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Tannery Waste Treatment: Leaching, Filtration and Cake Dewatering Using a Membrane Filter Press (a Pilot Plant Study)

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Abstract: In Alcanena (Portugal) the waste water treatment plant (WWTP) receives tannery waste, after a pretreatment for sulphides and the tanning exhaust baths have been sent to a recovery unit and the municipal waste water from Alcanena residential area. Physical, chemical, and biological treatment processes are involved, and the end products are sludge of ~71% moisture containing mainly organic matter, sulfides, iron, chromium, and other metals. The sludge is dumped, after stabilization, in a specially designed hazardous waste landfill.

In this study, tannery mixed sludge (from chemical and biological treatments) was leached and filtered. Leaching was carried out using sulfuric acid (pH 0.5) to release residual sulfides and metals from the slurry. Hydrogen sulfide (H_2S) was flushed out into an oxidation trap (hypochlorite/alkaline tank) in which H_2S transforms to soluble sulfate. The acidified sludge was fed into a membrane filter press where it was filtered, acid-washed, water–washed, membrane-squeezed, and vacuum-dried reaching lower moisture levels (20–30%). The process cycle is approximately 101–137 min in our experiments; however, from this work, a cycle of 90 min to produce cakes with 0.9 cm thickness in the industrial scale through cutting some operational time, reaching final moisture of ~20% at the end of the dewatering cycle, can be estimated. Filtration was carried out at different feed pressure (3–5 bar) with and without diatomite precoating. The effect of different amounts of diatomite body-feed was studied. Specific cake resistance, α, was found to increase with the increase in feed pressure and to decrease with diatomite precoating and the increased amounts of diatomite body feed. Cake washing was accomplished using 0.05 M H_2SO_4 (acid

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washing), to remove residual metals, followed by water washing, to remove cake acidity. Cake dewatering via membrane squeezing was applied using hot water (65°C), and cake moisture was dropped from ~71% before squeezing to 42% after squeezing. With vacuum application over the hot cakes, for 30 min, cake moisture decreased to ~20% for cakes with an average thickness of 0.9 cm. Cake chemical analysis showed chromium levels lower than 1000 mg/kg (the maximum Cr concentration allowed by the Portuguese legislation in a solid residue for use in agricultural soil). In addition, produced cake (without diatomite body feed) has a calorific value of 11,000 kJ/kg and accordingly it can be used as a source of energy.

Keywords: Leaching, filtration, membrane filter press, dewatering, tannery, waste, cake

INTRODUCTION

Tanning industry is considered as an intensive source of pollution. The quantities and qualities of emissions and waste produced strongly depend on the type of leather processed, the source of hides and skins, and the techniques applied. In general, tanning 1 tonne of raw hides to produce 200–250 kg leather, requires ~500 kg of chemicals, however, generates 450–730 kg solid waste and effluent which contains 5000–17000 mg/L COD, 2000–6700 mg/L BOD, ~3000–10,000 mg/L suspended solids, 100–400 mg/L chrome, and 200–670 mg/l sulfide in an effluent volume of 15–50 m^3 (1). A total of 80–90% of world tanneries use Cr (III) salts in their tanning processes (1). Hides that have been tanned with chromium salts have a good mechanical resistance, an extraordinary dyeing suitability, and better hydrothermic resistance in comparison with hides treated with vegetable substances (2). Chromium salts also have a high penetration rate into the interfibrillar spaces of the skin. This causes a better control on the process with a saving in production time. However, because only a fraction of the chromium salts used in the tanning process reacts with the skins, the rest of the salts remain in the tanning exhaust bath (2).

The waste water treatment plant (WWTP) located in Alcanena (Portugal) receives tannery waste, after a pretreatment for sulphides and the tanning exhaust baths have been sent to a recovery unit, in addition to the municipal waste water from Alcanena residential area. The effluents are subjected to mechanical, physico-chemical, and biological treatments based on the best available techniques for tannery waste treatment (1). The physico-chemical treatment processes generate a chemical sludge that consists of magnesium, calcium and chromium hydroxides (2, 3), and residual iron sulfides (1) in addition to organic matter such as debris from hide, oils, and grease (3). The activated sludge (biological treatment), which is a heterogeneous mixture of particles, microorganisms, colloids, organic polymers, and cations (4), produces waste that is relatively hard to be dewatered compared

with the chemical sludge. This is due to the small size of colloidal particles (2) that flow through the primary clarifier and are eventually removed in the secondary clarifier (5). It is recommended for waste water treatment plants that produce both chemical and waste-activated sludge to mix both sludges before dewatering to achieve better dewatering efficiency (5, 6). Chang et al. (3) found that dewatering of chemical sludge improve remarkably after being mixed with the waste activated sludge at 1 : 1 and 1 : 2 ratios of both sludge, respectively. The chemical sludge plays a role of skeleton builder that enhances the compactability of the waste-activated sludge (3). In WWTP (Alcanena, Portugal) the chemical sludge and waste-activated sludge are mixed together at a ratio of 3 : 2, respectively, prior to filtration using a conventional filter press, and approximately 500 m^3 of mixed sludge are produced per day and then filtered. The cakes produced which possess 71% moisture, are stabilized through the addition of a mixture of cement, ash, and lime. A total of ~70 tones of stabilized cakes of ~45% moisture, which are considered as hazardous waste, are generated per day and transported to a special landfill.

The order of priority in waste management and treatment is (1) prevention, (2) reduction, (3) reuse, (4) recycling and recovery, (5) thermal treatment for certain types of waste, and (6) landfill. The most common way to manage solid waste is disposal in controlled land sites (7). Due to the amount of chromium compounds and other pollutants, the sludge is considered as toxic and hazardous (2). Regulations about solid wastes are becoming more restrictive and the disposal of hazardous waste on land sites may cease to continue. Landfilling of wastes with high organic content and toxic substances is increasingly under pressure in European States. Council Directive 1999/31/EC on landfill of waste, adopted in 1999, is expected to have a considerable impact on trends to reuse and to recycle rather than to landfill (1). Studies to minimize the amount of tannery waste, to treat and to possibly exploit the waste products, are very important (2, 7).

A thermochemical treatment (the ENERSLIDGE™ process (8)) of the tannery sludge that is classified as hazardous waste was tested. The process thermochemically converts the carbonaceous materials, such as sewage sludges in the absence of oxygen, into oil, char, reaction water, and noncondensable gases in a dual stage reactor system. In the first reactor dried sludge (at 90–95% of total solids) is volatilized at temperature of 450°C with up to 50 wt% of the sludge, depending on its volatile solids content, being vaporized. In the second reactor, vapors from the first reactor are contacted with the char (the residue of the first reactor) to enhance catalytic gas-phase reactions, such as decarboxylation, deamination, desulphurization, dechlorination, etc. Another method is to stabilize the tannery sludge using different cement mixtures (9). The stabilized products are considered suitable for the manufacture of preformed building blocks according to Italian standards.

The aim of this paper is to produce cakes from the mixed sludge (chemical and waste-activated sludges) that is clean from residual sulfide

with chromium concentrations $<1000\,mg/kg$ (the maximum allowed chromium concentration in solid residues for use in agricultural soil by the Portuguese legislation (10)) and final moisture, 20%. Sulfide removal and metal extraction were achieved using sulfuric acid treatment that liberates residual sulfides which are oxidized in hypochlorite/alkaline trap, and releases high amounts of chromium (III) and other metals from the sludge. Filtration of treated sludge using a new technology of a membrane filter press (a Pilot plant scale) allows filtration, squeezing, and vacuum drying over hot cakes to achieve 20% cake moisture. This will also allow the use of produced cakes in agriculture and for other purposes such as clay products (2) and as an energy source by incineration.

