

**Post-treatment of the permeate of a submerged anaerobic membrane bioreactor
(SAMBR) treating landfill leachate**

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ABSTRACT

In this study, various methods were compared to reduce the Chemical Oxygen Demand (COD) content of stabilised leachate from a Submerged Anaerobic Membrane Bioreactor (SAMBR). It was found that Powdered Activated Carbon (PAC) resulted in greater COD removals (84 %) than Granular Activated Carbon (GAC-80%), an ultrafiltration membrane of 1kDa (75 %), coagulation-flocculation with FeCl₃ and polyelectrolyte (45 %), FeCl₃ alone (32 %), and polymeric adsorbents such as XAD7HP (46 %) and XAD4 (32 %). Results obtained on the <1 kDa fraction showed that PAC and GAC had a similar adsorption efficiency of about 60 % COD removal, followed by XAD7HP (48 %), XAD4 (27 %) and then FeCl₃ (23 %). The post-treatment sequence UF+GAC would result in a final effluent with less than 100 mg COD/L. Size Exclusion Chromatography (SEC) revealed that the extent of adsorption of low MW compounds onto PAC was limited due to low MW hydrophilic compounds, whereas the kinetics of PAC adsorption depended mainly on the adsorption of high MW aromatics.

Keywords: Submerged anaerobic membrane bioreactor; refractory organic substances; post-treatment.

INTRODUCTION

Landfill leachate is a complex wastewater with considerable variations in both composition and volumetric flow over time. The composition and concentration of contaminants are influenced by the type of wastes deposited, by hydro geological factors and the age of the

landfill. In general the leachate is highly contaminated with organic contaminants measured as chemical oxygen demand (COD) and biological oxygen demand (BOD), with ammonia, halogenated compounds and heavy metals, and is thus toxic to the environment. ^[1] Humic substances constitute an important group of compounds in the leachate organic matter. These substances are refractory anionic macromolecules of moderate (1 kDa - fulvic acids) to high (10 kDa - humic acids) molecular weight (MW) and they are the major contributors to residual COD in the stabilized leachate. ^[2] They contain both aromatic and aliphatic components with primarily carboxylic (60-90 %) and phenolic functional groups. ^[3] In most cases, the first step of plants treating leachate is a biological process for BOD, COD, and ammonia removal. ^[1-4] Biological processes are effective for new leachates containing mainly volatile fatty acids, but less so for stabilised leachate. In most cases, stabilised leachate from the biological stage still shows high COD values because the fulvic-like fraction increases with land fill age, ^[5-6] and after biological treatment. Usually, leachate is disposed of to sewer where there is likely to be a restriction on ammonia and COD concentrations, and inorganic compounds. ^[1-7-8] As a result, the search for other effective and efficient technologies for the treatment of stabilized landfill leachate has intensified in recent years.

Various physico-chemical methods, including adsorption, coagulation-flocculation, precipitation, oxidation, evaporation and membrane filtration or combination of processes have been applied to remove COD from leachate. ^[4] Activated carbon adsorption is most commonly used for the removal of recalcitrant organic matter from landfill leachate, and COD removals greater than 90 % could be obtained. ^[4-9] Coagulation-flocculation is an essential process to remove refractory organic substances in wastewater treatment, either as a pretreatment before a biological step, ^[10] or as a final polishing treatment step. ^[11] The

negative charge of colloids, such as that of dissolved humic acids, can react chemically with Fe (III) salts, forming Fe-humic acid precipitates. At an appropriate iron to humic ratio, the negative charge of the humic molecules is neutralized and settleable flocs are produced, depending on the pH and iron dosage. Ntampou et al. ^[11] have investigated the coagulation of leachate samples by the addition of ferric chloride. Maximum COD removals (up to 72 %) were achieved by the addition of 1135 mg FeCl₃/L. Aziz et al. ^[12] obtained 27 % and 51 % COD removal at FeCl₃ doses of 200 and 1200 mg/L, respectively. From the literature, the optimum coagulation-flocculation was obtained with iron chloride (1-4.8 g/L) under controlled acidic pH (4-6). Under these conditions, the treatment gives 50-60 % COD removal. ^[6-13] Stabilised leachate coagulation with FeCl₃ eliminates all high MW compounds (≥ 5 kDa) but does not trap compounds with a lower molecular weight. ^[5-6] Ultrafiltration (UF) has also been used in the removal of recalcitrant organic compounds and heavy metals from landfill leachate. This treatment process has the ability to remove solutes with a MW range of 10-100 kDa, as well as inorganic substances through electrostatic interactions between the ions and membranes. Bohdziewicz et al. ^[7] obtained 52 % COD rejection using UF, while Trebouet et al. ^[6] found that at least nanofiltration is required to obtain CODs lower than the requirements for discharge. Polymeric adsorbents have also been reported to be highly effective for the removal of non biodegradable compounds that contain humic substances, and in a study carried out by Rodriguez et al. ^[14], the removal of humic substances from stabilised leachate was evaluated using Amberlite XAD-8, XAD-4, IR-120 and granular activated carbon (GAC). GAC was found to achieve the highest removal of COD (93 %), followed by XAD-8 (53 %), XAD-4 (46 %) and IR-120 (31 %) at an initial COD concentration of 1300 mg/L.

Due to the novelty of this type of bioreactor combining anaerobic treatment and a submerged microfiltration unit in a single unit, there is a lack of information regarding the properties of

the permeate. The purpose of this study was also to determine the best physico-chemical treatment most suitable for further reducing the organic content of the permeate of the Submerged Anaerobic Membrane Bioreactor (SAMBR).

MATERIALS AND METHODS

Leachate of Municipal Solid Waste

The stabilised leachate used in this study was the permeate of a Submerged Anaerobic Membrane Bioreactor (SAMBR) treating leachate from a simulated feedstock of Municipal Solid Waste made of paper waste, kitchen waste and garden waste. ^[15] The SAMBR typically achieved 90% COD removal and the permeate SCOD was in the range 400 – 1200 mg/L and VFA concentration was less than 30 mg/L. The filtration through the 0.4 micron submerged membrane ensured a permeate free of suspended solids and large colloids.

Batch Adsorption Tests

Batch adsorption experiments were carried out using powdered activated carbon (PAC), granular activated carbon (GAC) (from Norit, Table 1) and the polymeric adsorbents Amberlite XAD7HP and XAD4 purchased from Sigma-Aldrich (Table 2).

Batch adsorption tests were performed in flasks containing 25 mL of SAMBR effluent. pH was adjusted with either H₂SO₄ or NaOH, and a magnetic stirrer was used at 200 rpm at 20°C. Initial samples were collected from the flasks before addition of PAC, and the adsorption experiments were carried out for 24 hours to ensure that equilibrium had been attained. Samples were filtered through a 0.2 microns filter (Minisart, Sartorius) and COD analysis was carried out according to Standard Methods. ^[16] The coefficient of variation (COV) for ten identical samples was 2.6%. Freundlich and Langmuir models were used to assess the adsorption capacity of the PAC and GAC. The Freundlich model is expressed as:

$$q_e = K_F \cdot C_e^{1/n} \quad (1)$$

where K_F (mg/g) represents the quantity of adsorbate adsorbed onto activated carbon for a unit equilibrium concentration, and n is a constant related to sorption intensity of adsorbent. A coefficient n greater than 1 represents favourable sorption conditions. Equation 1 can be easily linearised into logarithmic form for data fitting and parameter evaluation. ^[17]

The Langmuir isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sorption sites. The amount adsorbed by the adsorbent, and the equilibrium concentration of the adsorbate at a constant temperature, can be given by the Langmuir adsorption isotherm as:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (2)$$

where K_L and a_L are the equilibrium constants. Equation 2 can be linearised by plotting C_e/q_e against C_e which yields a straight line with slope a_L/K_L and intercept 1/K_L. The ratio a_L/K_L indicates the theoretical monolayer saturation capacity Q₀.

