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Direct Contact Membrane Distillation for Separation of Hcl From A Mixture of Acids

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ABSTRACT

HCl is separated from HCl –H_2SO_4 solution by membrane distillation process(MD). The flat – sheet membranes made from polyvinylidene fluoride (PVDF) and polypropylene (pp.). Plate and frame these types of membrane where used in the process. The feed is a mixture of HCl and H_2SO_4 acids compositions depended on metals treated object.HCl concentration increased in the permeate during the process but sulfuric acid increased gradually in the feed .During the concentration of solution acids concentrations in the feed at the beginning were 50 g/dm^3 of sulfuric acid and 50 g/dm^3 of hydrochloric acid at 333K feed temperature the permeate flux was 71 dm^3/m^2.d. At a higher concentration of HCl in the feed 111g /dm^3 and 61 g/ dm^3 of sulfuric acid at the feed temperature 333K volume permeate flux was 57 dm^3/ m^2.d . At a higher concentration of sulfuric acid in the feed 161 g/dm^3 and 60 g/dm^3 of HCl decrease the permeate flux from 71 to 35 dm^3/m^2.d at 333K . The permeate flux increase from 35 at 333K to 85 at 343 K increase the temperature caused an increase in permeate flux. Increases in sulfuric acid concentration from 50 to 161 g/dm3 decrease the volume permeate flux from 71 to 35 dm3 /m^2.d, HCl concentration was achieved a higher value 9.1 g/dm^3 during the process at the feed concentration 161g/dm^3 of sulfuric acid and 60g/dm^3 of hydrochloric acid at feed temperature 343K.

Key Words: membrane distillation, HCl separation, vapor permeation

فصل حامض الهيدروكلوريك من مزيج من حامض الهيدروكلوريك وحامض الكبريتيك بواسطة التقطير الغشائي

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الخلاصة

فصل حامض الهيدروكلوريك من مزيج حامض الكبريتيك و حامض الهيدروكلوريك بواسطة التقطير الغشائي، الغشاء عبارة عن ورقة مسطحة مصنوعة من PVDF و PP غشاء اللوحة والاطار استخدم في التجربة. المحلول متكون من مزيج من حامض الهيدروكلوريك وحامض الكبريتيك بتراكيز ابتدائية مختلفة وهذه النسب تعتمد على مشاريع معالجة المعادن خلال.

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عملية التقطير الغشائي وجد بأن حامض الكبريتيك يبقى محتجزا في الخط المغذي الداخل وبالتالي فان تركيز حامض الكبريتيك يزداد با لتدريج ، بينما حامض الهيدروكلوريك يتناقص تركيزه في الخط المغذي . خلال تركيز المحلول50 غم/دسم^{3}من حامض الهيدروكلوريك و 50غم/دسم^{3}من حامض الكبريتيك بدرجة حرارة 333كلفن حجم الحامض المتدفق كان 71دسم^3/م^2.يوم عندما يكون تركيز حامض الهيدروكلوريك مرتفع في الخط المغذي الداخل 111غم/دسم^{3}و 61غم/دسم^{3}من حامض الكبريتيك بدرجة حرارة 333كلفن حجم الحامض المتدفق كان 57دسم^3/م2.يوم .عندما يكون تركيز حامض الكبريتيك 161غم/دسم^{3}و60غم/دسم^{3}من حامض الهيدروكلوريك حجم المتدفق سوف يقل من 71 الى 35دسم^3/م^2.يوم، بينما حجم الحامض المتدفق يزداد من 35 الى 85دسم^3/م^2.يوم بدرجة حرارة 343كلفن زيادة تركيز حامض الكبريتيك في الخط المغذي الداخل من 161-50 غم /دسم^{3}يسبب تقليل الحجم المتدفق من 71الى 35دسم^3/م^2.يوم اعلى تركيز لحامض الهيدروكلوريك يمكن الحصول عليه خلال العملية هو9,1 غم /دسم ^{3} عندما يكون تركيز الخط المغذي الداخل كل من حامض الكبريتيك 161غم/دسم^{3}و60غم/دسم^{3}من حامض الهيدروكلوريك بدرجة حرارة 343كلفن.

الكلمات الرئيسية : التقطير الغشائي ، فصل حامض الهيدروكلوريك، تغلغل البخار.

