.

RESULTS AND DISCUSSION

Precipitation of Phenols and Other Organic Compounds

From preliminary experiments, a period of 2 h was found to be enough for the maximum precipitation of phenols and other organics to be achieved. There was no change in phenols and COD concentrations after 2 h of lime mixing with agitation. Accordingly, to optimize the amount of solid $Ca(OH)_2$ required for the maximum removal of phenols and organics, a 5 h period was chosen, as precipitation time.

As shown in Fig. 1, as the amount of solid $Ca(OH)_2$, which is added to OMWW, increased, concentration of phenols and COD decreased; however, almost no further removal took place with more addition of solid $Ca(OH)_2$ above 40 g per L of OMWW. Therefore, 40 g of lime were found optimum for precipitation of unwanted organics in 1 L of OMWW removing 71.2% of phenols and about 39% of COD, Table 2. Another study by Aktas et al. (6) has shown that about 41.5–46.2% of COD was removed by lime treatment, however, Tsonis et al. (18) found that the COD value dropped 20–30% by lime treatment. The variation in COD removal upon lime treatment in literature is perhaps related to the large variation of the OMWW chemical composition (7). BOD_5 and turbidity were also found to decrease by lime treatment, Table 2. On the other hand, total suspended solids (TSS) of OMWW increased by more than two folds after lime treatment. This is related to the precipitation of unwanted organics by lime in addition to an excess of insoluble $Ca(OH)_2$.

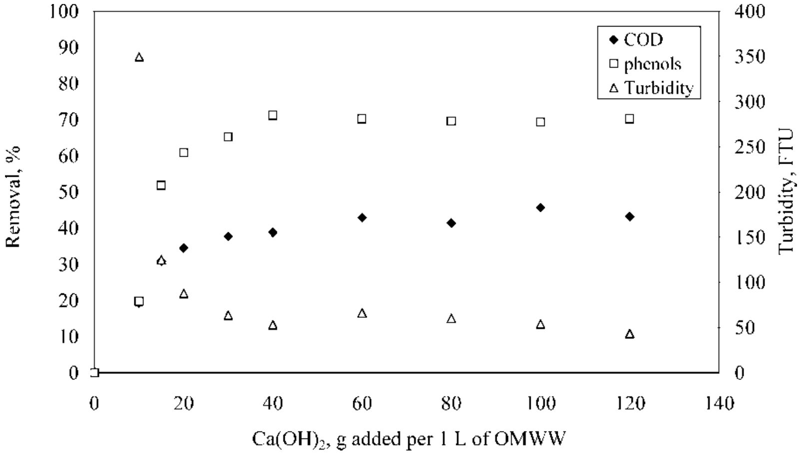

Figure 1. Removal of total organics (expressed as COD), phenols, and turbidity from OMWW by lime precipitation.

Table 2. OMWW characterization before and after precipitation using 40 kg of lime in 1 m^3 of OMWW

Tests	Before precipitation	After precipitation
[a]BOD_5, mg/L	1380	160
[a]COD, mg/L	51867	31706
[a]Phenols, mg/L	3395	980
[b]TSS, g/L	31	69

[a]Tests carried out using OMWW after the removal of suspended solids by filtration.

[b]Test carried out on OMWW slurry.

However, in this study using lime in the concentration 40 g/L, the treatment of OMWW with lime proved ineffective in removing color. Similar results have been presented elsewhere by other researchers (30–32). Accordingly, after solid separation the filtrate was treated for color removal using activated carbon, as shown later in the paper.

Filtration of Lime-Treated OMWW

The classical filtration theory described in Svarovsky (33) was used to model the filtration behavior of lime-treated OMWW. Cake growth occurs as solids in the feed collect and accumulate on a growing layer of the filter cake. The cake resistance, for incompressible cakes, remains constant as the cake grows and the pressure drop is linear across the cake. The specific cake resistance, α, and medium resistance, R_m, are determined using the following equation: (33)

$$\frac{t - t_s}{V - V_s} = \frac{\alpha \mu c}{2A^2 \Delta P} \cdot (V + V_s) + \frac{\mu R_m}{A \cdot \Delta P} \tag{1}$$

Filtration at Different Feed Pressure

Filtration kinetics was carried out for lime-treated OMWW slurry, with solid concentration of 69 kg/m^3 (on dry basis), with and without diatomite filter aid pre-coat under different feed pressure (3–5 bar). Figure 2 represents the filtrate volume-time behavior and Fig. 3 shows the variation of filtration rate against the accumulated filtrate volume. The filtration rate, which is high at the start of filtration, varies as the pressure builds and then shows a decrease as a result of the increased filtration resistance with the cake starting to form. The rate of filtration depends on the feed pressure. The higher the feed pressure, the higher the filtration rate for both filtration

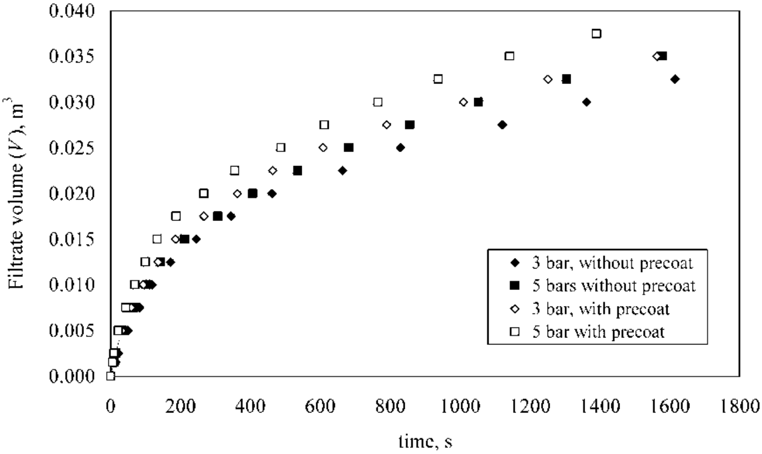

Figure 2. Filtration pattern of lime-treated OMWW with and without filter aid pre-coat.

cases (with and without pre-coat) with higher rate values for the filtration with diatomite pre-coat.