EXPERIMENTAL

Sludge Pretreatment Using Sulfuric Acid

The mixed sludge (chemical sludge and waste-activated sludge mixed in a ratio of 3 : 2, respectively) from WTTP (Alcanena Portugal) was delivered to our laboratory. Leaching studies were carried out for 100 mL of mixed sludge, on the bench, using different volumes of 50% sulfuric acid in a fume cupboard, and the reaction mixture was air-agitated for proper mixing. Released H_2S was allowed to pass through an oxidation trap from commercial hypochlorite, 5%, with sodium hydroxide, 1 M, in a 1 : 1 ratio. Sodium hydroxide absorbs H_2S that undergoes oxidation by hypochlorite (11, 12). After 3 h of acid mixing, the leached sludge was filtered using suitable Gooch crucible (G4). Cr, Fe, and Zn were analyzed in addition to chemical oxygen demand (COD) and total dissolved solids (TDS). Leaching was, then, carried out for 1 m^3 of the mixed sludge (solid concentration 73 kg/m^3) in the filtration feed tank at pH 0.5 as recommended from the bench studies. Cakes produced after leaching at pH 0.5 have chromium levels below the maximum allowed by the Portuguese legislation for use in agricultural soil (10). Concentrated sulfuric acid was mixed in a slow rate under constant mechanical stirring and air agitation. H_2S and the organic smell were allowed to pass through an oxidation trap of hypochlorite/sodium hydroxide solution as mentioned previously.

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) is 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. 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 membrane plate material is polypropylene with size for each plate 470 mm × 470 mm. The membrane plates are three-parts plates consisting of a flexible polypropylene membrane welded to each face of a rigid polypropylene body. A thorough description of the equipment, membrane plates, tubing, and filter cloth was published earlier in our previous study (13).

The filter is center fed from the central eye that also serves as the wash water inlet and the core-blow outlet. The upper left-hand eye is a filtrate port that also serves as the port for blowing air in and discharging filtrate and wash water. The eyes on the upper right-hand, bottom right-hand, and bottom left-hand are filtrate ports that also serve as discharge of wash water. The eyelets series on the top and bottom of each membrane connect filtrate to the discharge filtrate ports. The filter is opened, closed, and held at pressure with a single acting cylinder (OTC P55-S 470 mm), manually powered hydraulic system with a hydraulic pressure of 700 bar at operating conditions.

The filter cloth used is a polypropylene multifilament fiber (9 oz/sq yd or 0.305 kg/m^2), satin weave, 140 × 42 thread count. The cloth air flow rating is 3–5 cfm (cubic feet per minute) or 4–6 L/sec. The cloth consists of a single sheet that drapes over both sides of each plate. The cloths are hung over the plates, extending from top to bottom and held in place by eyelets which fit over the cloth pins on top of the plates. The filter cloth from top and bottom from both sides were threaded together using plastic ties.

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 (13).

Vacuum drying was applied over the hot cakes at 0.048 bar, using a liquid ring vacuum pump (Squire Cogswell Company, number C00-2240/1, Type: PM124-M30A) through the filtrate outlet ports and the central core (13). 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 (14), before reaching the vacuum pump.

The 13-steps dewatering cycle is listed in Table 1. Three dewatering cycles are processed per day producing ~4 kg and ~3 kg of solids after acid treatment (on dry basis) per batch (three cakes) for filtration with and without filter aid precoat, respectively.

Table 1. BSG dewatering steps

Step	Time required, (min)
1. Press close	2
2. Membrane drain	1
3. Diatomite precoat	10
4. Fill press	1–2
5. Filtration	15–50
6. Core blow	2
7. Wash	10
8. Squeeze	15
9. Air-drying	5
10. Hot squeezing with vacuum drying	35
11. Vent press	1
12. Open press	1
13. Retract plates and discharge cakes	3

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 $\pm$ 0.1 bar and an average pressure value between the maximum and minimum for the manometer for each stroke was recorded.

Filtration Cycles

A mechanical and air agitators were used to keep the acid-treated sludge 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 200 g diatomite with 90 L of tap water (2.22 g/L) in a 100 L tank. Precoating of filter aid was carried out by feeding the well-agitated diatomite slurry into the filter press at a rate of 35 L/min and the filtrate was returned to the precoat tank for recirculation. Precoating process was continued for 10 min.

Filtration and Drying Operations

Prior to diatomite precoating 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 (13). 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. Filtrate 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 (13).

Cake washing was applied at 5 bar, after core blow, through acid washing (80 L of 0.05 M H_2SO_4) to remove residual metals from the cake, and water washing (tap water) to remove residual acid from the cake. 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 of 6–7 bar following the squeeze filtrate volume with time until the squeeze filtrate was far-dropping. This stage was continued for 15 min and a sample of the squeezed filtrate was collected to be analyzed for Cr, Fe, and Zn concentrations.

Air drying was applied straight after the squeezing was accomplished using compressed air at 5 bar for about 5 min (13). Hot squeezing was applied again at the same pressure for about 5 min to restore the cake temperature prior to vacuum application.

Vacuum was applied at pressure of 0.048 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 (14). Straight after the dewatering cycle was completed and cakes were separated, cake moisture% 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.

Cake Characterization

Using Poresizer 9320, the porosity of the dry cake was measured via mercury intrusion by IPNLABGRAN (Laboratory of Characterization and Certification of Granular Materials, Pedro Nunes Institute, Coimbra, Portugal), Table 2. Cake chemical analysis, ash content, and calorific value were measured by INETI (Instituto Nacional de Engenharia, Tecnologia e Inovação, Lisbon, Portugal). Cr, Fe, and Zn were extracted by digesting 0.5 g of the cake in a 10 mL solution (5 mL conc. HNO_3 (15.5 M) and 5 mL H_2O_2, 130 vol. (11.6 M)) for 2 h in a microwave digester, MDS 2000, and then analyzed.

Table 2. Cake parameters

Cake parameters	Values
Total intrusion volume, mL/g	0.17
Total pore area, m^2/g	6.40
Median pore diameter, (volume) μm	1.15
Bulk density, g/mL	1.28
Apparent density, g/mL	1.64
Porosity,%	21.64

Analytical Methods

Analysis of metals was accomplished using atomic absorption (Perkin Elmer AAnalyst 200). TSS was measured for the sludge, as delivered and after acid leaching at pH 0.5, using method 2540 D described in Standard Methods Section (15). For the filtrate, COD was measured using a closed reflux method (method 5220D described in Standard Methods (15)) in an acidified Cr(VI) solution. Residual Cr (VI) was measured spectrophotometrically via 1,5 diphenylcarbazide method (16). TDS was also measured using method 2540C, described in the Standard Methods Section (15).

Experiments of acid leaching 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

Sulfuric Acid Leaching

From preliminary experiments, a period of 3 h was found enough for acid leaching experiments. Preliminary experiments showed better performance for H_2SO_4 than HCl or HNO_3 when used at the same molar concentration for the same period of time. Similar results were found by Shen et al. (17) showing that Cr extraction was better using H_2SO_4 than using HCl or HNO_3 with maximum leaching achieved in 2 to 3 h. In our study, H_2SO_4

transforms solid and soluble sulfides to H_2S, which was flushed out into an oxidation trap (as mentioned previously), and extracts Cr, Fe, Zn and other metals from the organic sludge.