1. INTRODUCTN

Membrane distillation is a process was used for separation of two aqueous solutions with different composition and temperature**, Tomaszewska ,and Mientka , 2009.** This process takes place at atmospheric pressure and a temperature may be lower than the boiling point**, Uchenna et al., 2014.** A physical role of support for liquid/gas interface was played by hydrophobic membrane, and PVDF membrane prevents solution passing through it because of its nature. The driving force in membrane distillation process caused by the difference in vapor pressure across the membrane originates from the composition and temperature gradients in the boundary layer adjacent to the hydrophobic membrane **, Tomaszewska, et al., 2000 and Tomaszewska, et al., 1998.** The separation mechanism in membrane distillation process is contacted with (solution-vapor) equilibrium system**, Lawson, et al., 1997.** When the feed contains a high concentration of volatile substance such as (HCl) with water, they all transferred from the feed side through the hydrophobic membrane pores to the distillate side**, Tomaszewska ,et al., 1995 and Sarti, et al., 1985.** When the feed contains non-volatile components, so only water vapor will transferred through the membrane pores **, Calabro, et al., 1991.**In this case the compositions of the distillate depends on the diffusion rates and volatility values for the different substances in the feed . The feed solution consisted of a mixture of sulfuric acid and hydrochloric acid with a different initial concentration , acids concentrations depends on metal treated objects, these solution is very harmful for natural environment , due to the solubility of metal oxide in sulfuric acid and hydrochloric acid , either of two acids can be used for cleaning these oxides will not be removed by the simple application or HCl only because it has a simple effect , so HCl will mix with sulfuric acid for cleaning purpose**, Tomaszewska, et al., 2001.** Till now membrane distillation process used to concentrate of non-volatile components because MD process has been investigated widely for concentration solution of non – volatile substances .By membrane distillation process a lot of pollution problems can be solved, so the quantity of the effluents could be reduced. Membrane distillation process used for obtaining pure water from the sea **,Drioli, et al., 1987.** Because it has been mostly investigated in salt solution of NaCl (sodium chloride) **, Lagnan, et al., 2000.** MD also has been applied to waste water treatment yielding a permeate that is less hazardous to environment the waste sulfuric acid solution can be treated by conventional methods such as (cooling, evaporation, distillation , thermal decomposition , solvent extraction), and advance method such as (membrane distillation , electro dialysis ,diffusion dialysis)**, Petal, et al., 2017.** The object of this project was to recover of volatile component from the solution and concentrate it, also to study the effect of temperature on the permeate volume flux and on the permeate concentration.

2. EXPERIMENTAL WORK

The membrane distillation process (MD)**, Tomaszewska, et al., 1995.** Consist of feed, permeate, and two thermo stated loops for feed and permeate to control the process temperatures. The module was plate and frame the membrane made from PVDF and supported with PP .The area of filtration was 0.045 m^2, membrane characteristic are pore size 0.22um, dimensions 0.26x11.6m, H_2SO_4 rejection 99%, normal boiling point $65C^0$ and maximum temperature$90C^0$ for the direct contact membrane distillation, the main element of the flat sheet system was the cell consisted of compartments cold and warm, separated by hydrophobic membrane PVDF the thermo stated feed was recycled to the warm side The vapor transported through the membrane was directly condensed in the permeate (cold side) the warm feed and cold permeate were circulated in counter current closed system as shown in **Fig.1**.The feed was a mixture of sulfuric acid and hydrochloric acid. The concentration of both sulfuric acid and hydrochloric acid were used in a wide range in order to investigate the effect of feed composition on the separation process. Its compositions depend on treated metal objects. The feed solutions contained HCl with initial concentration (50-111) g/dm^3 whereas sulfuric acid concentration (50-161)g/dm . the volume of feed was (3L), all experiments occurred at a feed temperature (TF in) 333 K or 343 k and the inlet temperatures of the cold receiving solution (TR in) was kept at 298 K by using thermo state loop contacting with cooler (chiller) when the permeate solution reached 298K thermo state will be turn off for all experiments, at the beginning of the process the cold system (permeate) supplied by (750ml) of distillate water to calculate the volume permeate flux, the change in the volume of distillate must be measured every hour. The concentration of Cl and H ions were measured by titration method. After each hour concentration of permeate was measured by titration method, materials were used unknown HCl solution, Phenolphthalein, NaOH solution, (2-50mL) Burette, Universal Stand, Titration Clamp,(250mL)flask,(25mL) graduated cylinder , pipet, and distilled water. Take a sample (10 ml), from permeate (HCl solution) and titration with (0.1 M) of NaOH , the base NaOH was put in the burette and acid was but in the flask, 2 drops of indicator put on the flask over the acid and titrate with base the solution was changed from colorless to pink and checked by pH meter.Volume permeate flux can be calculated by**, Tomaszewska , et al., 1999.**

$$LMH= (Vt+1 - Vt)/A.\ t \qquad dm^3/m^2.\ d \tag{1}$$

Where:

LMH: is the volume permeate flux

A: is membrane area, m^2

(Vt+1 –Vt) : are the difference in permeate volume at time t and t+1

t: the time ,h

2.1 Acids

Both hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) are strong mineral (inorganic) acids. They react with bases producing water and they react with metals producing H_2. HCl is found in Human body HCl drenches the stomach contents in an acid bath which kills harmful bacteria in the food. Sulfuric acid can be preparation out of the home.

2.1.1 Hydrochloric acid HCl

HCl is a solution of hydrogen chloride (HCl) gas that is dissolved in water, in the past the people called it (muriatic acid), it is widely used in industry.

Table 1. The specifications of HCl.