In order to observe the adsorption process over time, two kinetic models, first and second order models, were proposed which are the most common models being used to explain adsorption kinetics. ^[18] The first-order equation can be written as:

$$\frac{dq_t}{dt} = k_f (q_e - q_t) \quad (3)$$

where q_t (mg/g) is the amount of adsorbate absorbed at time t (min), q_e (mg/g) is the adsorption capacity in equilibrium, and k_f (min^{-1}) is the rate constant for first order kinetics. After integration, and by applying the initial conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, the equation becomes ^[17]:

$$\log(q_e - q_t) = \log q_e - \frac{k_f t}{2.303} \quad (4)$$

The second-order kinetics can be presented in the following form:

$$\frac{dq_t}{dt} = k_s (q_e - q_t)^2 \quad (5)$$

where k_s is the rate constant of second-order model (g/mg min). After integration and applying the same initial conditions as above, the equation becomes: ^[17]

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \quad (6)$$

The initial sorption rate, h , at $t=0$ can be defined as $h = k_s q_e^2$. The adsorption rate constant (k_f) and equilibrium adsorption capacity (q_e) of the first-order model were calculated from the slope and intercept of the plots of $\log(q_e - q_t)$ against t . The initial sorption rate (h), the equilibrium adsorption capacity (q_e) and the second-order rate constants (k_s) were obtained from the slope and intercept of the plots of t/q_t against t .

Ultrafiltration Test

PAC was used to study the adsorption of various molecular weight (MW) fractions of the effluent. The MWs of the effluent were separated using an Amicon cell (Model 8200, Amicon) and ultrafiltration membranes (Amicon/Millipore) with specific molecular weight cut-offs of 50, 10 and 1kDa following a parallel mode described in ^[19] which yielded various fractions according to the molecular weights: $MW < 1 \text{ kDa}$, $1 < MW < 10 \text{ kDa}$, $10 < MW < 50 \text{ kDa}$ and $MW > 50 \text{ kDa}$.

Coagulation-Flocculation Tests with Iron Chloride

Coagulation-flocculation tests were also carried out to study the effect of FeCl_3 on the removal of organics, and also to compare the effect of coagulation with adsorption. Iron chloride was chosen because it is widely used in wastewater treatment plants and is easily available. The effect of various Magnafloc polyelectrolytes such as E24 (Inverse emulsion range), MF10 (anionic powder), LT31 (cationic), MF333 (non-ionic) and MF4240 (anionic) were also studied as flocculant aids at a concentration of 0.5 mg/L to reduce the effluent COD. Their effects were studied alone and also when added after FeCl_3 .

Size Exclusion Chromatography (SEC)

In order to get more insights into the molecular weight of the recalcitrant organic substances produced by the SAMBR and the effect of the above post-treatments size exclusion

chromatography was used. A HPLC with an Aquagel OH-40 column (Polymer Labs) was used with deionised water as eluent at a flow rate of 0.5 mL/min. The sample volume was 50 μ L, and the column was maintained at 20°C with a Shimadzu UV detector set at 254 nm. Unbranched standards of polyethylene oxide and polyethylene glycol and glucose were used to calibrate the system.

RESULTS AND DISCUSSION

Activated Carbons

Effect of activated carbon dosage

The effect of adsorbent dose on the removal of organics from the SAMBR permeate was studied at an unchanged pH (8). It was found that 1, 5 and 10 g GAC/L resulted in 36, 70 and 80 % COD removal, respectively, after 24 hours. With PAC, COD removals of 39, 72 and 84 % at dosages of 1, 5 and 10 g/L, respectively, were obtained. Higher removals are obtained with increasing dose of GAC or PAC, which is in line with the literature. ^[1]

Effect of pH on adsorption of GAC

The chemical properties of both adsorbate and adsorbent may vary with pH, thus it is important to study the effect of pH on adsorption with activated carbon. The pH was tested using a GAC dosage of 5 g/L, and the optimum pH for GAC was observed to be at the unchanged pH value of the effluent stream (pH 8 – Fig. 1), where the highest COD removal was obtained (70 %). However, as the pH increased to 12 there was a decrease in COD removal: this is because at higher pHs values there is competition between the organics and the OH⁻ ions for the adsorption sites. However, the smaller OH⁻ ions are adsorbed better to produce metal hydroxide layers that inhibit further adsorption of organics from the effluent. Organic compounds adsorb poorly on activated carbon when they are ionized. This explains why non-ionised forms of acidic and basic compounds adsorb much better than their ionized counterparts on activated carbon. Hence acidic compounds adsorb better at low pHs, and basic species adsorb better at high pHs. At pH 12, the organic uptake was lower due to electrostatic repulsion between the negative surface charge and some solutes in the solution, whereas at pH 8 the solutes were undissociated and dispersion interactions predominated, thereby increasing electrostatic attraction between the solutes and the adsorption sites. At pH 8 adsorption of the organics was based mainly on the decrease in negative charge, or increase in positive charge, on the activated carbon which would decrease any surface refractory organic substances (ROS) repulsive interaction. In contrast, at pH 12 where an increase in negative charge on the activated carbon and competition between increased OH⁻ ions and the organics both contributed to reduce the COD removal capacity of the GAC.

Effect of surface area

PAC has finer particles and greater surface area, while GAC has more coarse particles. It was observed that adsorption kinetics and capacity increased as the surface area of adsorbent increased as can be seen from the steepness in the slope of the PAC compared to GAC in Figure 2. Adsorption using both types of activated carbon (PAC and GAC) was very fast, and after about 15 minutes of contact 73 % of the organics were removed (in the case of PAC). After about 1 hour of contact, equilibrium had been established and the adsorption rate did not change much in 24 hours for both PAC and GAC. At equilibrium 76 and 79 % of the organics have been successfully removed using GAC and PAC, respectively, causing the COD of the effluent to decrease from 745 to 180 and 160 mg/L, respectively.

Adsorption isotherms and adsorption kinetics

The equilibrium adsorption onto GAC and PAC was analyzed using Langmuir and Freundlich isotherms, and the data are shown in Table 3. The regression correlation coefficient R^2 was used to determine the linear equation of best fit. Freundlich was found to describe the best adsorption for both GAC and PAC, thus showing a multilayer adsorption on a heterogeneous adsorbent which is also observed in most studies with activated carbon.

^[4-9] Based on the K_F value of the Freundlich model, a higher adsorption capacity of PAC was confirmed.

A summary of the kinetic results can be seen in Table 3. Since the calculated correlation coefficients are closer to unity, the adsorption kinetics could be explained better by the

second-order kinetic model for both GAC and PAC. In particular, the value of h highlights the faster adsorption of PAC compared to GAC as there is a twelve-fold increase in the initial adsorption rate.