As the sludge pH decreases metal extraction increases, Fig. 1 (A,B,C). At pH 0.5, Cr, Fe, and Zn extraction reached 90, 95, and ~100%, respectively, with metal concentration in the dry sludge 890 mg/kg for Cr, 743 mg/kg for Fe, and <0.1 mg/kg for Zn. The residual organic matter probably adsorbed some metals or formed strong chemical bonds with them that some metals could not be released into the leaching solution (17). Cr (III) is one of the most readily adsorbed metals by the biomass in the acidic solutions (18). However, Cr levels in the dry sludge after acid treatment stays below its maximum allowed concentration in a solid residue by the Portuguese legislation (1000 mg/kg) for use in agricultural soil (10). COD value increases as the leaching pH decreases, reaching 440 mg/L at leaching pH 0.5, Fig. 1D. This is perhaps because some organic fractions, especially those with nitrogen groups, became positively charged as a result of acidification and, thus, become soluble in water. TDS increases as the pH decreases, Fig. 1D, due to the extraction of metals from the sludge such as Cr, Fe, Al, Ca, Na, Zn, and Mg. However, only Cr, Fe, and Zn were chosen for analysis in this study. TSS of the sludge was measured as delivered from WWTP (Alcanena) and found to be 73 kg/m^3, and it decreased to 53 kg/m^3 after acid leaching at pH 0.5.

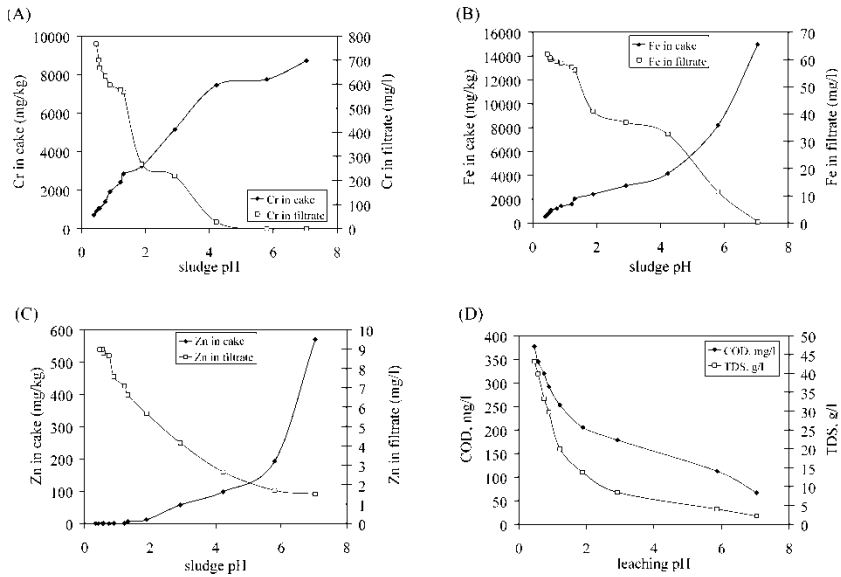

Figure 1. Leaching of waste sludge (TSS 73 kg/m^3) using 0.05 M sulfuric acid. (a) Cr, (b) Fe, (c) Zn, and (d) COD and TDS.

Filtration of Acid-Treated Tannery Sludge

The classical filtration theory described in Svarovsky (19) was used to model the filtration behavior of the acid-treated tannery sludge. 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 (19)

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

where μ is the viscosity of filtrate and A is area of filtration, $0.8143\,\mathrm{m}^2$ for three cakes.

The viscosity of the filtrate was assumed to be the same as water, $0.001\,\mathrm{Ns/m}^2$.

Filtration at Different Feed Pressure

Filtration kinetics was carried out for acid-treated sludge, with solid concentration of $53\,\mathrm{kg/m}^3$ (on dry basis), with and without diatomite filter aid precoat 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

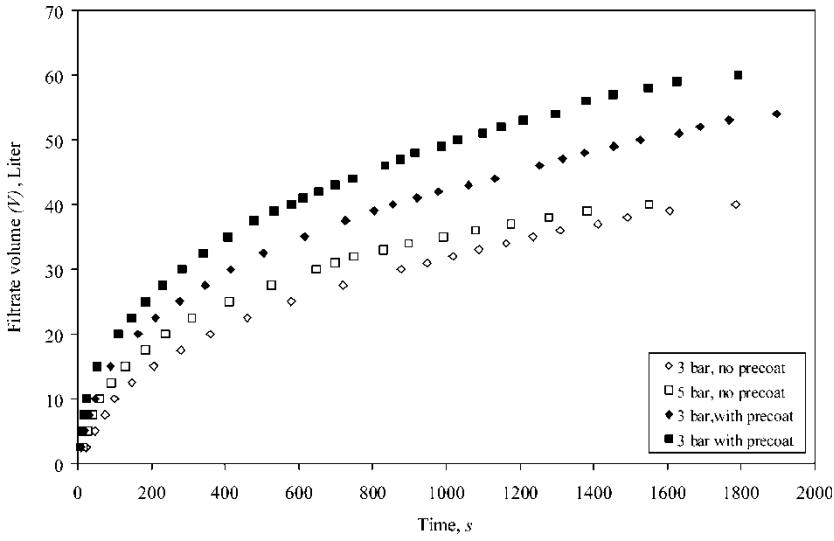

Figure 2. Filtration pattern of acid-treated sludge with and without filter aid precoat.

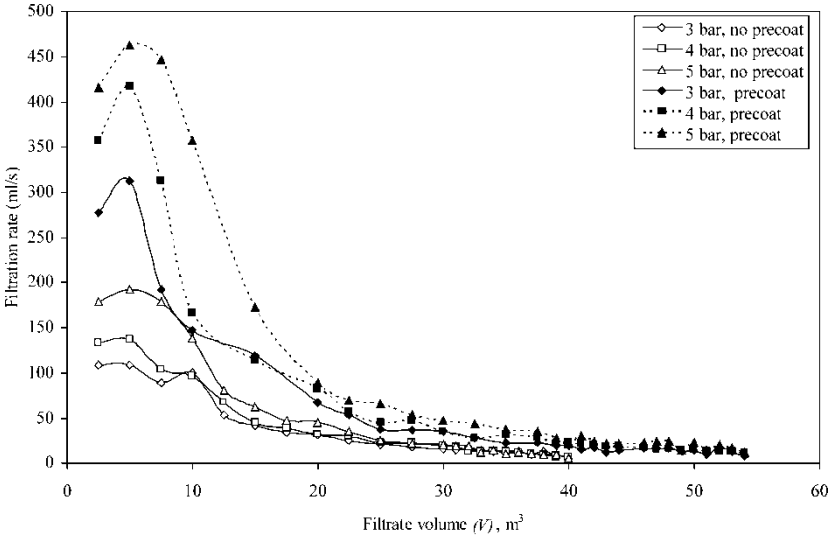

Figure 3. A plot of filtration rate for precoated and non-precoated cakes at different feed pressure.

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 cases (with and without precoat) with higher rate values for the filtration with diatomite precoat.