Plotting the adjusted inverse rate, $(t - t_s)/(V - V_s)$ vs. the adjusted filtrate volume, $(V + V_s)$, gives a straight line with a slope from which the specific cake resistance is determined (Fig. 4a and b). For the filtration system under study, careful data collection produced standard errors for the slope below 5% with r^2 values not less than 0.98. The specific cake resistance, α, was found to increase with feed pressure in both filtration studies (with and

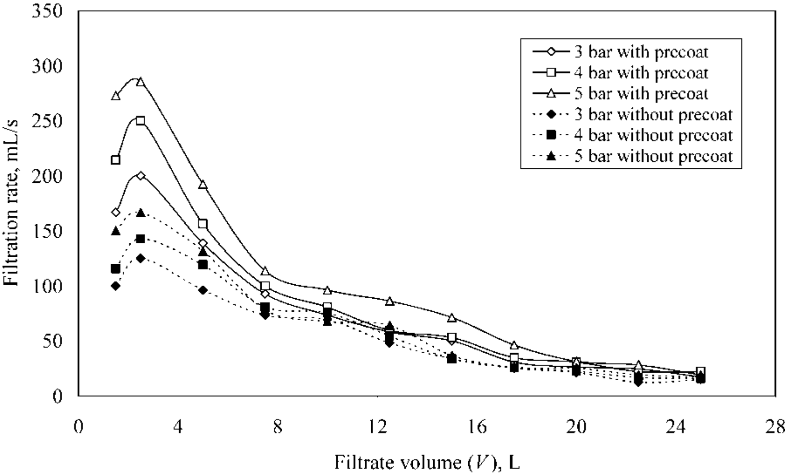

Figure 3. A plot of filtration rate for pre-coated cakes at different feed pressure.

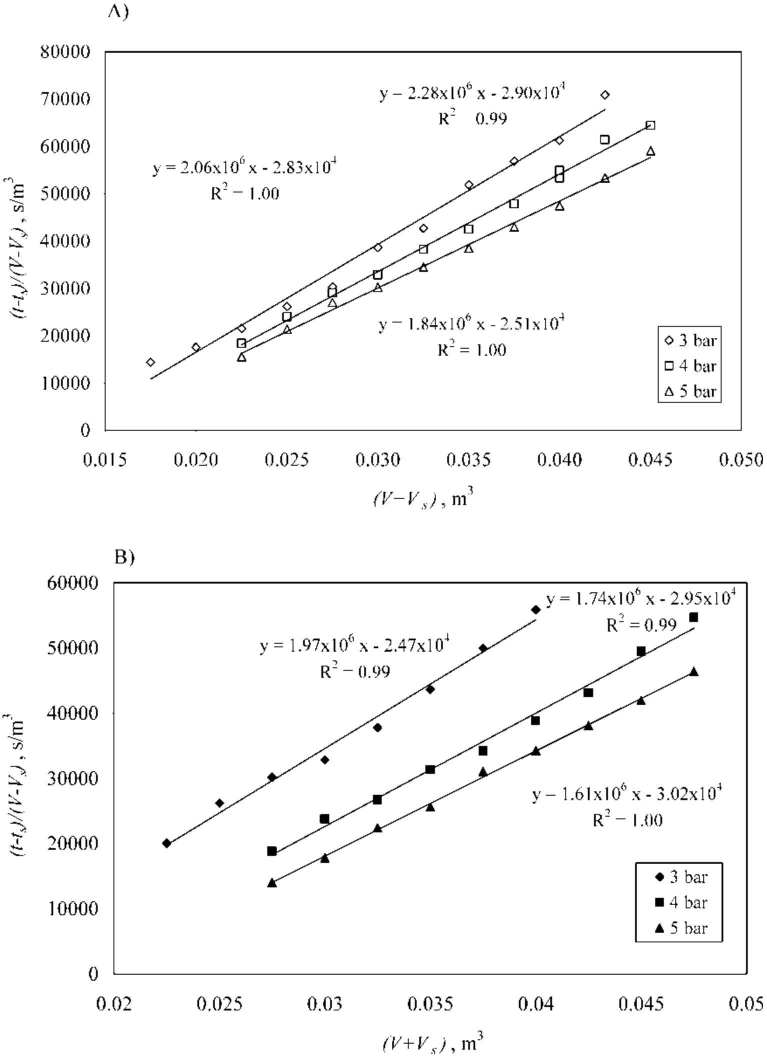

Figure 4. A plot of $(t - t_s)/(V - V_s)$ against $(V + V_s)$ at different feed pressure (slurry concentration: $69\,\mathrm{kg/m^3}$). (A) without filter aid pre-coat; (B) with filter aid pre-coat.

without pre-coat). This is because the cake becomes denser under high feed pressure providing fewer and smaller passages for the filtrate flow. On the other hand, the specific cake resistance decreases as a result of diatomite pre-coating, (Table 3). In other studies (27, 34), a decrease in the specific cake resistance with a higher filtration rate was observed by applying filter aid pre-coat. The diatomite pre-coat makes a bed over the filter cloth and

Table 3. Specific cake resistance (α) at different filtration conditions

Applied conditions					
Feed pressure (bar)	Slurry conc. (kg/m^3)	Diatomite body feed conc. (kg/m^3)	α, without filter aid pre-coat (m/kg)	α, with filter aid pre-coat (m/kg)	α, with filter aid pre-coat and diatomite body feed (m/kg)
3	69	—	1.31×10^{13}	1.14×10^{13}	—
4	69	—	1.58×10^{13}	1.34×10^{13}	—
5	69	—	1.77×10^{13}	1.55×10^{13}	—
5	23	—	—	2.26×10^{13}	—
5	46	—	—	1.77×10^{13}	—
5	69	17.25	—	—	1.08×10^{13}
5	69	34.50	—	—	8.85×10^{12}
5	69	51.75	—	—	6.73×10^{12}

the fine particles of the cake infiltrate into the void spaces of the diatomite bed protecting the filter cloth and offering less resistance to flow and accordingly higher filtration rates were obtained. In addition, filter aid pre-coat provides two distinct advantages in their use: (i) particles of a sub-micron size may be retained, yielding a clearer filtrate; and (ii) the cake is easily removed from the filter medium at the end of the dewatering process (34). However, the difference in α values between pre-coated and non-pre-coated cakes at similar feeding pressures is less than that shown earlier for brewer's spent grain at the same conditions (27). This could be related to the presence of insoluble $Ca(OH)_2$ particles in lime-treated OMWW that act as a minor body feed facilitating the filtration, to some extent, even in the absence of diatomite pre-coat.