COD removal of PAC on various MW fractions of SAMBR permeate

A marked difference in colour was observed among the various MW fractions, with the low MW fraction (< 1 kDa) being the least coloured, indicating that the light brown-yellow colour of the SAMBR permeate was due to compounds larger than 1 kDa which are difficult to degrade due to their humic nature. In this study it was found that the various fractions MW<1 kDa, 1<MW<10 kDa, 10<MW<50 kDa and MW>50 kDa contributed to 24.6 %, 20.4 %, 32 % and 23 % of the total effluent COD (≈ 1.2 g/L), respectively, therefore showing that all MW fractions contribute to relatively similar COD content in the range 20-32 %. Furthermore, the use of a 1 kDa membrane to treat the SAMBR effluent resulted in 75 % COD removal (= 100 % - 24.6 %), but the 1 kDa permeate still contained about 290 mg/L of COD. Wang et al. ^[2] also concluded that large MW ROS were the major COD components of aged raw landfill leachate, and that ROS with MWs larger than 1 kDa were the major colour contributors.

The experiment on various effluent fractions in Figure 3 shows that the rate of adsorption was similar and the final COD removal percentage for the fractions greater than 1kDa was approximately the same in the range 79-85 %. In contrast, only 67 % of the COD of compounds smaller than 1 kDa could be removed onto PAC. From these results PAC was

able to adsorb high and low MW compounds, and the adsorption was relatively fast as most of the COD of each MW fraction was adsorbed within 1 hour. The lower COD removal of low MW compounds is because larger molecules are preferentially adsorbed onto PAC compared with smaller molecules. ^[19] These large MW compounds can adsorb directly in the macropores of the PAC due to a strong affinity with PAC due to their high hydrophobicity and low solubility, whereas low MW molecules need to diffuse into the micropores to find free adsorption sites, and their lower affinity does not warrant adsorption, and may even cause desorption. These results show that in a process sequence SAMBR-UF-PAC, we will obtain 75 % COD removal in the UF unit resulting in an effluent of 290 mg/L, and then PAC will remove 67 % of the low MW compounds resulting in a final effluent containing less than 100 mg/L COD.

Coagulation-Flocculation Using Iron Chloride

There are two main mechanisms regarding the removal of humic substances from the aqueous phase by the application of coagulation/flocculation: (a) binding of cationic metal species to anionic sites, resulting in the neutralization of humic substances and the reduction of their solubility, and (b) adsorption of humic substances onto the produced amorphous metal hydroxide precipitates produced. Although it is not easy to distinguish between the two mechanisms, it appears that these are strongly pH-dependent as well as iron dosage dependent.

Effect of pH on coagulation

The effluent pH was approximately 8, and hence the humic substances were negatively charged, whereas Fe^{3+} ions are positively charged which resulted in charge neutralization of the humic substances. Using a constant concentration of 1 g/L FeCl_3 , the COD removal percentages at pH 5, 8 and 9 were 28, 6 and 2 %, respectively. These results show that optimum COD removal was obtained at a pH of 5 which is in agreement with results obtained in the literature. ^[12-20] The high concentration of positive soluble Fe species at acidic pHs increased the probability of adsorption and charge neutralization interactions with ROS indicating that sorption dominated as the primary mechanism for organic matter removal.

Effect of coagulant dosage

Iron (III) compounds accomplish destabilisation of colloids in three ways: (i) double-layer compaction; (ii) adsorption and charge neutralisation which includes coordination; and (iii) enmeshment in sweep flocs. The amount of electrolyte required to achieve coagulation by double-layer compaction is practically independent of the concentration of colloids in the dispersion. Sweep-floc coagulation is characterised by an inverse relationship between the optimum coagulant dosage and the concentration of colloids to be removed. Destabilisation by adsorption and charge neutralization is stoichiometric so the required dosage of coagulant increases as the concentration of colloids increases. However, results in Figure 4 obtained by varying the coagulant concentration showed an increase in COD removal of about 18 %

initially as the concentration of coagulant increases from 0.5 to 1 g/L, but with further increases from 1 to 3 g/L, the COD removal decreased by about 10 %; this is due to a restabilisation of colloids that occurs due to a charge reversal of the colloids as the concentration of the coagulant increases beyond 1 g/L. It was also observed that the increase in contact time reduced the stability of colloids formed as can be seen from the percentage of COD removed after 1 hour and 24 hours, respectively. The low percentage removal observed in our study contradicts the 70 % COD removal observed by Ntampou et al. ^[11] at 1.1 g FeCl₃/L, which indicates that the nature of the SAMBR effluent makes it less prone to coagulation because most colloids were retained within the SAMBR due to its submerged 0.4 micron membrane and the cake layer rejection. Our results thus demonstrate that coagulation-flocculation will not be an efficient way to treat the permeate of a SAMBR.

Effect of polyelectrolyte addition on flocculation-coagulation

Polyelectrolytes are polymers with ionisable groups: in polar solvents such as water, these groups can dissociate, leaving charges on polymer chains and releasing counterions into solution. When they were used alone (with no FeCl₃), a COD removal of 5 % was obtained with all five polyelectrolytes indicating that their charge had no substantial effect. The effect of the polyelectrolytes was then studied to determine their effects on the coagulation of organic compounds with FeCl₃ (1 g/L, pH 5). The results obtained showed that their addition had a positive effect on the percentage COD removal: 30 minutes after addition of FeCl₃ and the flocculants COD removals of 44-46 % were found as compared with only about 32 % with FeCl₃ acting alone. This is similar to Gotvajn et al. ^[1] who achieved 34 % with 1 g/L

FeCl₃ alone, and 51 % with FeCl₃ with 2.5 mg/L polyelectrolyte. The enhanced removal is due to the fact that polyelectrolytes can form additional inter-molecular bonds (bridging effect).^[21-22] The addition of polyelectrolyte therefore increases the rate of COD removal within a very short time interval. Using a concentration of 5 mg/L polyelectrolyte instead of 0.5 mg/L, a COD removal of 47 % was obtained showing that increasing the polyelectrolyte concentration did not significantly increase the amount of COD removed.

Adsorption onto Polymeric Adsorbents

It was found that XAD7HP performed better than XAD4: the respective COD removals were 46 and 32 %, while a combination of both (XAD7HP 10 g/L, then XAD4 10 g/L) resulted in 55 % COD removal. The pore size, surface area, polarity, contact time, pH and the hydrophobic nature of the adsorbent and adsorbate are among the parameters affecting the resin capacity for a particular material. An important factor is the matching of polarity between adsorbent and adsorbate, where an adsorbent with a higher polarity is more selective for polar compounds.^[17] XAD4, which is a styrene based resin, was expected to exert a stronger affinity for low MW hydrophobic compounds than the acrylic based ones such as XAD7HP which were both used in the experiment. Also, the smaller pore diameter of XAD4 was supposed to facilitate the adsorption of small MW compounds. Results, however, showed that the adsorption capacity of XAD7HP was better than that of XAD4. This can be explained by considering the fact that even though both resins have non ionic interactions with the adsorbate, XAD4 is a completely non polar resin while XAD7HP is a

moderately polar resin, and as such is able to adsorb non aromatic compounds from polar solvents.

Adsorption and Coagulation Tests on Low MW Compounds (MW<1 kDa)

Since 25 % of the COD from the SAMBR permeate is due to compounds smaller than 1 kDa, we investigated the removal of these compounds using other adsorbents and coagulants, namely GAC (10 g/L), iron chloride (1 g/L), XAD7HP and XAD4 resins (10 g/L) at pH 8. Initially the adsorption of the low MW compounds using the two different types of activated carbon showed in Figure 5 that PAC and GAC had similar adsorption capacities, with the removal rising to approximately 60 %. These findings have a clear economical consequence because GAC is much cheaper than PAC. Results in Figure 5 showed that PAC and GAC had the highest adsorption efficiency around 60 % COD removal after 1 hour of contact, followed by XAD7HP (48 %), XAD4 (27 %) and then FeCl₃ (23 %). The adsorption of low MW compounds was more effective using activated carbon as opposed to polymeric adsorbents as a result of their larger surface areas, and hence smaller pore size which are effective for the removal of low MW compounds.