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, Figs. 4 (A 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 without precoat). This is because the cake becomes denser under high feed pressure, providing fewer and smaller passages for the filtrate flow. On the other hand, α decreases as a result of diatomite precoating (Table 3). In other studies (13, 20), applying a filter aid precoat has led to an increase in the filtration rate and a decrease in the specific cake resistance. The diatomite precoat makes a bed over the filter cloth, and the fine particles of the cake infiltrate into the void space of the diatomite bed protecting the filter cloth and offering less resistance to flow. Accordingly, higher filtration rates were obtained. In addition, filter aid precoat provides two distinct advantages in its use: (i) particles of a submicron 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 (20).

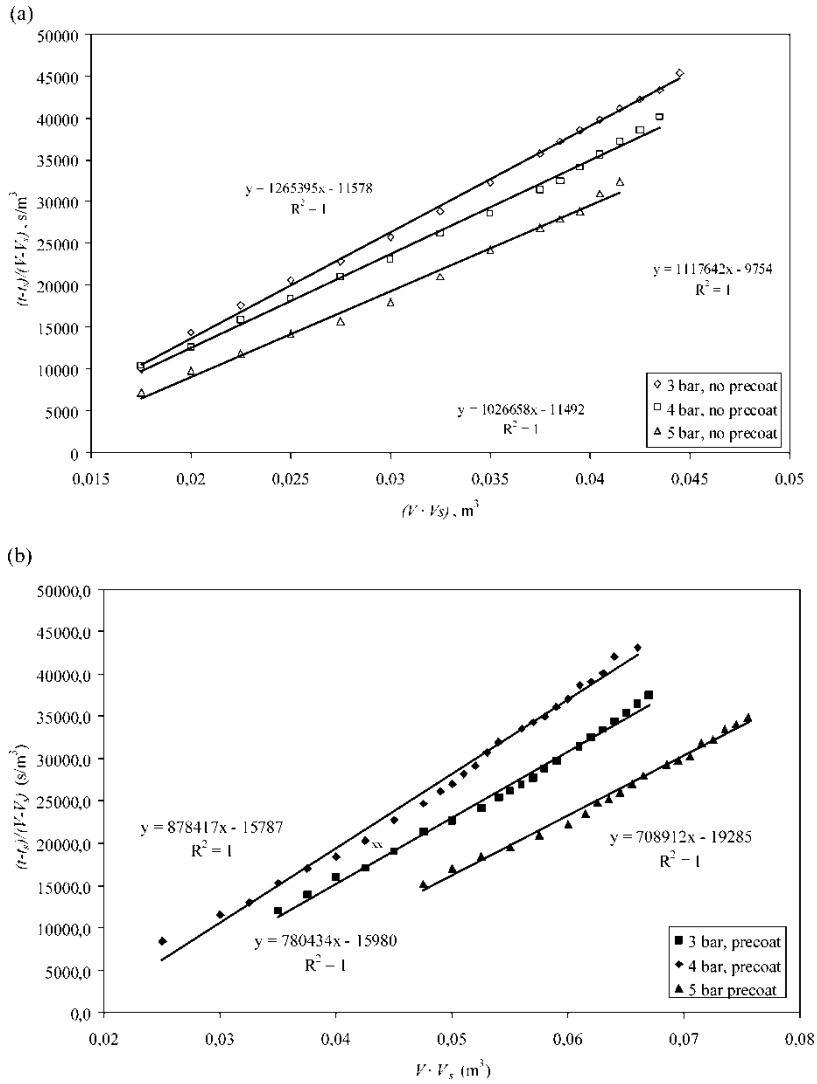

Figure 4. A plot of $(t - t_s)/(V - V_s)$ against $(V + V_s)$ at different feed pressure (sludge concentration: $53\,\mathrm{kg/m^3}$). (a) without filter aid precoat, (b) with filter aid precoat.

According to the classical filtration theory, the medium resistance, R_m, should normally be constant. However, the theory has been under criticism (19) 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 with unrealistically negative values. 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

Table 3. Specific cake resistance (α) at different filtration conditions. (sludge solid concentration is 53 kg/m^3)

Applied conditions			
Feed pressure (bar)	Diatomite body feed conc. (kg/m^3)	Diatomite precoat	α, Specific cake resistance (m/kg)
3	—	No	8.76×10^{12}
4	—	No	1.09×10^{13}
5	—	No	1.31×10^{13}
5	12	No	1.30×10^{12}
3	—	Yes	6.06×10^{12}
4	—	Yes	7.80×10^{12}
5	—	Yes	8.86×10^{12}
5	4	Yes	6.31×10^{12}
5	8	Yes	2.46×10^{12}
5	12	Yes	1.11×10^{12}
5	16	Yes	7.58×10^{11}

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 (13) and hafnium hydroxide (21) using a membrane filter press. Leu and Tiller (22) considered that some of the basic assumptions involved in flow through compressible porous media have shown to be incompatible with experimental data. The development of an adequate theory of filtration gets complicated because of the increase in the resistance of the septum (filtration medium) not only during the first few seconds, but also throughout the entire process in many cases (22, 23), and the variation of the cake resistance during the filtration process as a result of subsequent closure of passages as small particles migrate downstream in the cake (22).

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 (24). The following empirical equation has been proposed to consider cake compressibility (25):

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

α_o is a constant that represents the specific cake resistance at zero compressive pressure and s is the compressibility coefficient of the cake. The s values vary between 0 for incompressible cakes and 1 for highly compressible ones (20). Plotting α values against the filtration pressures on a log-log scale shows

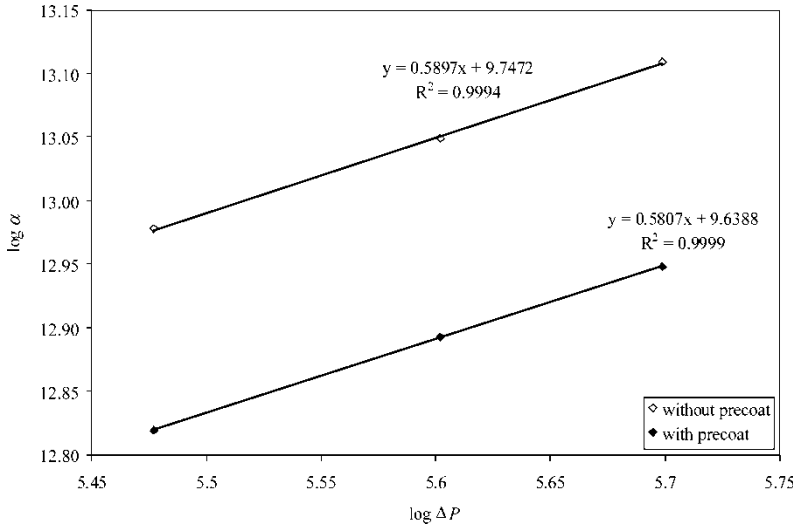

Figure 5. A plot of log α vs. log ΔP.

a straight line whose slope gives the cake compressibility coefficient, s (Fig. 5). The values of α_o and s are 4.35×10^9 m/kg and 0.581 ($r^2 = 0.999$), and 5.59×10^9 m/kg and 0.590 ($r^2 = 0.999$), for filtration with and without precoat, respectively. The s values, shown here, indicate the compressible character of the cakes.