Molar density	36.46 $gmol^{-1}$
Appearance	colorless
Density	1.18 g/cm^3
Melting point	-114.22 C^0 (-173.60 F^0,158.93 K)
Solubility in water	823 g/l (0 C^0) 720 g/l (20 C^0) 561 g/l (60 C^0)
Boiling point	-85.05 C^0 (-121.09 F^0, 188.10 K)
Vapor pressure	4352 Kpa at (21.1 C^0)
Viscosity	0.311 CP (-100 C^0)

2.1.2 Sulphuric acid H2SO4

Sulphuric acid is a strong acid produced by the dissolving of sulphur trioxide in water.

$$SO_3 + H_2O \longrightarrow H_2SO4$$

Sulphuric acid is a colourless, viscous corrosive liquid which has a specification as shown in table2.

Table 2. The specification of sulphuric acid.

Vapour pressure	0.001 mm Hg(20 C^0)
Viscosity	26.7 CP (20 C^0)
Odour	odourless
Melting point	10 C^0
Density	1.84 g/cm^3
Boiling point	337 C^0 (610 K)
Solubility in water	miscible
Molar mass	98.079 g/mole

3. RESULT AND DISCUTION

3.1 Effect of Operating Time

The effect of operating time on permeate flux was studied in direct contact membrane distillation. When the feed containing initially 50g/dm^{3}HCl and 50g/dm^3H_2SO_4, and at temperature 333K as shown in **Fig.2**. Only hydrochloric acid gaseous and water vapor transferred through the membrane pores to the permeate during MD process but sulfuric acid remained in the feed and its concentration increasing gradually reached a value of 100g/dm^3 ,**Fig.2** show the changes in the concentration of HCl and H_2SO_4 with time .At the beginning of membrane distillation process both acids was gradually increase, because of only water vapor was transferred through the membrane, so HCl concentration slightly increase in the feed , this behaviour is agreement with **,Tomaszewska and Mientka, 2009.** After one hour permeate concentration was 0.67g/dm^3 but during 5 hours the permeate concentration increased to 1.8g/dm^3, and the volume permeate flux was 71dm^3/m^2.d from Eq(1).

3.2 Effect of Feed Concentration

When a higher concentration of HCl in the feed after the first hour the component appeared in the permeate of the concentration process, was 3.0991g/dm^{3}as shown in **Fig.3**, and during 5 hour permeate concentration reached 5.39g/dm^3,and the volume permeate flux was 57.39dm^3/m^2.d.When the initial concentration of sulphuric acid was equal to 161g/dm^3 the permeate flux decrease to 35dm^3/m^2.d as shown in **Fig.4**,these declines of volume permeate flux was caused by the decreasing in water vapour pressure being in equilibrium with the feed solution.When added non-volatile solute to solution caused decrease in water vapour pressure, this behaviour is agreement with **,Gryta , et al., 2001**. The viscosity of the feed increase because of increase the concentration of sulphuric acid this is another factor, sulphuric acid has higher viscosity compared with another acids, so decrease the diffusivity .Diffusivity adversely related with viscosity, and also when the sulphuric acid weight present be higher than HCl caused a declines in HCl flux, this behaviour is agreement with ,**Tomaszewska, et al., 1994.**

3.3 Effect of Feed Temperature

In the case of acid mixture with the initial concentration 161g/dm^3 H_2SO_4 ,and 60g/dm^3 of HCl at 343K the increase in feed temperature to 343K a faster concentration of sulphuric acid and hydrochloric acid on the feed side. In the membrane distillation process the initial composition of the feed, were the same as for temperature 333K, the distillate consist of HCl solution with higher concentration, due to the gas/liquid phase equilibrium. An elevation of temperature caused, higher partial pressure of volatile components, and large mass transfer of water vapour and HCl across the membrane pores .The partial pressure of HCl under these conditions was so high, that the volume permeate flux was twice higher than for 333K, this behaviour is agreement with ،Tomaszewska **and Mientka, 2009.** And achieved a value 85.4dm^3/m^2.d.The concentration of HCl in the permeate achieved a value of 9.1g/dm^3, this increases in HCl concentration in the permeate caused by the water vapour was transferred through the membrane pores to the permeate with HCl vapour, during the concentration of acids mixture containing of both HCl and sulphuric acid the H_2SO_4 was completely retained on the feed side, this behaviour is agreement with **,Tomaszewska, et al., 1999.** Thus its concentration constantly increased, as shown in **Fig.5** can be seen, the increase of HCl in the permeate due to an increase in the feed temperature. From the data initially the concentration of both acids were gradually increased at the beginning of MD process only water vapour was transferred across PVDF membrane. When the concentration of HCl and sulphuric acid in the feed achieved the value of 71.35g/dm^3 and 201.26g/dm^3 respectively, the HCl transfer through the membrane pores was noticed **Fig.5**. Large volume permeate flux in order to large mass transfer of water through the membrane.