According to the classical filtration theory, the medium resistance, R_m, should normally be constant. However, the theory has been under criticism (33) since medium resistance, in practice, often appears as unrealistically small or even negative. In the current study, R_m is known with far less certainty than the specific cake resistance, and R_m values, in this study, appeared unrealistically negative. The uncertainty of the intercept is too large to be used for medium resistance determination. The larger error in R_m results from the extrapolation necessary for the intercept determination. The unrealistic R_m values could be because of the increased medium resistance, as a result of the penetration of some solids into the filter medium, and the variation of the cake resistance along the filtration process. Similar results with large errors in medium resistance were also found in filtration studies of brewer's spent grain (27) and hafnium hydroxide (35) using a membrane filter press. Leu and Tiller (36) considered that some of the basic assumptions involved in flow-through compressible porous media have been shown to be incompatible with experimental data. The development of an adequate theory of filtration gets complicated because of the following two factors (36):

a. The increase in the resistance in the septum (filtration medium) not only during the first few seconds, but also throughout the entire process in many cases (36, 37).
b. Variation in cake resistance, continuing throughout the process as a result of subsequent closure of passages as small particles migrate downstream in the cake (36).

The fact that a pore could be blocked by particles much smaller than the pore itself was recognized early in filtration literature (36).

Most cakes formed from biological materials are compressible. As liquid flows through a compressible bed of particles, viscous drag on the particles produces compressive pressure which causes α to increase and porosity to decrease toward the filter medium (38). The following empirical equation has been proposed to consider cake compressibility (39):

$$\alpha = \alpha_o(\Delta P)^s \tag{2}$$

α_o is a constant that represents the specific cake resistance at zero compressive pressure and s is the compressibility coefficient of the cake. s values vary between 0 for incompressible cakes and 1 for highly compressible ones (34). Plotting the specific cake resistance values against the filtration pressures on a log-log scale shows a straight line whose slope gives the cake compressibility coefficient, s (Fig. 5). The values of α_o and s are 5.92×10^9 m/kg and 0.599 ($r^2 = 0.998$), and 8.26×10^9 m/kg and 0.585 ($r^2 = 0.999$), for filtration with and without pre-coat, respectively. The values of the compressibility factor, s, shown here, indicate the compressible character of the cakes.

Filtration with Diatomite Pre-Coat and Body Feed

Diatomite was dispersed in the OMWW through proper agitation, as mentioned earlier, and pumped together with the slurry into the press through the feed pump. Filtration pattern, in the presence of different doses of diatomite body feed, is presented in Fig. 6. An increase in the filtration rate was observed with the increase in the amount of diatomite body feed (Fig. 7). An additional decrease in the specific cake resistance, α, was obtained with the addition of diatomite as a body feed, after pre-coating (Table 3), and as the diatomite body feed dose increases, α further decreases (Fig. 8). A similar decrease in α values with the increase in the amount of diatomite body feed was found earlier (34, 40). With diatomite body feed, as filter cycle progresses, the body feed produces a fresh new

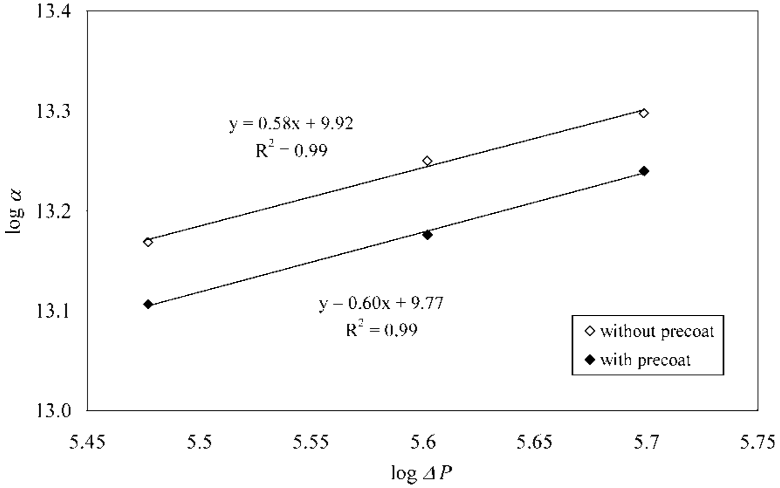

Figure 5. A plot of log α vs. log ΔP.

filtering surface, reducing cake resistance and facilitating the entrapment of the particles. This provides additional microscopic channels through which clarified fluid can flow, thus keeping the permeability and porosity high. Diatomite body-feed filtration can be considered as a dynamic filtration where the filtering surface is constantly renewing itself. In this case, cake

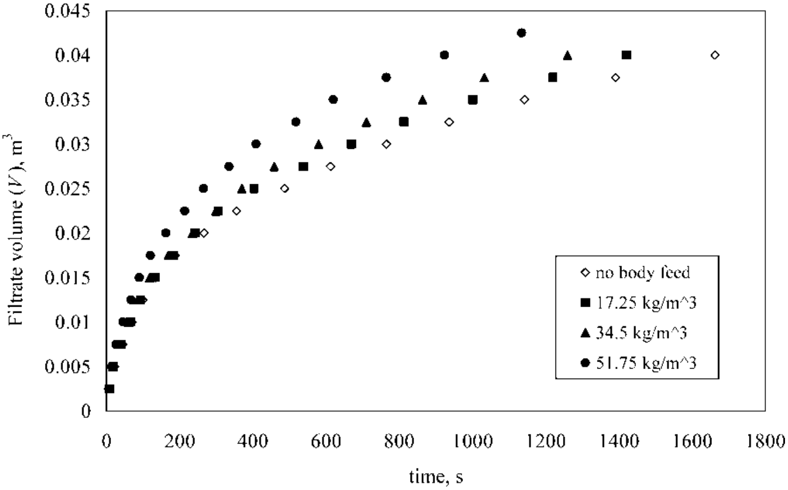

Figure 6. Filtration pattern for pre-coated cakes with different doses of diatomite body feed.