Filtration with Diatomite Body Feed

Diatomite was dispersed in the nonfiltered slurry through proper agitation, as mentioned earlier, and pumped together with the slurry into the press through the feed pump. Filtration pattern for precoated and non-precoated cakes in the presence of diatomite body feed is presented in Fig. 6 (A, B). An increase in the filtration rate was observed with the increase in the amount of diatomite body feed (Fig. 7). An additional decrease in α was obtained with the addition of diatomite as a body feed, after precoating (Table 3), and for precoated cakes, 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 (20, 26). With diatomite body feed, as filter cycle progresses, the body feed produces a fresh new 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. In this case, cake thickness increases and the solids of the incoming suspension cannot clog its channels with excessive accumulation (27, 28).

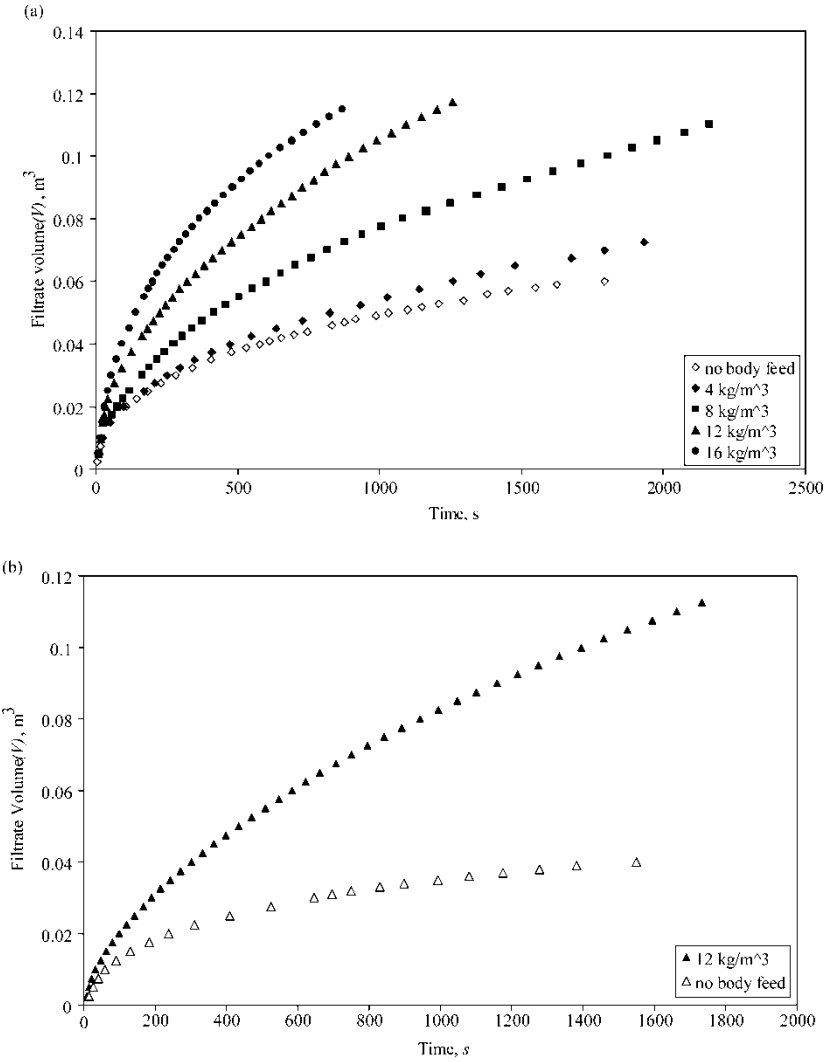

Figure 6. Filtration pattern at feed pressure of 5 bar for cakes with and without diatomite body feed. (a) precoated, (b) non-precoated.

Cake Washing

Cake washing was preferred to take place prior to the squeezing step. It was found that squeezing decreases cake volume and porosity, producing denser cakes. Thus applying cake washing under pressure would cause the membranes to deflate, having larger size than the squeezed cake, and new passages for wash effluents can develop between the filter medium and the

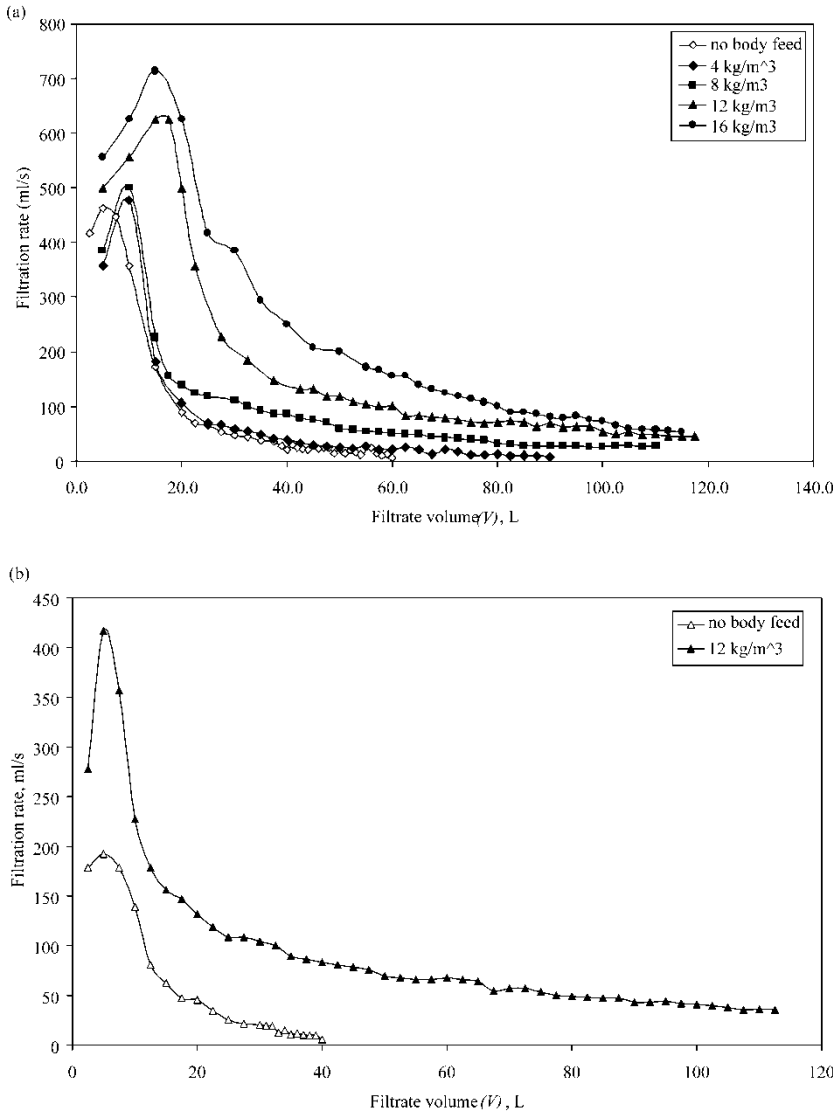

Figure 7. Filtration rate against filtrate volume for filtration with and without diatomite body feed at feed pressure of 5 bar. (a) precoated, (b) non-precoated.

cake, resulting in less-efficient washing. Chromium levels in the cake that was squeezed before washing were higher than 2000 mg/kg. Accordingly, cake washing was applied prior to the squeezing step. Cake washing was applied at a pressure of 5 bar through acid washing (0.05 M H_2SO_4), to remove residual metals, and water washing (tap water), to remove the cake acidity. The acid washing requires ~80 L (seven times the volume of three cakes)