The volume permeate flux is a function of feed temperature As shown in **Fig.6** Due to an increase in feed temperature the volume permeate flux increase at the same concentration 111/61g/dm^3, this behaviour is agreement with**, Tomaszewska, et al., 1999.** The volume permeates flux in MD with PVDF membrane was lower than permeate flux in case polytetrafluroethethylene (PTFE) membrane. The PVDF was thickener, which creates longer path way for vapour pressure diffusion. A change in membrane type causes a change in heat and mass transfer. There is a large difference in values of volume permeate flux between(333-343)K feed temperature, as the temperature of the liquid increases due to the increasing in kinetic energy of the molecules, thus increasing vapour pressure. During the MD process of acids mixture HCl gaseous transport through the membrane pores is too high, that mean that the concentration of HCl in permeate is higher than in the feed under process conditions, as shown in **Fig. 7**.The final concentration of HCl achieved in the permeate reached practically the same concentration in the feed and permeates were practically the same. From the data at temperature of the feed equal to 333K the concentration of HCl in the permeate achieved a value of 3.0991g/dm^3, but at temperature 339K achieved a value of 5.9g/dm^3, and at temperature 343K achieved a value of 7.79g/dm^3.

4. CONCLUSIONS

1. HCl permeate flux increase with an increase in concentration of HCl in the feed.

2. Volume permeates flux decrease with an increase in sulfueric acid concentration in the feed.

3. Feed temperature strongly influences on the permeate flux, volume permeate flux increase with an increase in feed temperature.

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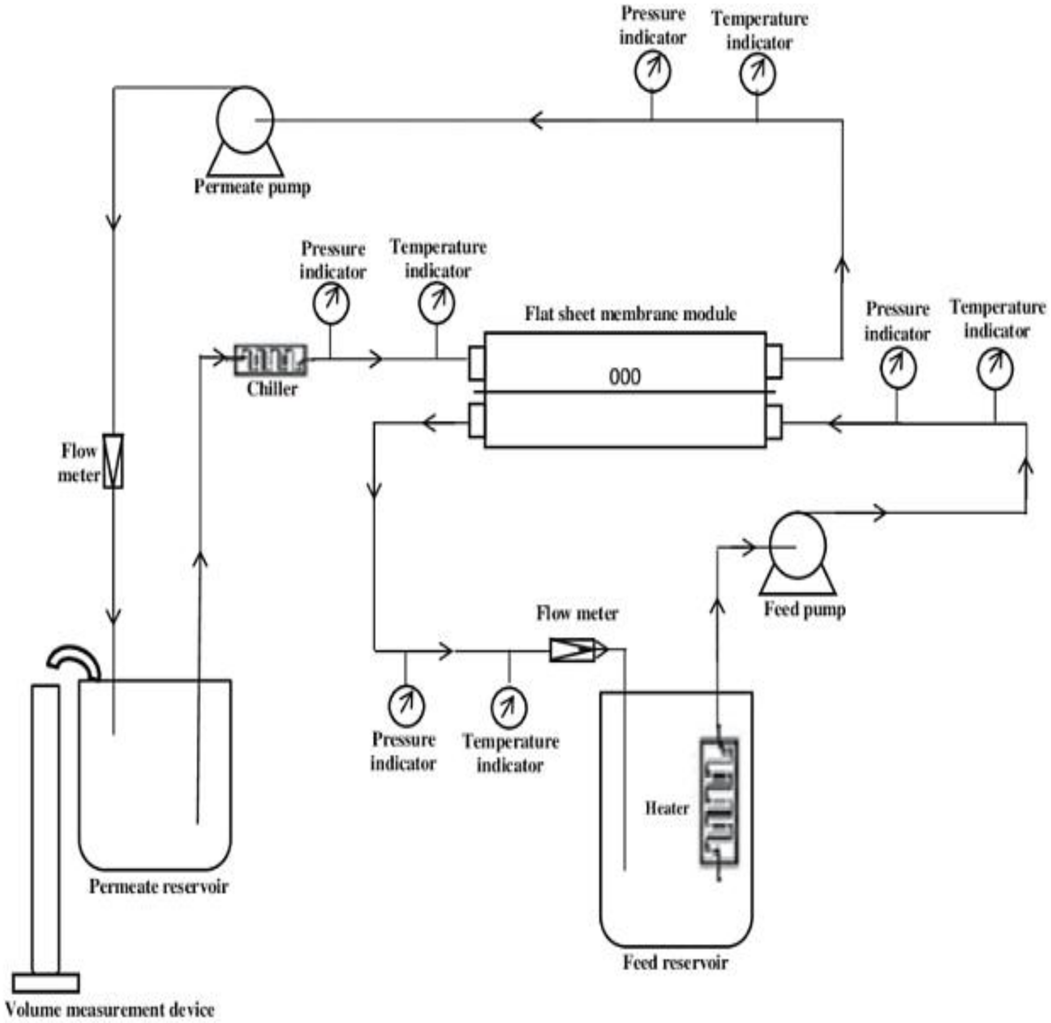