The better adsorption of low MW compounds by XAD7HP compared to XAD4 indicates that there are relatively polar components in the lower MW fraction that XAD7HP can adsorb, but not XAD4. The nature of the <1 kDa compounds could also influence the rate of adsorption, as XAD4 will preferentially adsorb hydrophobic aromatics which are not readily available in the lower MW fraction of the effluent. In fact, from a COD balance, about 70 % of low MW are hydrophilic compounds which could not be removed by XAD4. This is in

agreement with Croue et al. [23] who observed that the lower the MW of the natural organic matter, the less its hydrophobic character and aromatic carbon content.

Size Exclusion Chromatography Results

Activated carbons

The SEC allowed us to shed more light on the mechanisms taking place during adsorption rather than using COD data only as reported in the literature. Standards are shown in Figure 6A where it can be seen that high MW compounds elute first because they do not penetrate as deep as low MW into the gel pores. The following equation ($R^2 = 0.984$) was derived from the standard elution times and MW (in Da):

$$MW = 4.22 \cdot 10^{10} \cdot \exp(-0.985 \cdot t) \quad (7)$$

Where t is the elution time in minutes. Interestingly, it was observed that the SAMBR permeate chromatograph (FIG.. 6B) was made of two clear peaks at elution time of 13 and 17.5 min corresponding to MW of 116 kDa and 1.3 kDa, respectively.

Figure 6B shows that GAC and PAC efficiency was highest at 10 g/L which is consistent with the observations made with the COD analysis.

The kinetics of adsorption onto GAC and PAC at 10 g/L was also studied in terms of size exclusion chromatography. Figure 7 confirms that both high and low MW compounds were adsorbed in the first minutes of contact; however, PAC removed low MW compounds much

faster than GAC which contradicts Figure 5 where COD removal occurred within 5 minutes on both GAC and PAC. It should be born in mind that COD analysis encompasses all compounds, aliphatic as well as aromatics, whereas SEC analysis at 254 nm detects preferentially aromatics. Therefore, although the COD removal followed the same kinetics for GAC and PAC, low MW aromatic compounds absorbing at 254 nm were adsorbed much faster on PAC than on GAC. Furthermore, the adsorption of these low MW aromatic compounds reached equilibrium very quickly as no more adsorption took place after 5 minutes. This indicates that there is a fraction of low MW aromatics that could not be removed no matter how long the contact time. This is due to the nature of these low MW aromatics that are hydrophilic and will not adsorb onto PAC or because of diffusional limitations. DeWalle and Chian ^[24] also found that the low MW fraction, consisting of mostly polar organic compounds, were poorly adsorbed.

Polymeric adsorbents

Figure 8 shows that after the addition of XAD7HP high and low MW aromatics were removed; however, there was not much difference in the amount of aromatics removed when XAD4 was added to the filtered effluent from the XAD7HP-treated sample. Based on the absorbance, about 20 % of high MW and 60 % of low MW aromatics were removed. This indicates that a large fraction of the high MW compounds could not be removed because of their MW. Indeed, XAD7HP is recommended for non-polar compounds up to 60 kDa. So the high MW compounds from the SAMBR permeate could not enter the pores of XAD7HP for efficient removal. On the other hand, about 60 % of low MW aromatic compounds could be

removed because of their hydrophobicity which indicates that 40 % of low MW aromatic were hydrophilic and exhibit a low affinity for XAD7HP. XAD4 used after XAD7HP could not remove much more of the low MW compounds as most of them had already been removed by XAD7HP.

CONCLUSIONS

Various post-treatment strategies were investigated to reduce the COD content of the permeate of a novel anaerobic membrane bioreactor. PAC was more effective in removing COD (84 %) from the SAMBR effluent compared to GAC (80 %), FeCl₃ with 0.5 mg/L polyelectrolyte (45 %), FeCl₃ alone (30-34 %), and the polymeric adsorbents XAD7HP (46 %) and XAD4 (32 %). Ultrafiltration (1 kDa cut-off membrane) could remove 75 % COD. PAC and GAC were the best adsorbents of low MW compounds (<1 kDa) with about 60 % COD removal, compared to XAD7HP (48 %), XAD4 (27 %) and then FeCl₃ (23 %) after 1 hour of contact time. The post treatment sequence UF+GAC following the SAMBR will result in a final effluent with less than 100 mg/L COD. A better understanding of the SAMBR permeate has been gained in this study: the SEC analysis revealed that the SAMBR permeate was made of two main peaks with aromatic compounds of MW 116 and 1.3 kDa. SEC revealed that the low MW aromatic compounds were adsorbed within 5 minutes onto PAC, but at a slower rate onto GAC. The high MW aromatic compounds were adsorbed at a slower rate compared to the low MW aromatic compounds.

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REFERENCES

- [1] Gotvajn, A.Z.; T. Tisler; J. Zagorc-Koncan. Comparison of different treatment strategies for industrial landfill leachate. *Journal of Hazardous Materials* **2009**, *162*(2-3), 1446-1456.
- [2] Wang, J.; D. Shen; Y. Xu. Effect of acidification percentage and volatile organic acids on the anaerobic biological process in simulated landfill bioreactors. *Process Biochemistry* **2006**, *41*(7), 1677-1681.
- [3] Hong, S.; M. Elimelech. Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of Membrane Science* **1997**, *132*(2), 159-181.
- [4] Kurniawan, T.A.; W.-H. Lo; G.Y.S. Chan. Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. *Journal of Hazardous Materials* **2006**, *129*(1-3), 80-100.
- [5] Chian, E.S.K. Stability of Organic-Matter in Landfill Leachates. *Water Research* **1977**, *11*(2), 225-232.
- [6] Trebouet, D.; J.P. Schlumpf; P. Jaouen; F. Quemeneur. Stabilized landfill leachate treatment by combined physicochemical-nanofiltration processes. *Water Research* **2001**, *35*(12), 2935-2942.

- [7] Bohdziewicz, J.; M. Bodzek; J. Gorska. Application of pressure-driven membrane techniques to biological treatment of landfill leachate. *Process Biochemistry* **2001**, *36*(7), 641-646.
- [8] Robinson, A.H. Landfill leachate treatment. in *5th International Conference on Membrane Bioreactors*, Cranfield University, UK 2005.
- [9] Diamadopoulos, E. Characterization and treatment of recirculation-stabilized leachate. *Water Research* **1994**, *28*(12), 2439-2445.
- [10] Tatsi, A.A.; A.I. Zouboulis; K.A. Matis; P. Samaras. Coagulation-flocculation pretreatment of sanitary landfill leachates. *Chemosphere* **2003**, *53*(7), 737-744.
- [11] Ntampou, X.; A.I. Zouboulis; P. Samaras. Appropriate combination of physico-chemical methods (coagulation/flocculation and ozonation) for the efficient treatment of landfill leachates. *Chemosphere* **2006**, *62*(5), 722-730.
- [12] Aziz, H.A.; S. Alias; M.N. Adlan; A. Fafidah; M.S. Zahari. Colour removal from landfill leachate by coagulation and flocculation processes. *Bioresource Technology* **2007**, *98*(1), 218-220.
- [13] Millot, N.; C. Granet; A. Wicker; G.M. Faup; A. Navarro. Application of G.P.C. processing system to landfill leachates. *Water Research* **1987**, *21*(6), 709-715.
- [14] Rodriguez, J.; L. Castrillon; E. Maranon; H. Sastre; E. Fernandez. Removal of non-biodegradable organic matter from landfill leachates by adsorption. *Water Research* **2004**, *38*(14-15), 3297-3303.
- [15] Trzcinski, A.P.; D.C. Stuckey. Continuous treatment of the Organic Fraction of Municipal Solid Waste in an anaerobic two-stage membrane process with liquid recycle. *Water Research* **2009**, *43*(9), 2449-2462.
- [16] APHA, *Standard Methods for the Examination of Water and Wastewater*. 1999, Washington D.C: American Public Health Association.