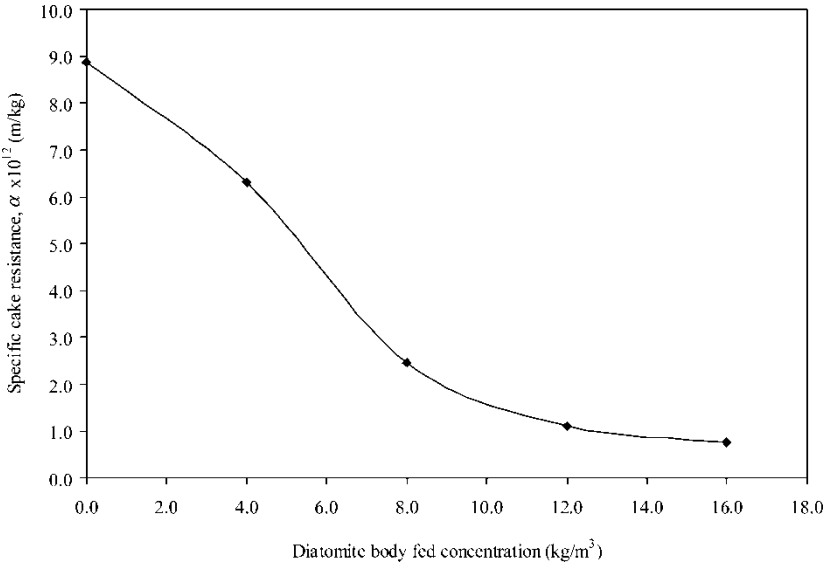

Figure 8. Variation of specific cake resistance with the amount of diatomite body feed at the same precoating conditions.

to have the filtrate with ~0.5 mg/L of Cr, 0.3 mg/L of Fe, and <0.1 mg/L for Zn at the end of acid washing (Fig. 9A). To remove the cake acidity, water washing was applied at 5 bar and 80 L were found enough to remove the cake acidity with final pH of water washing, 4.5 (Fig. 9B). Analysis of water washing showed 0.1 mg/L of Cr and 0.05 mg/L of Fe and <0.05 mg/L for Zn.

The acid wash was collected and added to the filtrate for metal recovery; however, the washing water after being collected was acidified by sulfuric acid to 0.05 M concentration to be used for the acid washing in a following filtration cycle.

Cake Dewatering via Membrane Squeezing

Squeezing step is considered as a crucial step to the success of the dewatering process (13, 21). The cake produced by conventional pressure filtration at 5 bar contains about 71% moisture. Squeezing, by passing water (at room temperature) at squeezing pressure of 7 bar for 15 min through the membranes, decreases the moisture content to ~55% for cakes with 0.9 cm thickness (after complete drying). Squeezing using hot water (65°C) at the same conditions uniformly dewaters the cake to 42%. Squeezing patterns under different conditions are shown in Figs. 10 and 11. Squeezing causes the particles in the filter cake to rearrange so that they are more densely packed.

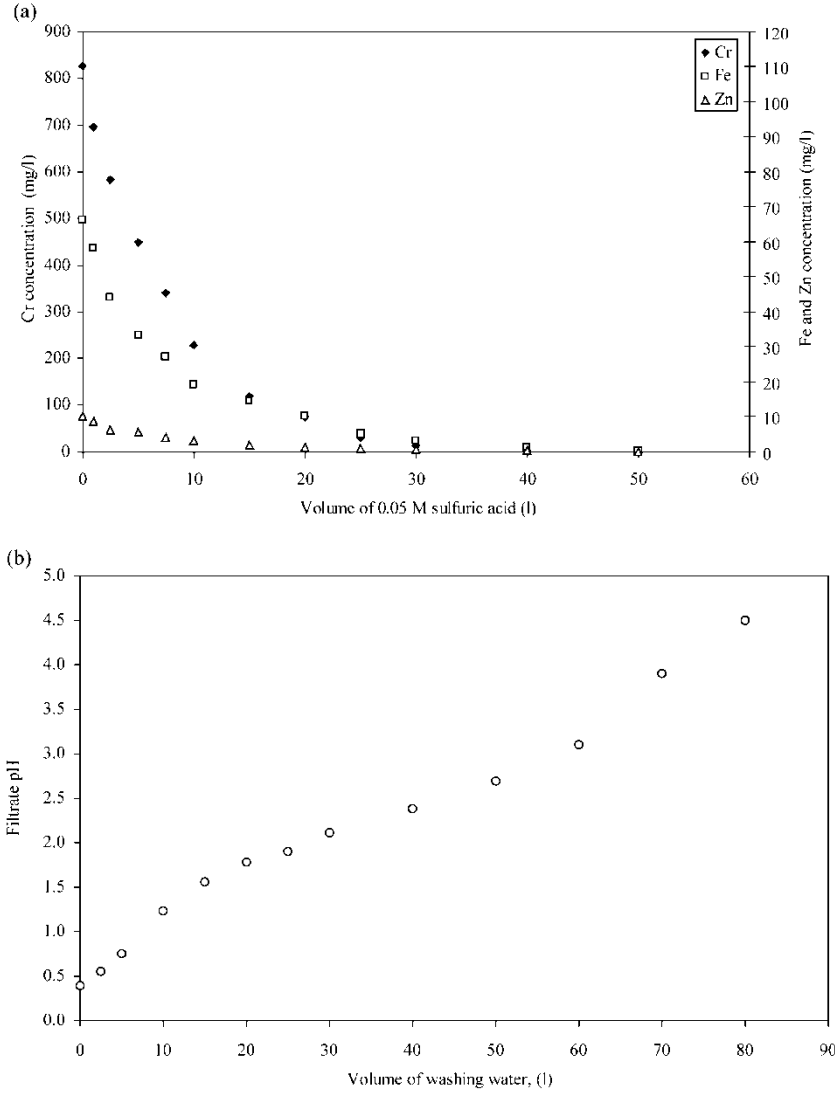

Figure 9. Typical washing of precoated and non-precoated cakes produced at feed pressure of 5 bar. (a) acid washing, (b) waster washing.

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 (13).