Figure 1. Schematic diagram of MD process**.**

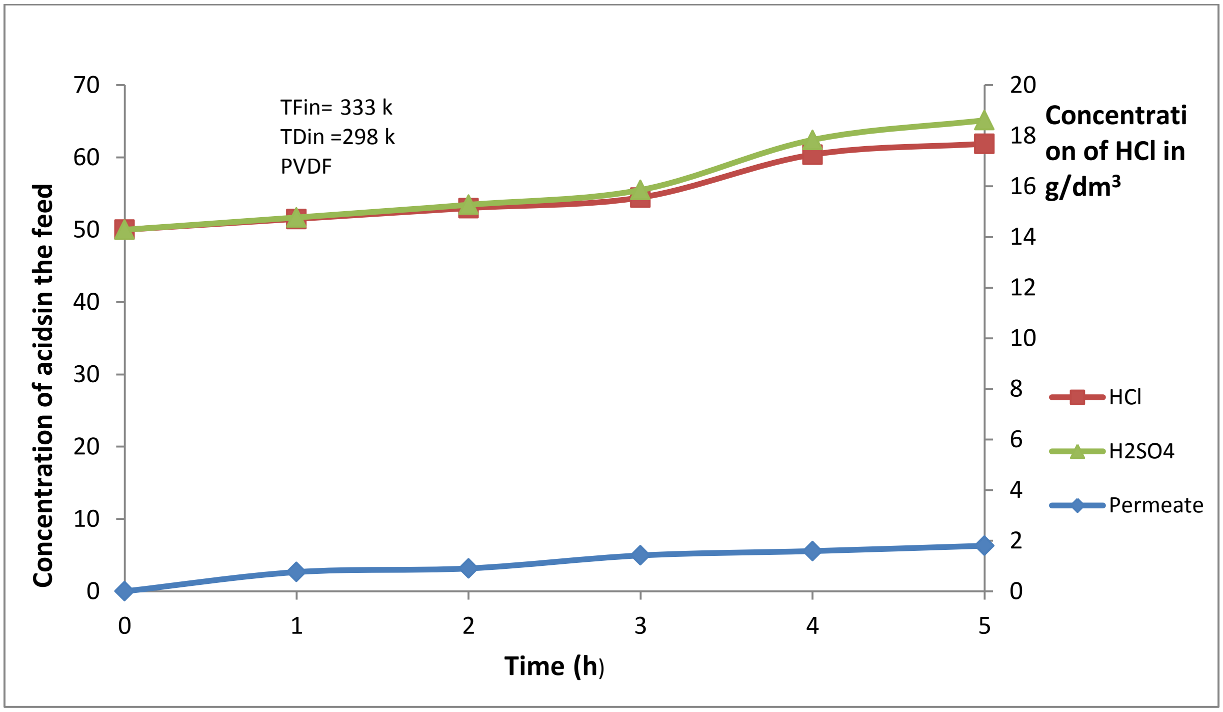


Figure 2. Gradual concentration of HCl /H_2SO_4 model solution by MD at feed temperature 333k, CHCl /CH_2SO_4= 50/50 g/dm^3.

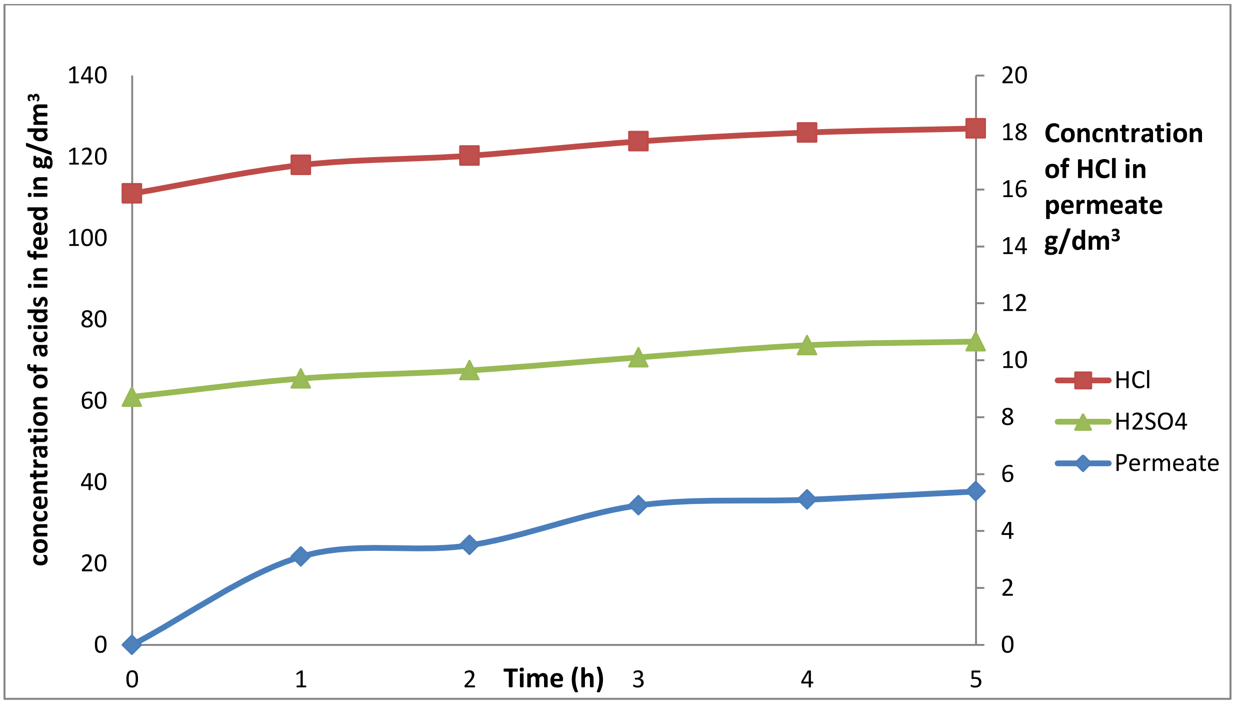


Figure 3. Gradual concentration of HCl/H_2SO_4 model solution by MD at feed temperature 333k, CHCl /C H_2SO_4= 111/61 g/dm^3.