- [17] Abdullah, M.A.; L. Chiang; M. Nadeem. Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents. *Chemical Engineering Journal* **2009**, *146*(3), 370-376.
- [18] Nadeem, M.; A. Mahmood; S.A. Shahid; S.S. Shah; A.M. Khalid; G. McKay. Sorption of lead from aqueous solution by chemically modified carbon adsorbents. *Journal of Hazardous Materials* **2006**, *138*(3), 604-613.
- [19] Barker, D.J.; G.A. Mannucchi; S.M.L. Salvi; D.C. Stuckey. Characterisation of soluble residual chemical oxygen demand in anaerobic wastewater treatment effluents. *Water Research* **1999**, 2499-2510.
- [20] Zhang, C.; Y. Wang. Removal of dissolved organic matter and phthalic acid esters from landfill leachate through a complexation-flocculation process. *Waste Management* **2008**, *29*(1), 110-116.
- [21] Baraniak, B.; M. Niezabitowska; J. Pielecki; W. Wojcik. Evaluation of usefulness of Magnafloc M-22S flocculant in the process of obtaining protein concentrates from peas. *Food Chemistry* **2004**, *85*(2), 251-257.
- [22] Mahvi, A.H.; M. Razavi. Application of Polyelectrolyte in Turbidity Removal from Surface Water. *American Journal of Applied Sciences* **2005**, *2*(1), 397-399.
- [23] Croue, J.-P.; D. Violleau; C. Bodaire; B. Legube. Removal of hydrophobic and hydrophilic constituents by anion exchange resin. *Water Science and Technology* **1999**, *40*(9), 207-214.
- [24] Dewalle, F.B.; E.S.K. Chian. Removal of Organic-Matter by Activated Carbon Columns. *Journal of the Environmental Engineering Division-Asce* **1974**, *100*(NEE5), 1089-1104.

FIGURES CAPTIONS

Figure 1. Effect of pH on COD removal percentage with 5 g/L of GAC.

Figure 2. Comparison of adsorption kinetics and capacity of GAC and PAC at 10 g/L. The error bars indicate the standard deviation.

Figure 3. Evolution with time of the COD removal percentage of various MW fractions on PAC 10 g/L.

Figure 4. Evolution with time of the COD removal percentage with 0.5, 1 and 3 g/L FeCl₃ at pH 5.

Figure 5. Evolution with time of the COD removal percentage of the low MW fraction (< 1 kDa) from the SAMBR permeate with various adsorbents and coagulants. Symbols: diamond = PAC; full square = GAC; triangle = FeCl₃; open square = XAD7HP; star = XAD4.

Figure 6. (A) Standards for size exclusion chromatography. (B) Effect of GAC and (C) PAC dosage on size exclusion chromatography after 24 hours of contact time.

Figure 7. (A) Size exclusion chromatographs at various times during the adsorption onto 10 g/L GAC and PAC (B).

Figure 8. Size exclusion chromatographs of the SAMBR permeate before and after adsorption onto polymeric adsorbents XAD7HP and XAD4.

TABLES CAPTION

Table 1. Properties of the GAC and PAC used in this study.

Table 2. Properties of the resins XAD7HP and XAD4 used in this study.

Table 3. Isotherm constants of Langmuir and Freundlich models and kinetic constants for first and second order model for adsorption onto GAC and PAC.

