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Treatment of waste water from metal working by ultrafiltration, considering the effects of operating conditions

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Abstract

In this study the effects of operating parameters on the ultrafiltration of metal working fluids were considered and the optimum conditions for filtration were estimated. In order to reduce the number of experiments an experimental design method (Taguchi) was applied. Seven parameters including pH, oil concentration, temperature, salt (NaCl, $CaCl_2$), feed velocity, and pressure were studied at three levels (low, medium, and high). The oil was water soluble cutting oil and the membrane was an ultrafiltration membrane (C100F) which was supplied by the NADIR Company. The filtration was done at total recycle conditions.

During the experiment samples from feed and permeate were collected in order to measure the retention of oil, the zeta potential, and the oil drop size.

The obtained results showed a flux increase with increasing pH. The highest flux was achieved at alkaline conditions but the highest retention was observed when the pH was acidic (lower limit in experiment). It was also observed that the zeta potential was mostly affected by pH and $CaCl_2$. The biggest zeta potential resulted in the lowest permeate flux. The drop size measurement showed that a bigger drop size usually gave a higher flux. The effect (increase in flux) of salt addition implied that at acidic conditions the effect was smaller than at alkaline conditions. As a conclusion, an alkaline pH, a high pressure, a high temperature and a low amount of $CaCl_2$ gave the optimum conditions.

Keywords: Metal working fluid; Experimental design; Salt; Flux

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1. Introduction

Finishing, rolling and cutting operations in metal working industries usually consume oil or water soluble lubricant for cooling and/or removing metal from the surface. During the application, these emulsions that undergo thermal degradation or become contaminated thus need to be periodically replaced. The produced effluent contains different substances like oil, surfactant, corrosion inhibitor, and biocide which are hazardous and toxic for the environment and must be treated before disposal. The methods used in the treatment of MWF (metal working fluid) waste effluent are based on the separation of the oily phase from the aqueous phase and then treating each phase independently [1–3]. Traditional treatment methods require high energy consumption or the application of a variety of chemicals, which decreases the efficiency and increases the costs of the process. Moreover, the presence of some substances like biocides makes the effluents difficult to treat with normal biological waste water treatments. It has been found that membranes are a good option to overcome this problem. Nevertheless, the application of membranes involves two hurdles to overcome; concentration polarisation and membrane fouling. Both phenomena result in decreasing permeate flux what significantly influences the capital and operational costs of membrane systems. That is why there is a great concern to find the methods, which mitigate concentration polarisation and fouling.

Control of the process conditions seems to be the easiest way of influencing filtration performance and thus preventing conditions resulting in flux decline. It has been proven that there is a strong dependency between transmembrane pressure and flux decline [4]. It has also been shown that this dependency is quite complex and other factors including the feed velocity [4] as well as the feed concentration [2], pH [5] and the type of membrane process [2,3] have to be taken into consideration. Still, adjusting the operating conditions can be limited by the applied equipment and costs involved, and that is why more and more research is being done on the modifications of the feed, which could enhance the performance of the filtration.

Adding salt to the feed which results in a destabilisation of the emulsion is one of the methods to modify the feed. It was proven that adding $CaCl_2$ significantly influences the flux decline [1,2,4]. Although, several researches [1,2,4,6] have been done applying MF, UF and NF with the combination of a coagulation/flocculation step there is still a lack of information on the influences of salt at different conditions.

The objective of this study was to estimate the best operational conditions in ultrafiltration of wastewater from metal working fluids. The conditions taken into consideration included transmembrane pressure, feed velocity, temperature and pH of the feed. Moreover, the influence of different salt concentrations on the performance of the process was examined. Different combinations of sodium chloride and calcium chloride concentrations were applied.

2. Materials and methods

2.1. Materials

The membrane used in the experiments was a flat sheet regenerated cellulose membrane (C100F) with a cut off of 100 kg/mol and a surface area of 44 cm^2, provided by NADIR Gmbh.

The emulsions prepared were based on cutting oil (saBesto cut + cool, Würth). The other chemicals were NaOH, HCl (37 w/w%) and sodium chloride (analytical grade, 95%), which were purchased from Merck and calcium chloride-2-hydrate (95%) from Riedel-de Haën.

2.2. Preparation of the feed

The feed used in the experiment was based on the cutting oil above. The prepared emulsions differed in their salt concentrations — a combination of 0, 0.1 and 0.5 g/L of the two mentioned salts was used. The emulsions differed in pH as well — alkaline conditions were achieved by adding NaOH whereas neutral and acid conditions were gained by adding HCl. In each case the starting point for adjusting the pH was in the range of 9.0–9.5. Different oil concentrations were used, 0.5, 1.5 and 3.0 v/v%. The total volume of the feed was 5.5 L.

2.3. Filtration

Different operating conditions were applied including different pressures (0.5, 1.5 and 3.5 bar), flow velocities (2.6, 2.9 and 3.3 m/s), as well as temperatures (25, 35 and 40°C). In order to have a constant concentration permeate was returned to the feed tank. Fig. 1 shows a schematic presentation of the filtration equipment. The filtration was run each time for 30 min and after this time samples of the permeate were collected to measure the total organic carbon (TOC), the zeta potential of the emulsion droplets and the amounts of the salts. The samples of the feed were collected before filtration and after 25 min of filtration. The amount of calcium and sodium were measured using atomic adsorption (GBC 932AA, Shimadzu). The zeta potential was measured by a Delsa 440 device. TOC was measured using the TOC-meter, model 5050A, Shimadzu.