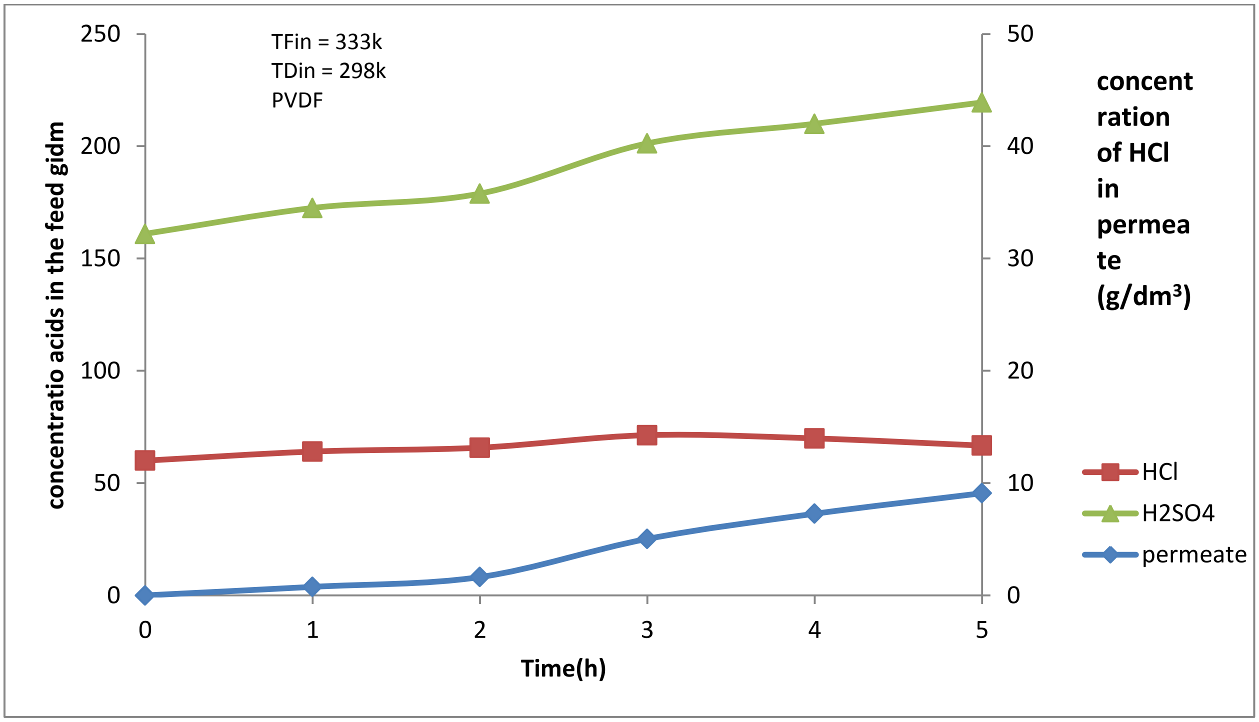


Figure 4. Gradual concentration of HCl/ H_2SO_4 model solution by MD at feed temperature 333 K, CHCl /C H_2SO_4= 60/161 g/dm^3.