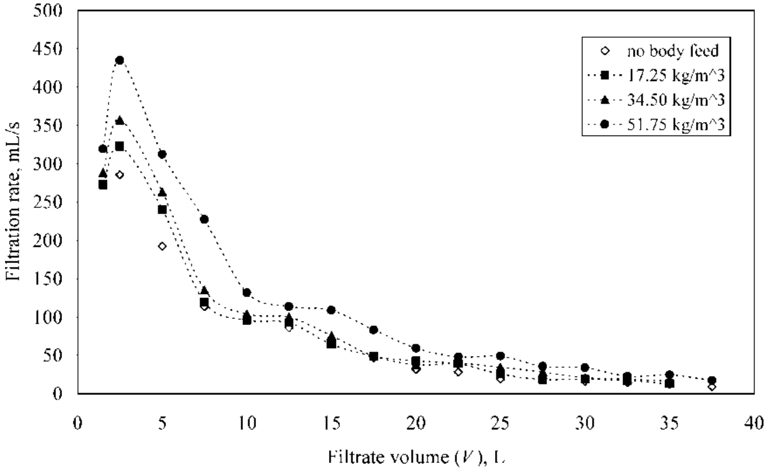

Figure 7. Filtration rate against volume with diatomite body feed variation.

thickness increases and the solids of the incoming suspension cannot clog its channels with excessive accumulation (41, 42).

Filtration at Different Slurry Concentration

Using a slurry concentration in the range of 23–69 kg/m^3 (on slurry dry basis), the filtration was carried out only with diatomite pre-coat under a feed pressure of 5 bar. The kinetics of filtration are presented in Fig. 9 with

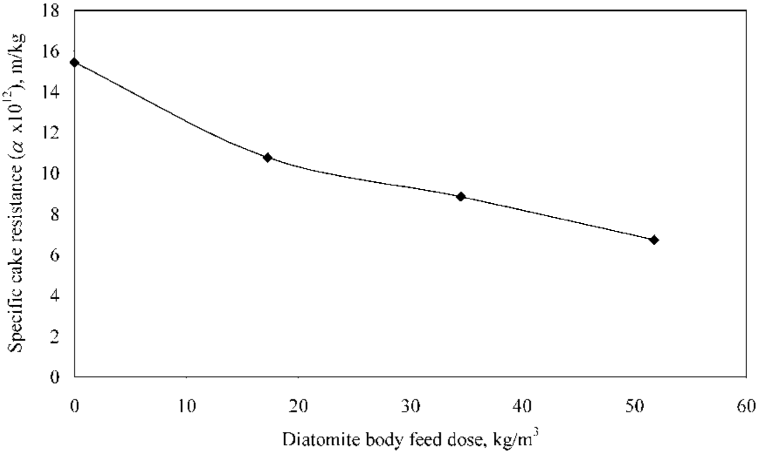

Figure 8. Variation of specific cake resistance with filter aid dose at the same pre-coating conditions.

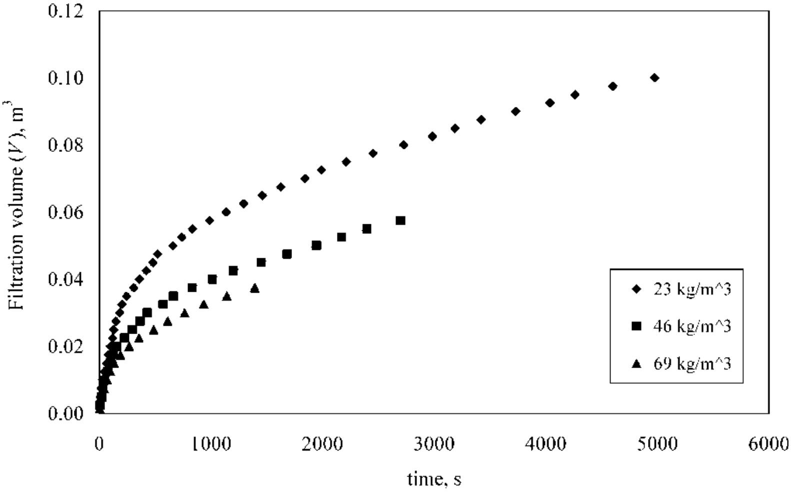

Figure 9. Filtration of lime-treated OMWW at different slurry concentrations.

a faster filtration for lower slurry concentration. The rate of filtration depends on the slurry concentration with higher rate values obtained for slurries with lower solid concentration. The specific cake resistance, α, was found to decrease with the increase in slurry concentration (Table 3).

It is noticed that α varies not only with feed pressure, but also with cake depth. As the cake thickness depends on the concentration of the particles in a slurry, α is correlated to slurry concentration as shown in the following equation (38):

$$\alpha = \alpha_o c^{-m} \tag{3}$$

It is observed that α decreases not only with the diatomite pre-coat, but also with the increase in slurry concentration, Table 3, and the log-log plot of the specific cake resistance, α, and slurry concentration, c, gives a straight line with a negative slope with m value of 0.347 ($r^2 = 0.999$) (Fig. 10). Lower slurry concentration produces less solid content into the press giving more chances for the particles to be arranged under pressure, leaving fewer voids between the particles, producing denser and thinner cakes with higher α value (27). However, if the slurry concentration increases, more solid is produced in the filter chambers in a short time, giving less chances for particles to arrange and thus more voids are available between the particles and thicker cakes are produced with a lower α value (27).