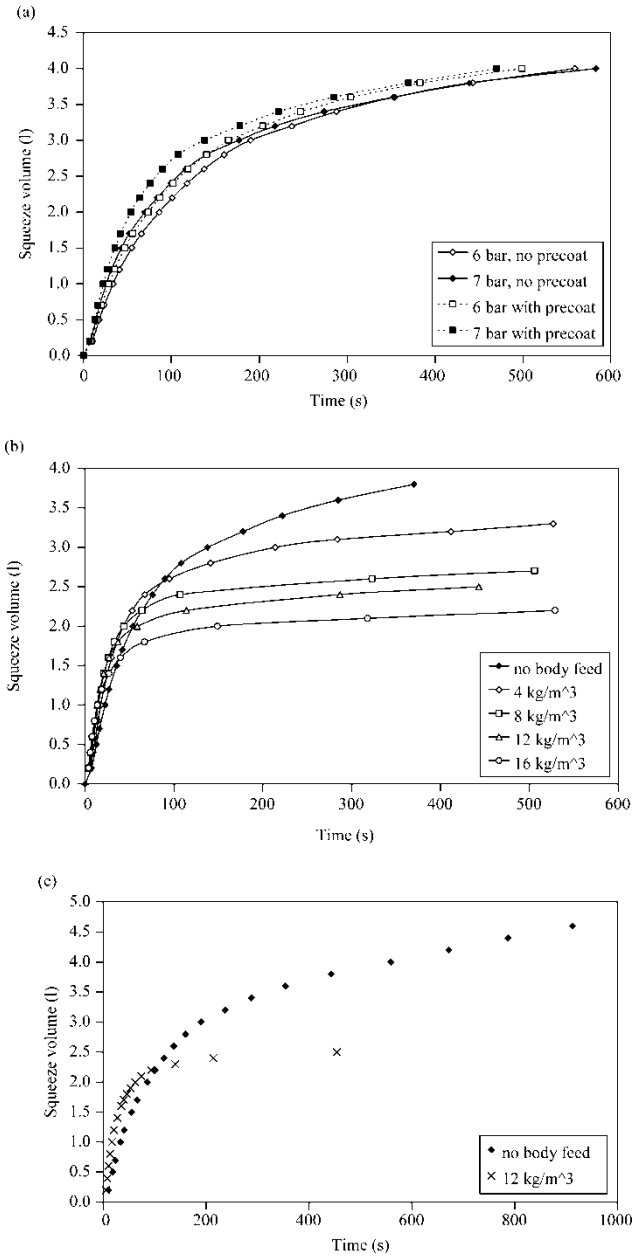

Figure 10. Squeezing pattern for the cake. (a) at different squeezing pressure for precoated and non-precoated cakes, (b) at different doses of diatomite body feed for precoated cakes. (expressed as kg of diatomite per $1\,m^3$ of sludge) at squeezing pressure of 7 bar, (c) non-precoated cakes with and without diatomite body feed at squeezing pressure of 7 bar.

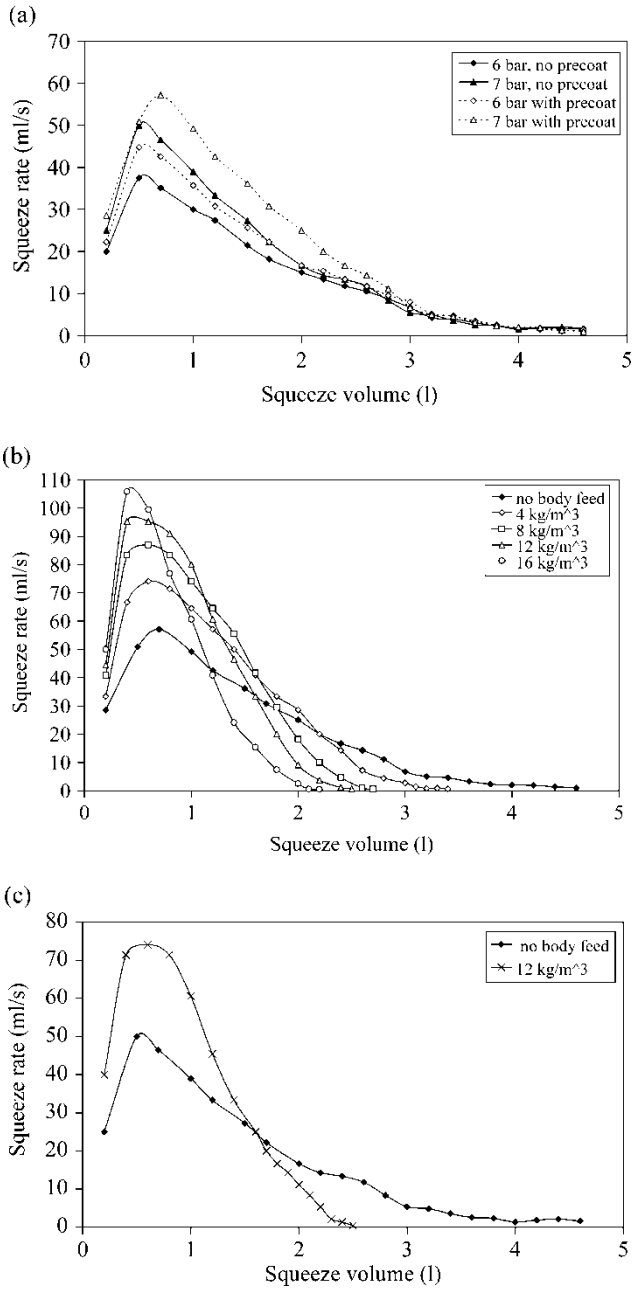

Figure 11. Cakes squeezing pattern. (a) at different squeezing pressure for precoated and non-precoated cakes, (b) at different doses of diatomite body feed for precoated cakes at squeezing pressure of 7 bar, (c) non-precoated cakes with and without diatomite body feed at squeezing pressure of 7 bar.

Most of the squeeze water was flown out of the cake in the first 5 min with flow rate higher at higher squeezing pressure (Fig. 11A). In addition, higher squeeze rates were achieved from precoated cakes than from non-precoated ones at the same squeeze pressure, and this could be because the filter cloth is protected by the filter aid precoat from blinding that is caused by unfiltered particles through filtration without filter aid precoat. The increased squeezing pressure results in increased dewatering and the maximum squeezing pressure, 7 bar, showed the best squeezing performance.

Squeezing rate at squeeze pressure, 7 bar, for precoated cakes with different doses of diatomite body feed is shown in Fig. 11B. 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 squeeze 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 min). However, as the cakes gets drier, thicker cakes that were 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 a decreasing squeezing rate with the progress of time with less squeeze volume received at the end of the squeezing stage. Consequently, more moisture content was achieved in thicker cakes. Similarly, the presence of diatomite body feed for non-precoated cakes has also led to thicker cakes and thus less squeeze volume is received at the end of the squeezing step (Fig. 11C). Another reason for the high moisture content in the cakes produced with diatomite body feed is that the diatomite particles are hard to squeeze and they absorb some moisture.

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, 800 mL of water are removed during the cake blow in each dewatering cycle. About 250 mL from that amount are from the central core (13) and the rest (550 mL) 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 the air blow. Vacuum drying over the hot cakes was then applied simultaneously with continued squeezing. The key success of this step is based on the fact that water boiling point decreases under low pressure developed by vacuum. Vacuum application at 0.048 bar would lower the water boiling point down to 32°C in an ideally sealed system (13). However, the actual boiling point referred in the US Filter manual (14), in the cake chambers under vacuum, was 45°C, which is still lower than the squeeze water temperature.

An economic period of vacuum application (30 min) was chosen for drying cakes with different thickness. That vacuum application period was based on preliminary studies and a previous publication on dewatering of brewer's spent grain (13) using the same dewatering equipment. Higher moisture content was found for thicker cakes than that for thinner ones (Fig. 12). Cake thickness is an important factor for the efficiency of filter cake drying under vacuum. A 20% moisture was achieved for cakes with 0.9 cm thickness. For cakes that are thicker than 0.9 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 warm squeeze water through the membranes to the cake bulk becomes inefficient, resulting in less water evaporation and consequently 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 0.9 cm, where best dewatering performance was achieved. Unlike a conventional filter press, which must build the cake by packing the chambers with