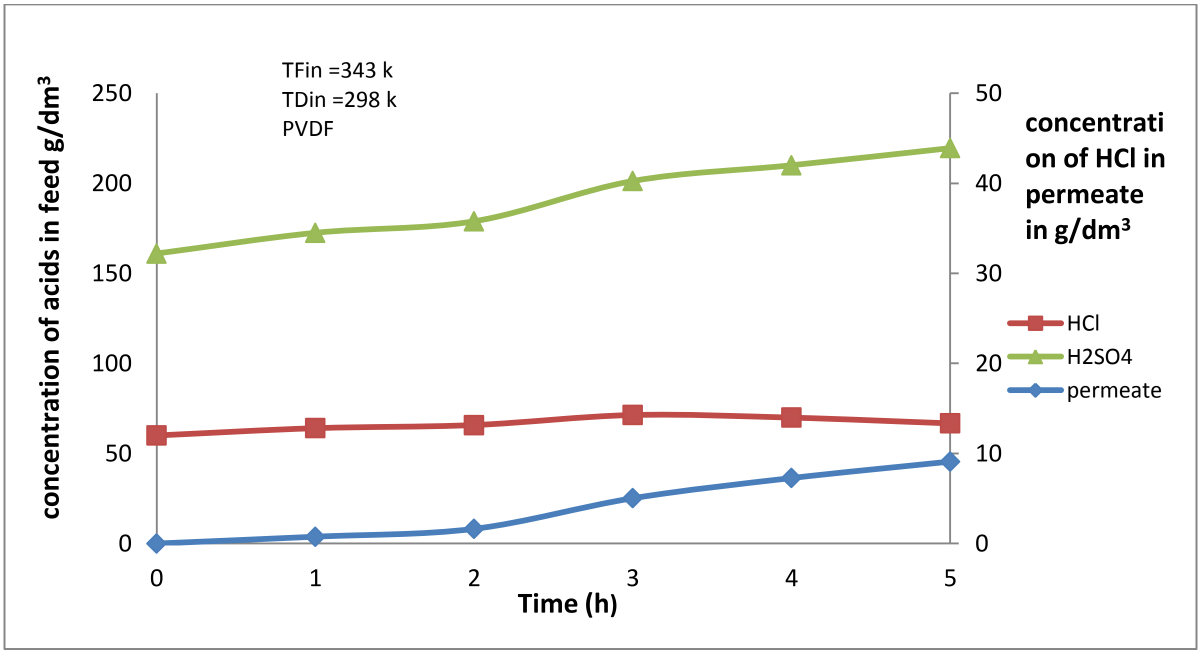


Figure 5. Gradual concentration of HCl/H_2SO_4 model solution by MD at feed temperature 343K, C HCl/C H_2SO_4 = 60/161 g/dm^3.

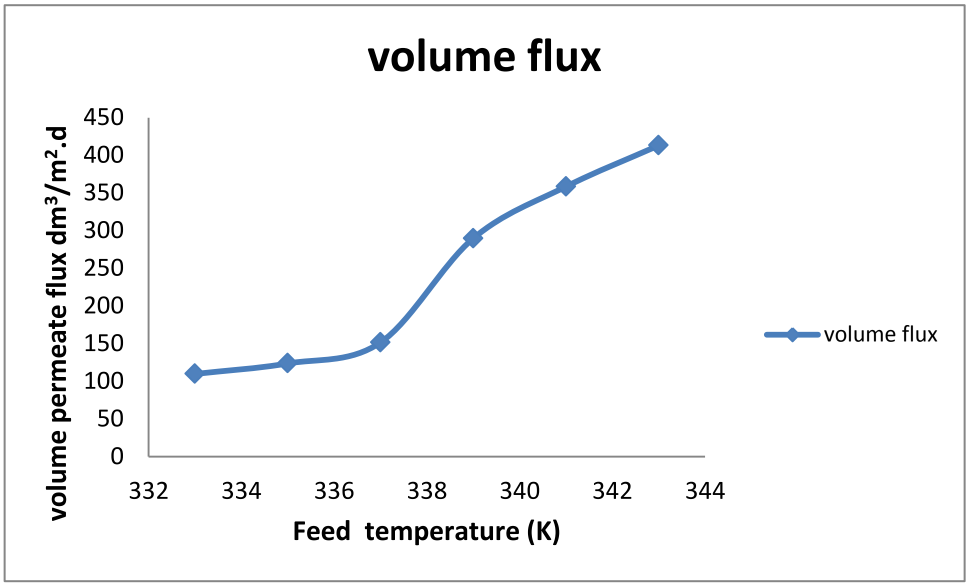


Figure 6. The effect of temperature on volume permeate flux at a feed concentration C HCl/ C H_2SO_4 = 111/61 g/dm^3.