Cake Dewatering via Membrane Squeezing

Squeezing step is considered as a crucial step for the success of the dewatering process (27, 35). OMWW cake produced by conventional pressure filtration at

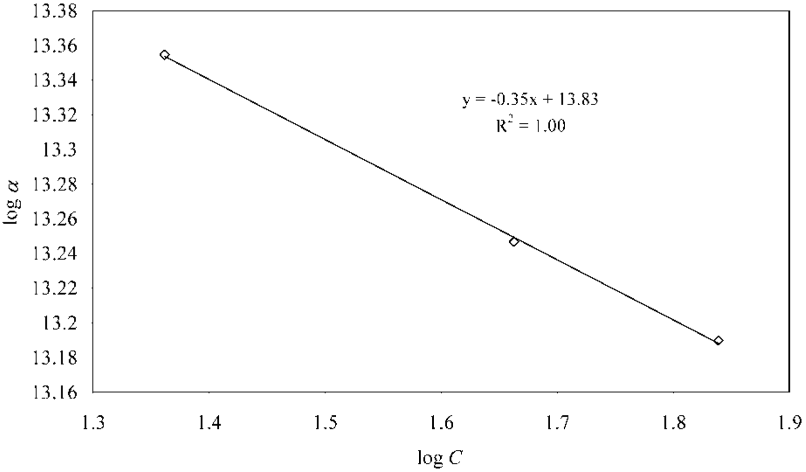

Figure 10. A plot of Log α against log C (C: slurry concentration).

5 bar contains about 64% moisture. Squeezing, by passing water (at room temperature) at squeezing pressure of 6.5 bar for 15 min through the membranes, decreases the moisture content to about 42% for cakes with 1 cm thickness (after complete drying). Squeezing using hot water (65°C) at the same conditions uniformly dewaters the cake to 35%. Squeezing patterns under different conditions are shown in Fig. 11. Squeezing causes the particles in the filter cake to rearrange that they are more densely packed. The fluid in the voids between the particles must flow out and leave the cake through the filter cloth. The pressure gradient between the cake and the filter cloth provides the driving force for the fluid flow. As the cake becomes drier, it bears an increasing fraction of the imposed pressure, causing the pressure on the fluid to decrease. The decreasing pressure gradient causes the dewatering rate to decrease as the dewatering proceeds (27).

Cold squeezing provides less squeezing rate than hot squeezing under the same squeezing pressure of 7 bar (Fig. 11a). The hot squeezing is believed to mobilize retained filtrate among the cake particles that it is released faster with a larger amount of squeeze liquid than the cold squeeze. Most of the squeeze water was flown out of the cake in the first 5–7 min with flow rate higher at higher squeezing pressure (Fig. 11b). In addition, higher squeezing rates were achieved from pre-coated cakes than from non-pre-coated ones at the same squeezing pressure, and this could be because the filter cloth is protected by the filter aid pre-coat from blinding caused by unfiltered particles through filtration without filter aid pre-coat. The increased squeezing pressure resulted in increased dewatering and the maximum squeezing pressure, 7 bar, showed the best squeezing performance.

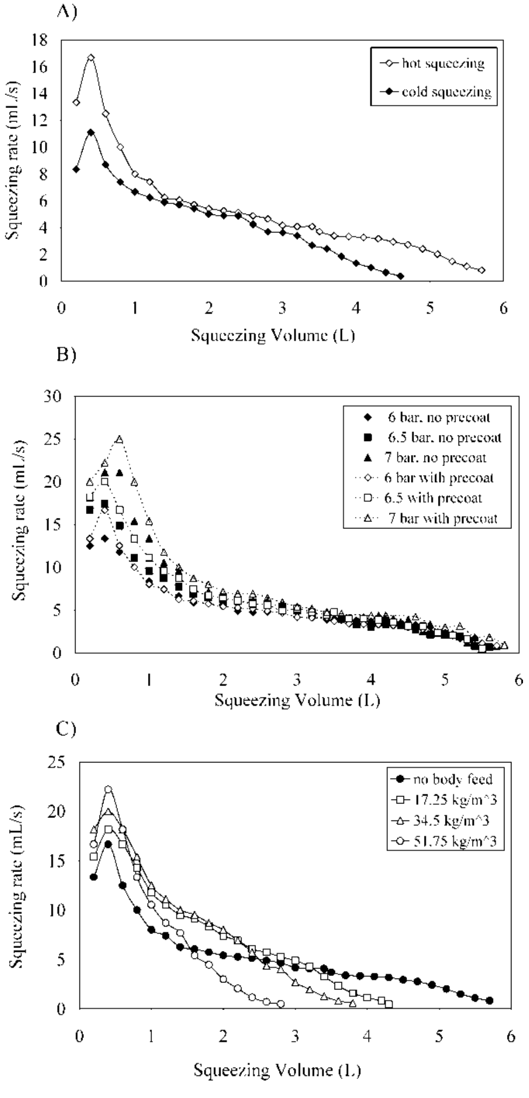

Figure 11. Cakes squeezing pattern: (A) Using cold and hot water (65°C) at squeezing pressure 7 bar. (B) At different squeezing pressure for pre-coated and non-pre-coated cakes. (C) Using different doses of diatomite body feed (expressed as kg of diatomite per 1 m^3 of OMWW slurry) for pre-coated cakes at squeezing pressure of 7 bar.

Squeezing rate at squeeze pressure of 7 bar, for pre-coated cakes with different doses of diatomite body feed is shown in Fig. 11c. For cakes with higher doses of diatomite body feed, higher squeezing rates were obtained in the early stages of squeezing, followed by a sharp decrease in the squeezing rate with less volume of total fluid received at the end of squeezing. As diatomite body feed increases, the cake permeability, porosity, and thickness increases. The increased permeability and porosity leads to higher squeezing rates in the early stages of squeezing (5–7 min). However, as the cakes gets drier, thicker cakes produced with larger doses of diatomite body feed possess more solids than thinner ones, bearing higher fraction of the squeezing pressure. Thus, less pressure is applied on the fluid in thicker cakes than in thinner ones, resulting in the decrease of squeezing rate with the progress of time with less squeeze volume received at the end of the squeeze stage. Consequently, higher moisture content was achieved in thicker cakes.

Cake Air Blow

Air blowing is an important dewatering step and used to displace water from the microscopic channels between the particles in the filter cake. Blowing also removes water from piping and channels inside the press prior to vacuum application. Approximately 750 mL of water are removed during the cake blow in each dewatering cycle. About 250 mL are from the central core and the rest is believed to be from the cakes, as well as piping and channels in the press.