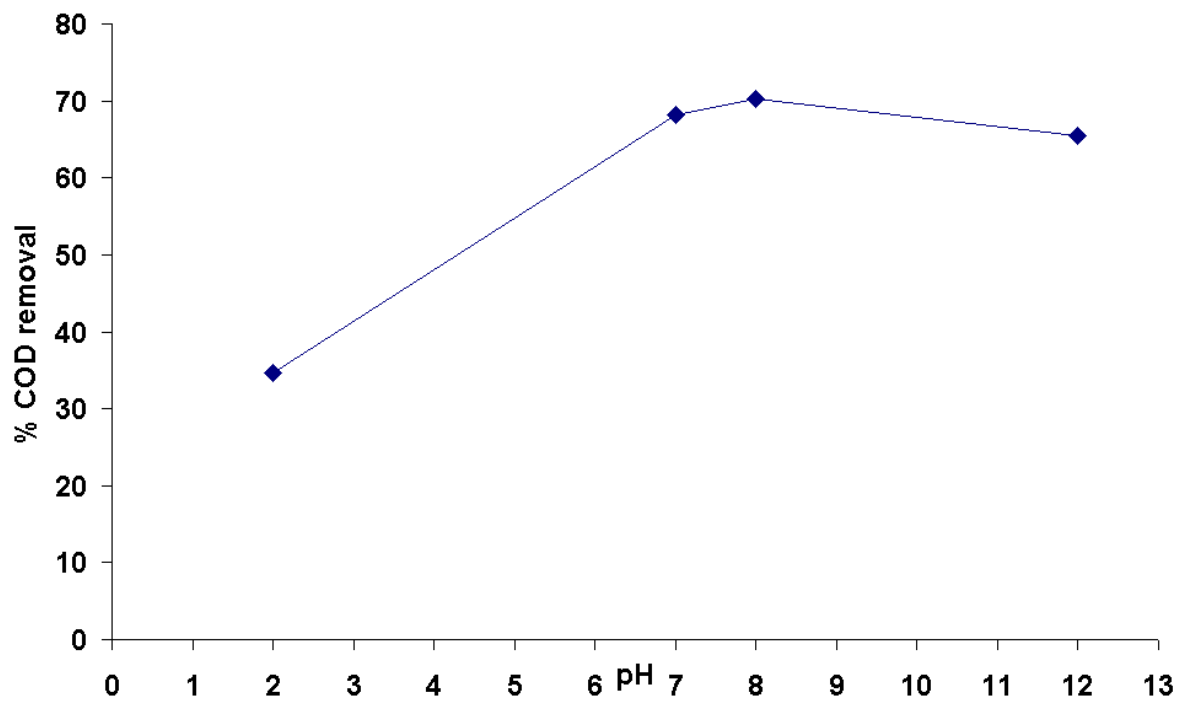


FIG. 1

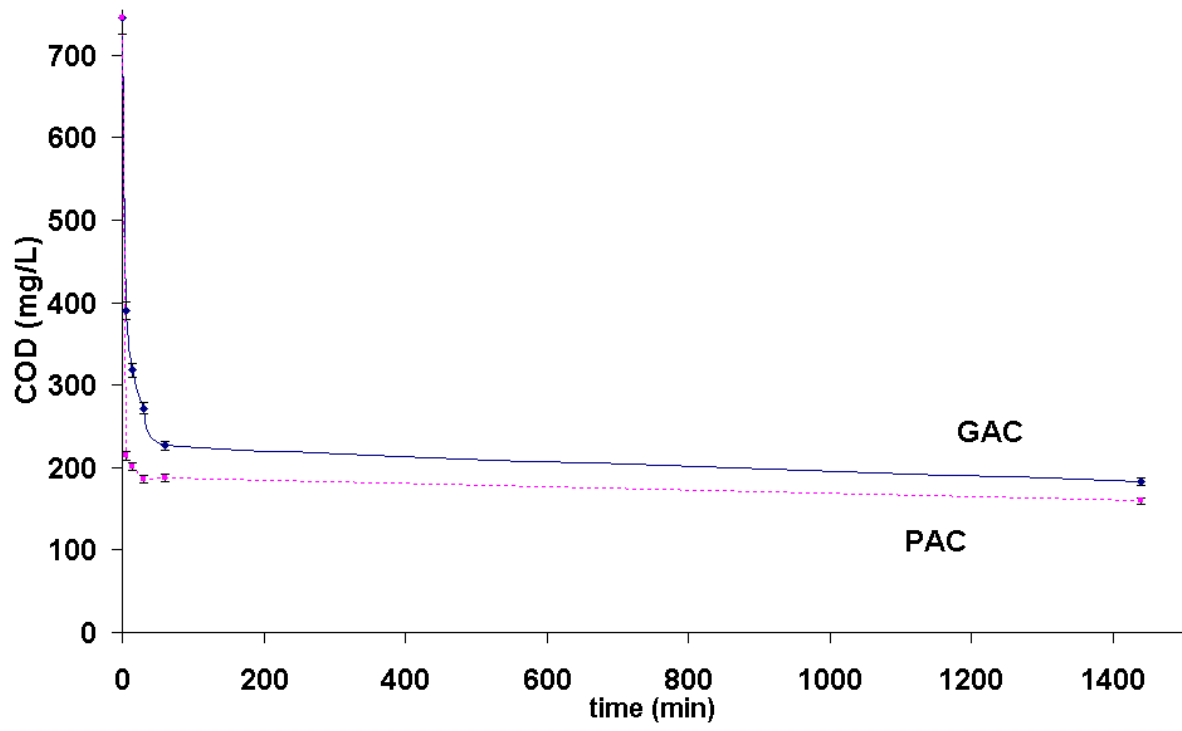


Fig 2

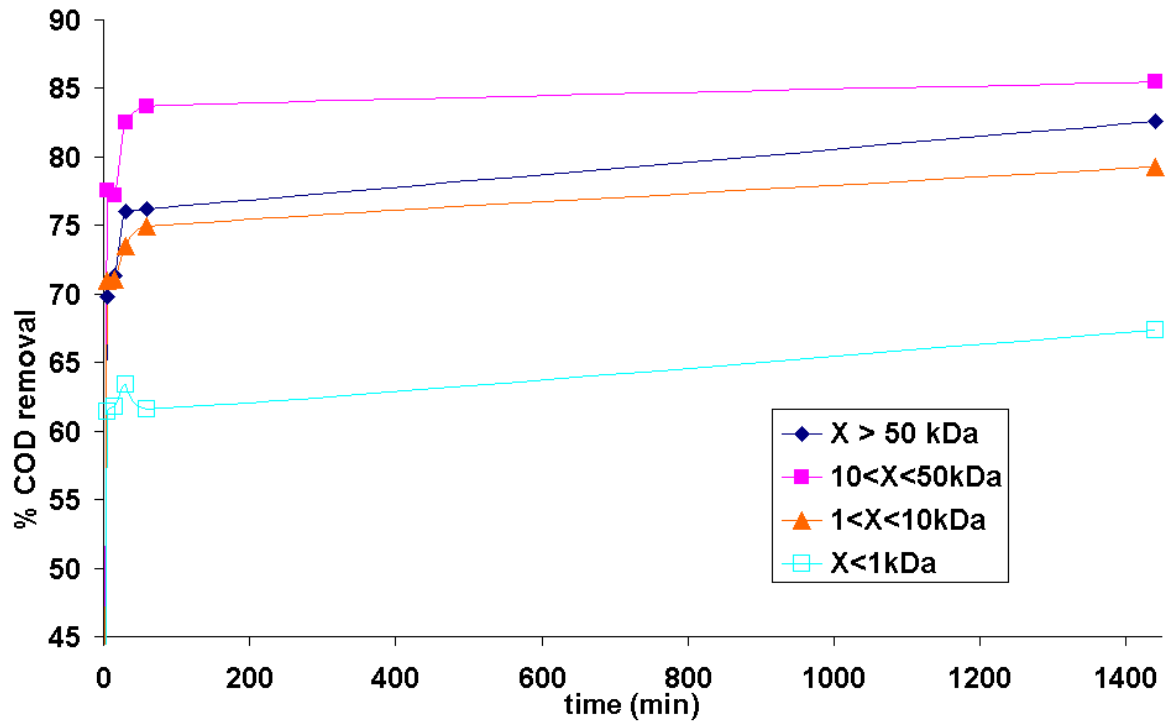


FIG3

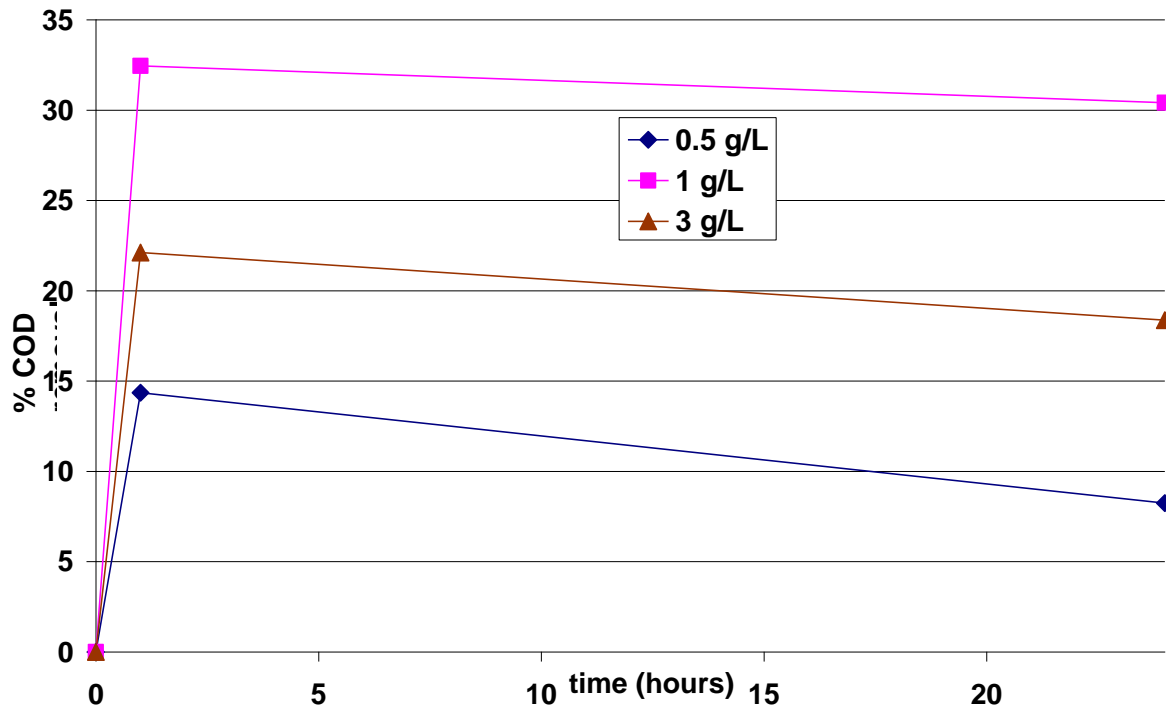


FIG4

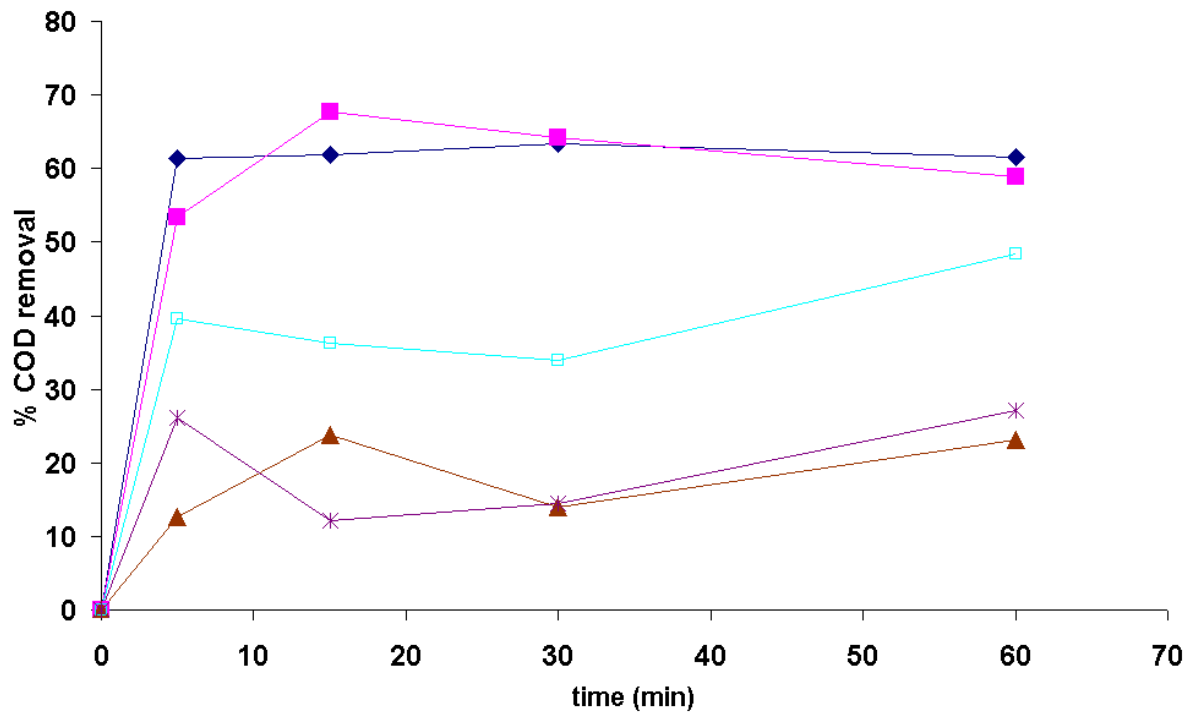


FIG5

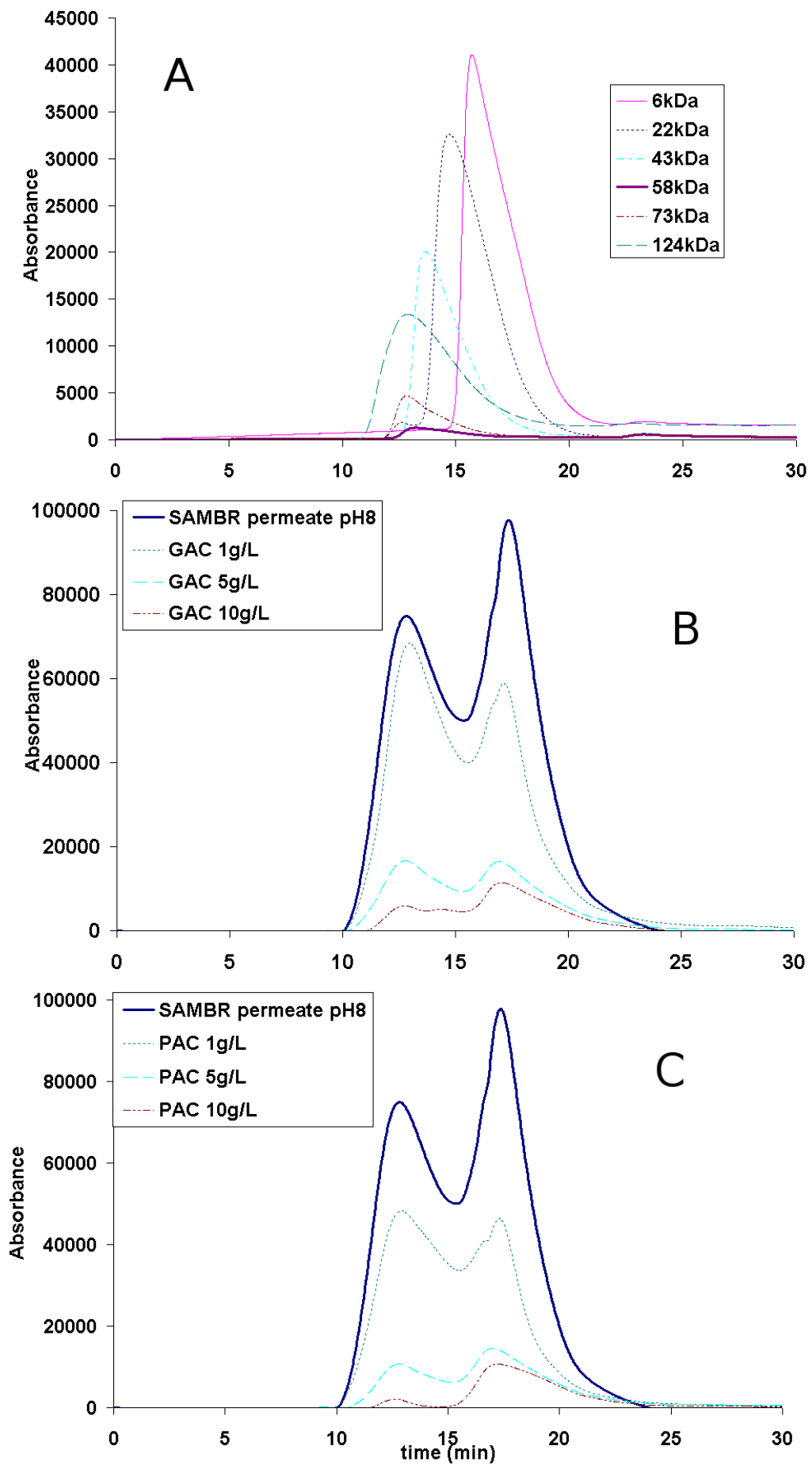


Fig6

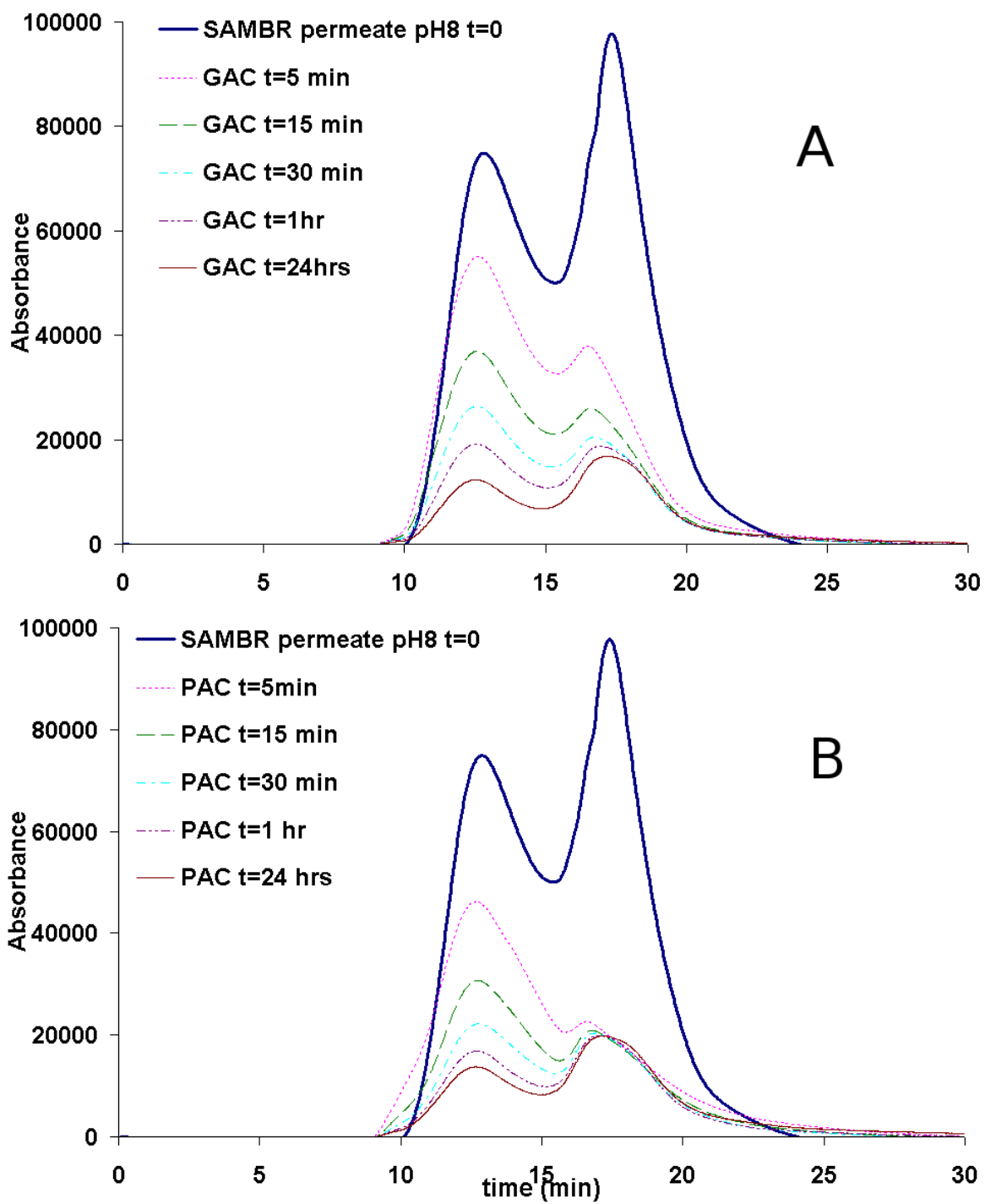


FIG7

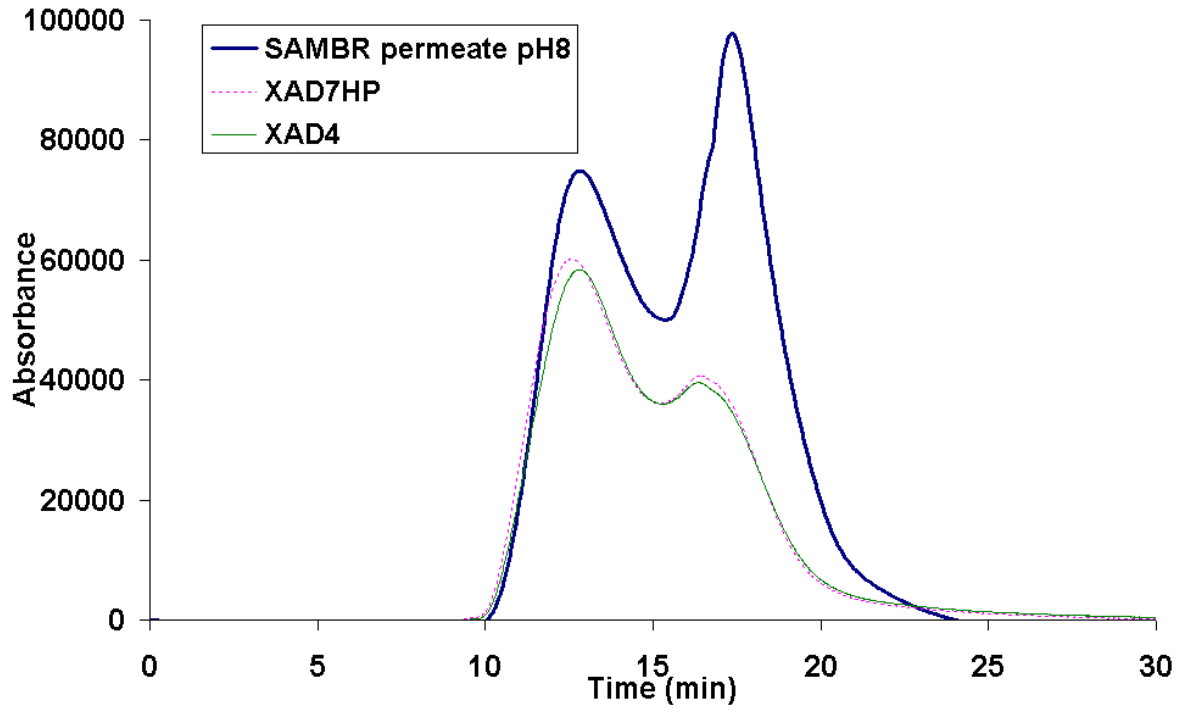


FIG8

Table 1. Properties of the GAC and PAC used in this study.

Properties	GAC	PAC
Name	PK025-1	SAE2
Surface area BET (m ² /g)	775	925
Methylene Blue adsorption (g/100g)	11	12
Iodine Number	600	850