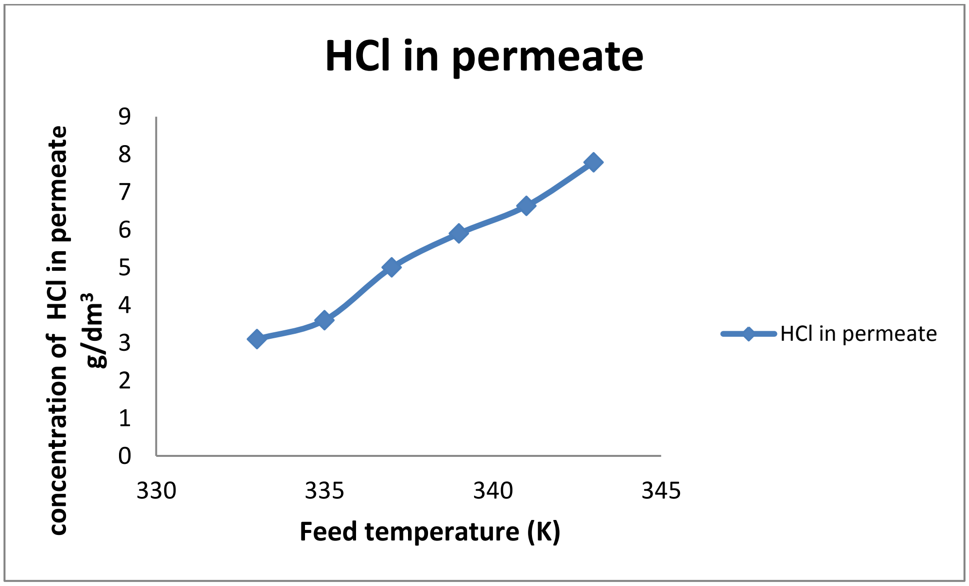
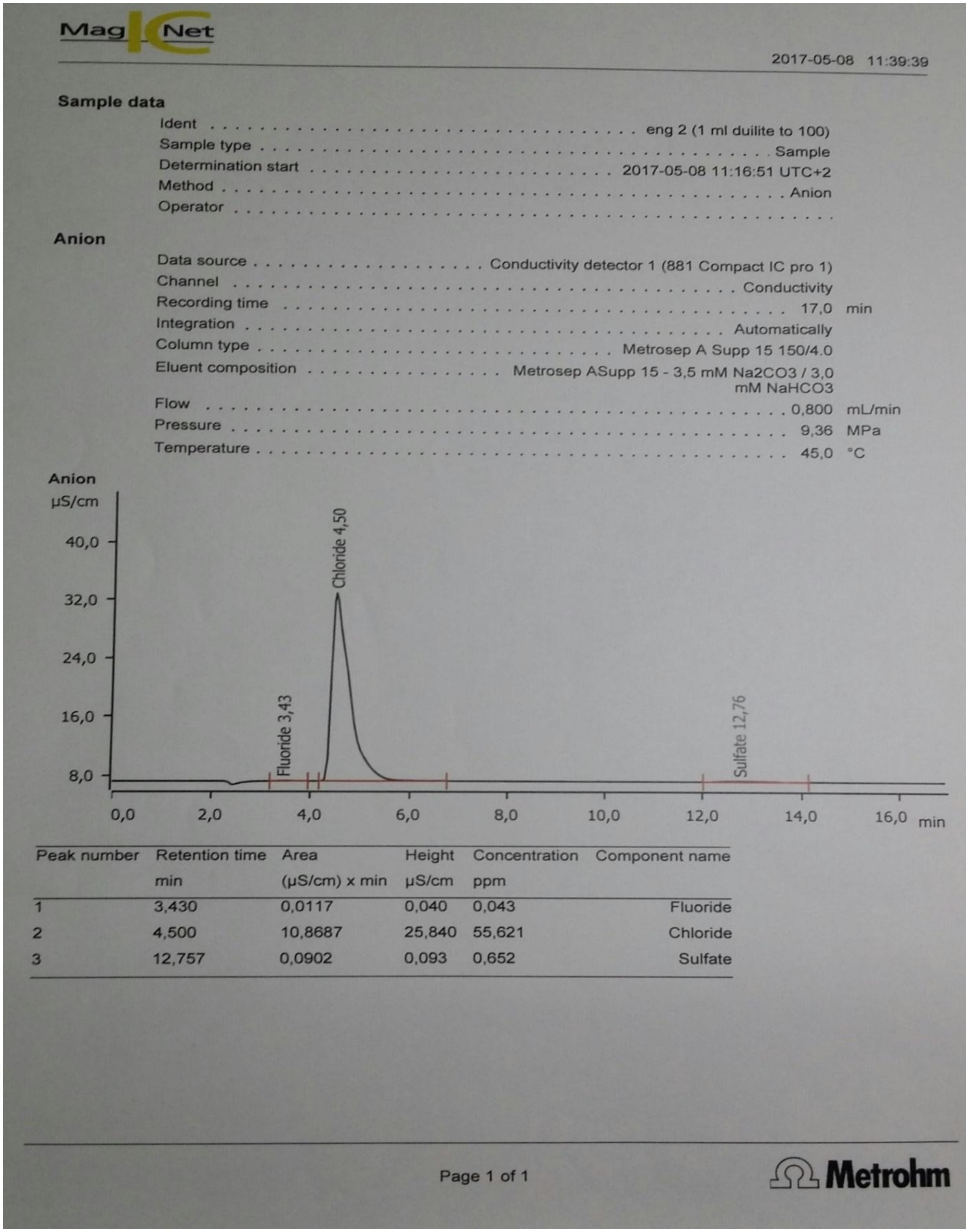


Figure 7. The effect of temperature on HCl concentration in the permeate at a feed concentration of C HCl/C H_2SO_4 = 111/61 g/dm^3.



MagIC Net

2017-05-08 11:39:39

Sample data

Ident . . . . eng 2 (1 ml duilite to 100)
Sample type . . . . Sample
Determination start . . . . 2017-05-08 11:16:51 UTC+2
Method . . . . Anion
Operator . . . .

Anion

Data source . . . . Conductivity detector 1 (881 Compact IC pro 1)
Channel . . . . Conductivity
Recording time . . . . 17,0 min
Integration . . . . Automatically
Column type . . . . Metrosep A Supp 15 150/4.0
Eluent composition . . . . Metrosep ASupp 15 - 3,5 mM Na2CO3 / 3,0 mM NaHCO3
Flow . . . . 0,800 mL/min
Pressure . . . . 9,36 MPa
Temperature . . . . 45,0 °C

Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	3,430	0,0117	0,040	0,043	Fluoride
2	4,500	10,8687	25,840	55,621	Chloride
3	12,757	0,0902	0,093	0,652	Sulfate

Page 1 of 1

Metrohm

Figure 8. The ionic content test of the permeate at a feed concentration of 50 /50 g/dm^3**.**