Filter Cake Drying

After the air blow step was accomplished, squeezing was applied again using hot water (65°C) for 10 min to restore the cake temperature after a loss caused by air blow. Vacuum drying over the hot cakes was then applied simultaneously with continued squeezing. The success key of this step is based on the fact that water boiling point decreases under the low pressure developed by vacuum. Vacuum application at 0.0481 bar would lower the water boiling point down to 32°C in an ideally sealed system. The actual boiling point referred in the US Filter manual (28), in the cake chambers under vacuum, was 45°C, which is still lower than the squeezing water temperature.

An economic period of vacuum application (30 min) was chosen for drying cakes with different thickness. Higher moisture content was found for thicker cakes than for thinner ones (Fig. 12). Cake thickness is an important factor for the efficiency of filter cake drying under vacuum. For cakes with 1 cm thickness 20% moisture was achieved. For cakes that are thicker than 1 cm, it becomes difficult to achieve high levels of cake dryness with economic periods of vacuum application. This could be because of the fact that as the cake gets thicker, the heat transfer from the

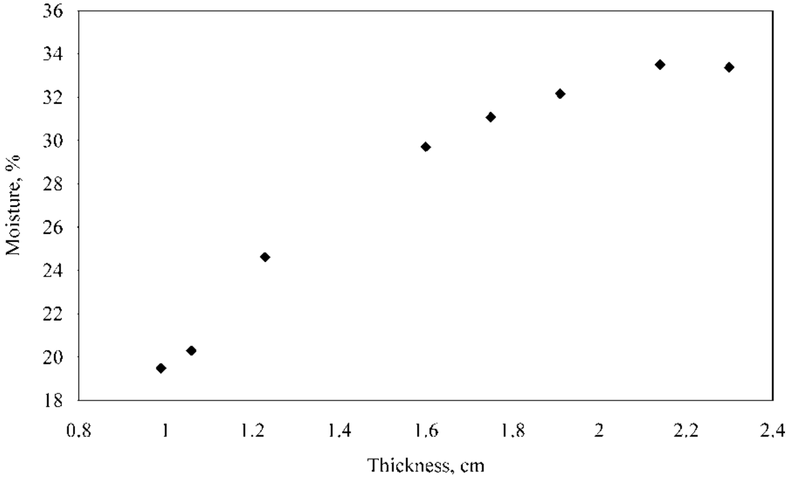

Figure 12. A plot of cake moisture against cake thickness using 30 min vacuum time.

warm squeeze water through the membranes to the cake bulk becomes inefficient, resulting in less water evaporation and consequently in a less dry cake.

To achieve better dewatering properties of the filter cake at the end of the dewatering cycle, cake thickness should be controlled not to be larger than 1 cm, where best dewatering performance was achieved. Unlike a conventional filter press, which must build the cake by packing the chambers with slurry fed under high pressure alone, the membrane filter press provides the possibility to stop feeding and to begin the squeezing step well before the flow rate has significantly dropped. This would have a control over cake thickness for maximum squeeze volume and better vacuum drying performance with economic periods of application. A summary of the whole dewatering process representing the moisture content at the end of each stage of the operation is shown in Fig. 13.

Cake Discharge

The cake release behavior of squeezed, air-blown, vacuum-dried filter cakes is dependent on the cake thickness and on the use of filter aid pre-coat. Diatomite pre-coated cakes, after releasing the press, separate very easily from the filter cloth regardless of the cake thickness. Non-pre-coated cakes with thickness up to 1 cm separate easily, while those with larger thickness show a difficulty in separation from the filter cloth with cake breaking. Such cakes possess high moisture content, and heat transfer from squeezing hot water through the membranes into the cakes' bulk is not efficient. By the end of the vacuum application, the cake surface in both sides is drier than the cake bulk and sticks to the filter cloth. Thus with plates opening, the cake breaks from the cake bulk.

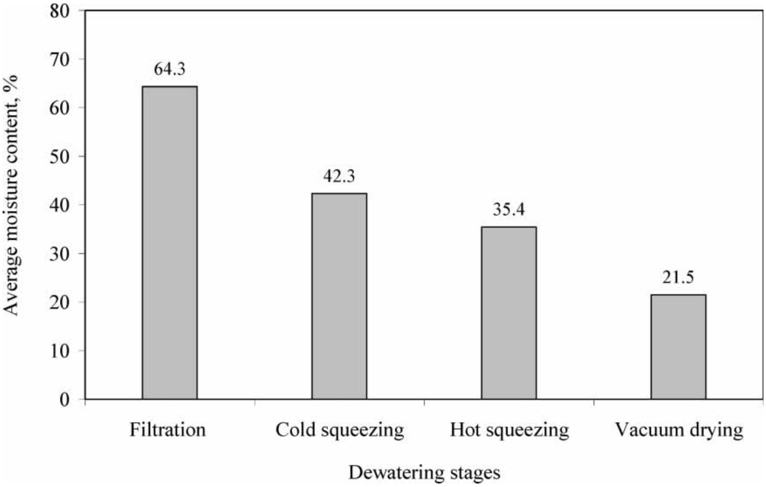

Figure 13. A plot of cake moisture at the end of every stage of the dewatering process (Thickness of dry cake: 1 cm).

Cake Characterization

At the end of the dewatering process, an average moisture value of 20% was obtained for cakes with a thickness of 1 cm. The cakes produced with the dewatering system, in the current study, experience more water evaporation by storing in open air, reaching an equilibrium moisture value of about 9% in a period of about 2–3 days. Cake chemical analysis for a produced cake without filter aid is shown in Table 4. Ash content seems high due to the lime treatment. The lower calorific value was also measured and found to be 15.71 MJ/kg. Typical calorific values of other organic components such as food wastes, wood, leather, and paper are 4.65, 18.61, 17.45, and 16.75 MJ/kg, respectively (43). This suggests the use of produced cakes as a source of energy due to their high calorific value.