Particle size		
≥ 1 mm (18 mesh) (% mass)	10	-
≤ 0.25 mm (60 mesh) (% mass)	5	-
≥ 150 μm (% mass)	-	3
Effective size (μm)	300	22
Uniformity coefficient	1.9	-
Ash (mass %)	15	-
pH	Alkaline	Alkaline
Moisture (max. mass %)	2	6

Table 2. Properties of the resins XAD7HP and XAD4 used in this study.

Properties	XAD7HP	XAD4
Matrix	Methylacrylate ester	Polystyrene-divinylbenzene
Surface area BET (m ² /g)	450	725
Pore diameter (Å)	90	40
Pore volume (mL/g)	1.14	0.98
Density	1.06 – 1.08	1.02 – 1.08
Particle size	20 – 60 mesh	20 – 60 mesh
Polarity	Intermediate polarity	non-polar
Target compounds	Non-polar up to 60 kDa	Low MW hydrophobic

Table 3. Isotherm constants of Langmuir and Freundlich models and kinetic constants for first and second order model for adsorption onto GAC and PAC.

Isotherm constants			Kinetic constants		
Model	GAC	PAC	Model	GAC	PAC
Langmuir			1 st -order		
K _L	0.366	0.459	k _f (min ⁻¹)	0.036	0.035
a _L	-0.00087	-0.00058	q _e (mg/g)	32.07	13.56
R ²	0.94	0.947	R ²	0.848	0.435
Freundlich			2 nd -order		
K _F	0.0875	0.213	h (mg/g min)	15.02	182.98
n	0.766	0.852	k _s (g/mg min)	0.005	0.058
R ²	0.999	0.997	q _e (mg/g)	54.55	56.11
			R ²	0.999	1