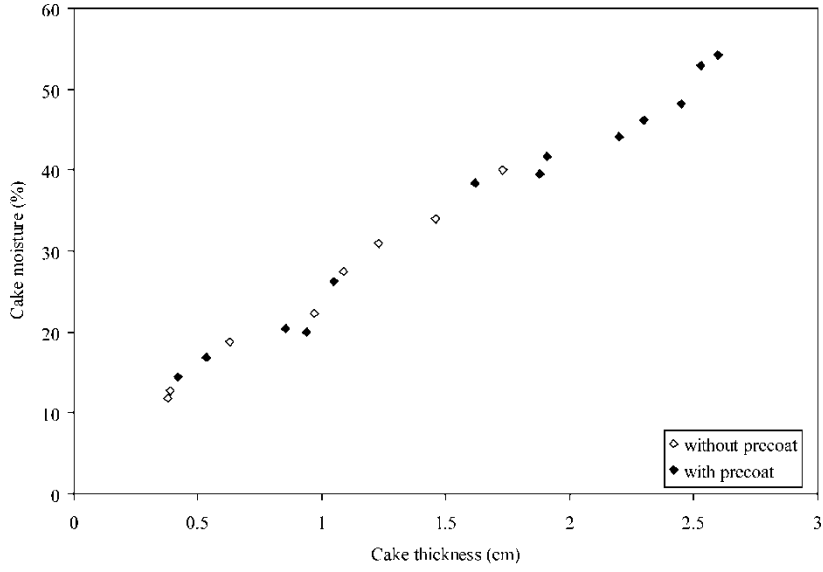

Figure 12. A plot of cake moisture against cake thickness using 30 min vacuum time.

slurry fed under high pressure alone, the membrane filter press provides the possibility to stop feeding and to begin the squeeze 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 cake is dependent on the cake thickness and on the use of filter aid precoat. Diatomite precoated cakes, after releasing the press, separate very easily from the filter cloth regardless of the cake thickness. Non-precoated 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 squeeze hot water through the membrane into the cake 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. In our experiments, the process cycle is approximately 101–137 min as detailed in Table 1; however, in an industrial scale, the process cycle is about 90 min.

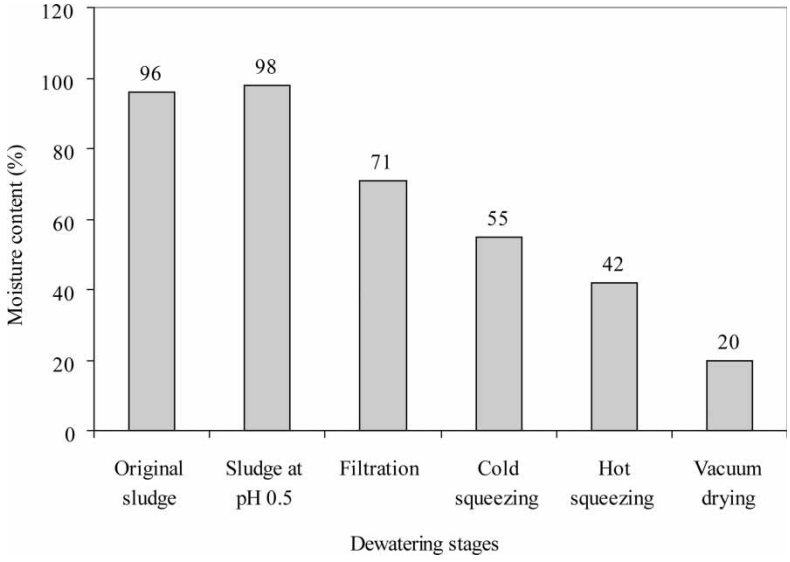

Figure 13. A plot of cake moisture at the end of every stage of the dewatering process. (Thickness of dry cake: 0.9 cm.)

Cake Characterization

At the end of the dewatering process, an average moisture value of 20% was obtained for cakes with a thickness of 0.9 cm. The cakes produced with the dewatering system, in the current study, experience more water evaporation by storing in open air (on the shelf at room conditions), reaching an equilibrium moisture value of ~8.2% in a period of approximately 2 days due to its high porosity (Table 2). Cake chemical analysis for a produced cake without filter aid is shown in Table 4. The calorific value was also measured and found to be 11,000 kJ/kg. Typical calorific values of other organic components such as food wastes, wood, leather, and paper are 46,500, 65,000, 17,500, and 17,000 kJ/kg, respectively (29). This suggests the use of produced cakes as a source of energy due to its high calorific value. In addition, nitrogen content in the cake is quite high (Table 4) and is beneficial for the soil especially after the Cr content was lowered below 1000 mg/kg (the maximum allowed limit by the Portuguese legislation). In fact, the presence of diatomite body feed would further dilute the Cr concentration in the cake due to the addition of clean diatomite solid. For example, for cakes produced without diatomite body feed and for that produced by mixing 16 kg/m^3 diatomite body feed in the sludge, Cr concentration in the produced cakes is 890 and 680 mg/kg, respectively.

As a result of sludge acid leaching, the filtrate will have high concentrations of metals, especially Cr. Some research has been carried out to treat the filtrate by separating the main metals present (Fe^{3+}, Cr^{3+}, and Zn^{2+}). A study is presented elsewhere (30) for the treatment of the filtrate and acid washings where it is proposed to selectively extract Fe(III) from the filtrate using a 5% solution of Cyanex 272 leaving Cr(III) and Zn(II) in the raffinate. Fe(II) is stripped from the organic phase by 50 g/L H_2SO_4. Cr(III) present in the raffinate can be selectively precipitated over Zn(II).

Table 4. Cake chemical analysis

Cake analysis	Values, wt%
Dry matter under shelf storing conditions	91.7
Carbon	28.7
Total hydrogen	4.7
Nitrogen	4.4
Sulfur	8.4
Total oxygen	16.3
Ash at 750°C	37.5

CONCLUSION

The integrated process presented in this study, including leaching the mixed sludge from Alcanena WWTP with sulfuric acid at pH 0.5 (to remove the sulfide and to extract chromium and other metals from the sludge) followed by filtration with cake dewatering using a membrane filter press allowed to obtain filtration cakes with 890 mg/kg of Cr (on dry basis) and 20% moisture content (in the case of the optimal cake thickness of 0.9 cm). This allows the filtration cakes to be used not only in agricultural soil, but also in ceramics production and as a source of energy (due to the high calorific value of the produced cakes).

In the filtration step, the specific cake resistance, α, was found to increase with feed pressure in the filtration studies and this is because the cake becomes denser under high feed pressure providing fewer and smaller passages for the filtrate flow. The presence of diatomite precoat decreases the specific cake resistance and offers higher filtration rate. The precoat makes a bed over the filter cloth and the fine particles of the cake infiltrate into the void space of the diatomite bed protecting the filter cloth from clogging that happens in the absence of the precoat. Accordingly, the diatomite precoat offers less resistance to flow.

The addition of diatomite as a body feed leads to a higher filtration rate with an additional decrease in the specific cake resistance. As filter cycle progresses, the body feed produces a fresh new filtering surface and facilitates the entrapment of the particles and reducing cake resistance. This provides additional microscopic channels through which clarified fluid can flow, thus keeping the permeability and porosity high. As the amount of diatomite body feed increases, the permeability and porosity of the cake increases, offering a further decrease in the cake resistance. However, care must be taken into account to control the cake thickness not to exceed 1 cm. Thicker cakes, due to the presence of diatomite body feed, have poor dewatering properties due to the nonefficient squeezing as a result of high solid content, and nonefficient vacuum drying due to the high moisture content after squeezing and the poor heat transfer to the cake bulk.

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
c	feed slurry concentration, kg/m^3
ΔP	total filter pressure drop, Pa

R_m filter medium resistance, m^{-1}
α_o constants
s compressibility coefficient

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