Filtrate Post-Treatment

After lime precipitation and filtration, the filtrate still contains 28.8% phenols and 61% of total organics that are expressed as COD components. Another post-treatment is required for removing such unwanted organics from the OMWW filtrate. Adsorption over activated carbon was tested, in this study, to treat the filtrate from the phenols and other organics that were not removed by lime precipitation. Activated carbon remains as the principal adsorbent in full-scale water treatment. It is expected that the application of adsorption to control contamination of water, by toxic and carcinogenic

Table 4. Cake chemical analysis

Cake analysis	Values, wt%
Dry matter under shelf storing conditions	91
Carbon	38.2
Total Hydrogen	6.3
Nitrogen	0.9
Sulfur	0.3
Total Oxygen	21.7
Ash at 600°C	32.6

organic compounds, will increase in the future. Activated carbon was used for the treatment of OMWW as studied by Galiatsatou et al. (26) Even though the study showed an efficiency of the removal of phenols and total organics by activated carbon, the direct treatment of OMWW by activated carbon adsorption would require large amounts of activated carbon, which would be costly in terms of industrial application. However, the use of activated carbon, as a post-treatment for OMWW with less phenols and total organics, after lime precipitation and filtration processes, seems effective and cheaper than its use as a direct treatment. From preliminary studies, the variation of initial pH from 3 to 12 did not affect the removal efficiency of phenols and total organics. Accordingly, the filtrate as produced from the filtration experiments with pH 12 was used for the adsorption studies.

The removal efficiency of phenols and total organics has increased with the increase of carbon dose (Fig. 14a). However, the sorption capacity expressed as mg/g decreases, as shown in Fig. 14b. Total removal by precipitation and activated carbon sorption, in this study, reached 99.7% for phenol removal and 80% for COD removal. The use of activated carbon adsorbent for the post-treatment of organic multicomponent solution, OMWW, seems promising. However, an extensive study of the activated carbon for the post-treatment of OMWW will be conducted in the near future, together with other treatment techniques available.

Preliminary Cost Estimation

In Table 5 the operating cost of treatment of the process now proposed is presented and compared with the operating costs of some processes reported in the literature. These costs have the limitations of being from different sources involving OMWW and countries with different characteristics. All costs presented were updated to 2005 by using *Chemical Engineering* Plant Cost Index (CEPCI) published regularly in the journal *Chemical Engineering*.

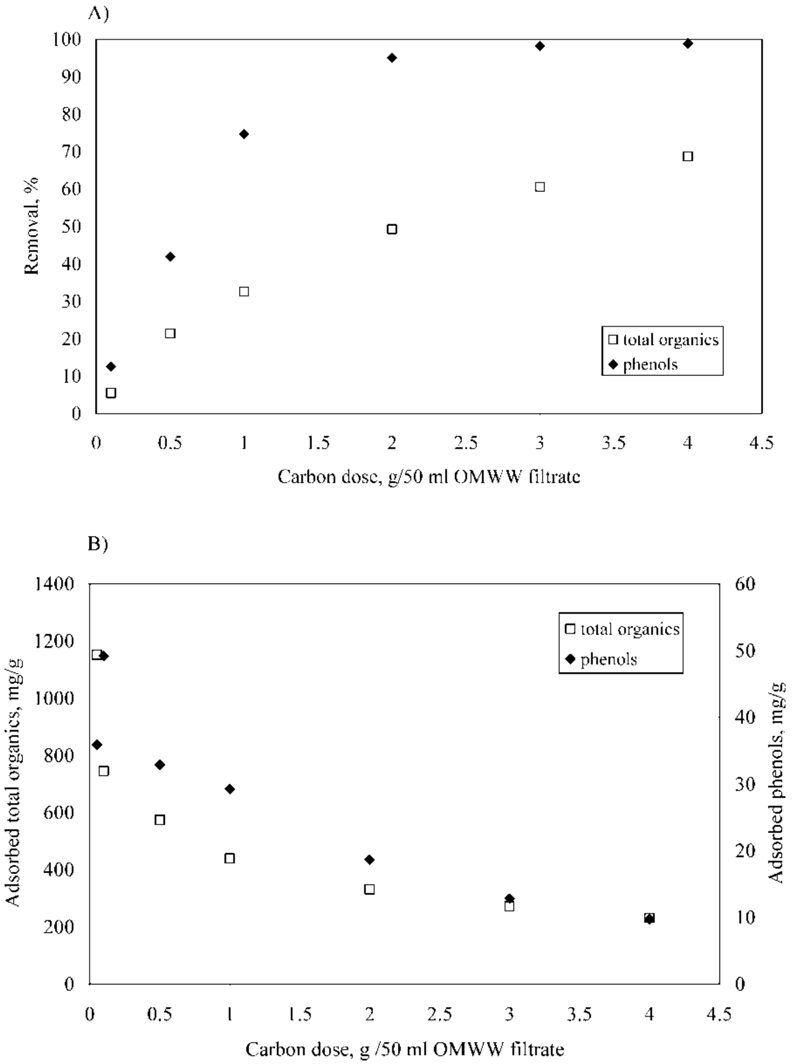

Figure 14. Removal of phenols and total organics from OMWW filtrate, as a post-treatment, using different doses of activated carbon. (A) Removal extent of phenols and total organics (expressed as COD) for several activated carbon doses; (B) Carbon sorption capacity for phenols and total organics for several activated carbon doses.

The operating cost of the treatment process proposed in this work was established by considering the costs of chemicals (calcium hydroxide) and power. The possibility of using the dewatered filter cakes as fuel for heating the squeezing water was taken into account. Labor and maintenance

Table 5. Comparison of the operating costs of the proposed study with other processes for OMWW treatment

Process	Operating cost (€/m^3 OMWW)	Source and year
This study	7.20	—
MINOS process	38.00	MINOS (2004) (44)
AquatecOLIVIA process	4.20–6.50	Schmidt and Knobloch (2000) (45)
Thermal treatment (gasification with energy recovery)	11.70	Caputo, Scacchia, and Pelagagge (2003) (46)
Acid treatment	1.64	Kestioglu, Yonar, and Azbar (2005) (47)
Coagulation with $Al_2(SO_4)_3$	2.60	
Coagulation with $FeCl_3$	2.18	
Oxidation with O_3 and UV	10.33	
Oxidation with H_2O_2 and UV	10.78	
Adsorption on activated carbon	115.39	
Flocculation	8.48	Sarika, Kalograkis, and Mantzavinos (2005) (19)
Coagulation with $FeCl_3$	1.96	

costs were not considered. The cost of filtrate post-treatment was also not considered. The use of activated carbon in the concentrations obtained in the bench studies would increase the operating cost of treatment in 120 €/m^3, which is a prohibitive value. Presently bench studies of advanced oxidation of the filtrate by using H_2O_2 and UV radiation are underway, so that a more cost-effective filtrate post-treatment could be obtained. Activated carbon could nevertheless be used as the last stage of this process to remove traces of organic compounds that are refractory to chemical oxidation.

The operating cost of the proposed process without filtrate post-treatment compares favorably with the operating costs of oxidation and adsorption processes, as well as with a thermal gasification treatment process (11.70 €/m^3) where OMWW is mixed with olive husks, dried and fed to a gasifier. The resulting gas is fed to a turbine or to an internal combustion engine for energy production.

It also compares favorably with MINOS process (38.00 €/m^3), where OMWW is filtered in successive stages and the phenolic compounds contained in the filtrate are adsorbed in resins. The filter cakes are mixed with olive leaves and composted. The resin is stripped with an organic solvent and the phenolic compounds are recovered as the residue of the thermal recovery of the solvent. Relevant fractions of phenolic compounds are separated by chromatography. The adsorption outflow is finally depurated in a nanofiltration/reverse osmosis system.

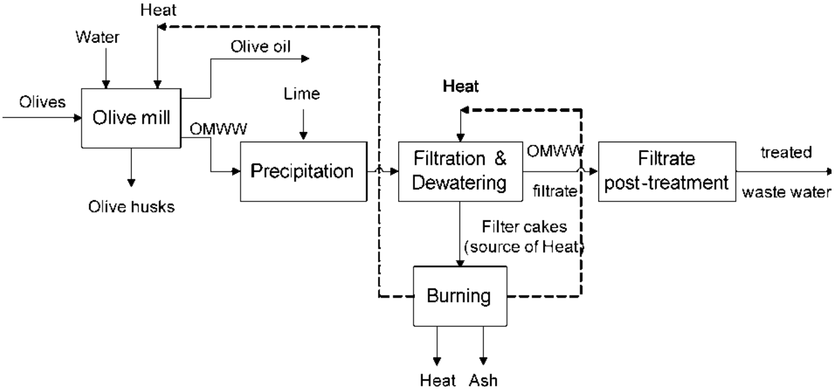

Figure 15. Schematic diagram of the integration of the proposed treatment process in the olive oil production process by using the filter cakes as a source of heat.

AquatecOLIVIA process involving a biological anaerobic process in two steps with biogas production in both and subsequent treatment of the dewatered sludge from both steps by composting (4.2–6.5 €/m^3) allowed obtaining slighter lower operating costs, but OMWW dilution is required and the start-up costs in the beginning of each season are higher.

The cost of calcium hydroxide precipitation alone (3.4 €/m^3) is in the order of the coagulation processes costs presented and much lower than the costs of flocculation.

The proposed process allows the establishment an integrated process in the Olive mill as shown in Fig. 15. Taking into account a case study of a Portuguese Olive Mill that processes 100 ton/day of olives and produces 80 m^3/day of OMWW, by using the integrated process proposed it is possible to produce 5520 kg/day of dewatered filter cakes (dry basis). Burning this waste would allow to production of 86.72 GJ/day of thermal energy. About 50% of this energy would be enough for the thermal needs of the olive mill and of the dewatering process and a surplus for other uses is even obtained. This option would decrease the thermal costs of the treatment process and it would be quite feasible since most olive mill plants include a boiler where wood, olive husks, and other materials are used as fuel.

CONCLUSION

Treatment of OMWW was accomplished via an integrated process including, consecutively, lime precipitation, filtration with cake dewatering, and filtrate post-treatment via activated carbon adsorption. The addition of 40 kg of $Ca(OH)_2$ to 1 m^3 of OMWW slurry from a continuous three-phase olive mill plant has led to the removal of ~71% of phenols, ~39% of total organics, expressed as COD, and ~88% of BOD_5 with a rise in the total suspended solids (TSS) from 31 g/L to 69 g/L after precipitation. Thus, lime treatment alone is not enough for the OMWW treatment, since the filtrate still contains large amounts of the unwanted organics. Separation of the solids by filtration using a novel technology of membrane filter press with cake dewatering via membrane squeezing followed by vacuum drying over hot cakes was undergone. Diatomite pre-coating has decreased the specific cake resistance and with diatomite body feed the specific cake resistance showed a further decrease with a higher filtration rate due to the increased permeability and porosity of the cake. Membrane squeezing using hot water (65°C) followed by vacuum application over the hot cakes for 30 min are considered as a success key for dewatering the produced cakes reaching levels of cake moisture of ~20% for cakes with an average thickness of 1 cm. Cake thickness is an important property for the overall dewatering process. For cakes that are thicker than 1 cm, both membrane squeezing and following vacuum drying would not be efficient. Produced cakes can be used as an energy source due to its lower calorific value of 15.71 MJ/kg.

A post-treatment for the filtrate is required and activated carbon adsorption was examined for the removal of the remaining phenols and total organics. Activated carbon showed good removal efficiency for phenols and total organics, and total removal by the end of the combined treatment processes reached 99.7% for phenol and 80% for total organics (expressed as COD). A combined process seems promising to solve such a difficult environmental problem. The thermal energy produced by the burning of the produced cakes would be enough for the thermal needs of both the olive mill and the proposed treatment process.

NOMENCLATURE

t	time of filtration, s
t_s	time elapsed when the feed pressure becomes constant, s
V	volume of filtrate produced in time t, m^3
V_s	filtrate volume produced when the feed pressure becomes constant, m^3
α	specific cake resistance, m/kg
μ	viscosity of filtrate, 0.001 Ns/m^2
c	feed slurry concentration, kg/m^3
A	area of filtration, 0.8143 m^2 for 3 cakes
ΔP	total filter pressure drop, Pa
R_m	filter medium resistance, m^{-1}
α_o, m	constants
s	compressibility coefficient

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