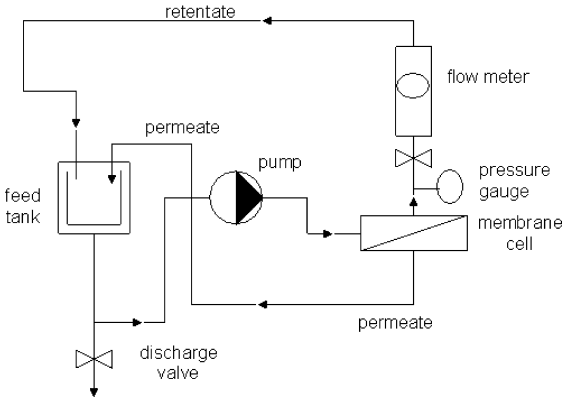

Fig. 1. A schematic presentation of the filtration equipment.

After filtration the membrane was flushed for 10 min at a pressure of 1.5 bar and at moderate flow velocity with distilled water. Then distilled water was filtered for 30 min at 1.5 bar and after that the water flux was measured. If the flux was below a preset value (345 L/(m^2 h)) a cleaning was undertaken.

2.4. Cleaning procedure

Cleaning was done using an alkaline cleaning solution (Ultrasil 110, Henkel). The cleaning solution was heated to 40°C, then the filtration was run for 45 min at a pressure of 0.5 bar and using a moderate flow velocity.

The whole system was flushed after filtration with distilled water. Verification of the cleaning procedure was done by comparing the water flux after filtration with the initial water flux at similar conditions.

3. Results and discussion

The set of experiments consisted of 18 trials and was designed using the Taguchi approach. The Taguchi method provides the possibility to consider systematically and simultaneously the effects of multiple variables on the response with a proper number of experiments. The method is based on the new definition of quality which was introduced by Taguchi; the best quality will be achieved when the variation around the target is minimised. In statistical form for a set of experiments with multiple factors the response quality is expressed as the ratio of the desired factor (signal) compared to uncountable factors (noise) [7]. There are a few programs which can

Table 1
Experimental set, factor levels and the corresponding *S/N* (signal/noise)

Trial/factors	A[a]	B[a]	C[a]	D[a]	E[a]	F[a]	G[a]	H[b]	I[b]	*S/N*
1	5	0.5	25	0.5	2.6	0	0	100	100	40.0
2	5	1.5	35	1.5	2.9	0.1	0.1	185	149	44.3
3	5	3	40	3.5	3.3	0.5	0.5	153	150	43.6
4	7	0.5	25	1.5	2.9	0.5	0.5	129	125	42.1
5	7	1.5	35	3.5	3.3	0	0	213	236	46.9
6	7	3	40	0.5	2.6	0.1	0.1	83	78	38.1
7	11	0.5	35	0.5	3.3	0.1	0.5	214	278	47.6
8	11	1.5	40	1.5	2.6	0.5	0	190	209	45.9
9	11	3	25	3.5	2.9	0	0.1	190	191	45.6
10	5	0.5	40	3.5	2.9	0.1	0	186	223	46.1
11	5	1.5	25	0.5	3.3	0.5	0.1	84	100	39.2
12	5	3	35	1.5	2.6	0	0.5	70	108	38.9
13	7	0.5	35	3.5	2.6	0.5	0.1	106	130	41.4
14	7	1.5	40	0.5	2.9	0	0.5	125	128	42.0
15	7	3	25	1.5	3.3	0.1	0	111	140	41.8
16	11	0.5	40	1.5	3.3	0	0.1	388	388	51.8
17	11	1.5	25	3.5	2.6	0.1	0.5	200	203	46.1
18	11	3	35	0.5	2.9	0.5	0	146	157	43.6

[a] Factors: A: pH, B: oil concentration (v/v%), C: temperature (°C), D: pressure (bar), E: flow velocity (m/s), F: $CaCl_2$ concentration (g/L), G: NaCl concentration (g/L).

[b] Response: H and I: Flux, L/(m^2 h), H and I are repetition experiments.

be used to calculate this ratio (*S/N*) and do the relevant analysis. In this study the design of experiments and the analysis was done using Qualitek-4 software (version 4.7). "The larger — the better" criteria were chosen for *S/N*.

Table 1 shows information about the experimental set including factor levels, the consequent response (here permeate flux), and the corresponding *S/N* ratio for each trial. The aim of the experiment was to maximise the *S/N*, and the following equation was used to calculate this ratio for a trial:

$$S/N = -10\log_{10}\left(\frac{1}{\mathrm{MSD}}\right) \tag{1}$$

where, MSD is the mean square deviation.

The calculated ratio shows the influences of each trial on the response.

As can be seen from Table 1, the biggest value of *S/N* was achieved for trial 16 where pH was in the alkaline range, oil at the lowest level, and there was no $CaCl_2$.

The *S/N* is also expressed for a factor. It indicates the effect of each factor on the response independently. It is calculated by averaging the *S/N* at different levels. For example for the first factor (pH) in Table 1, at low level (pH = 5), the *S/N* is equal to the average value of *S/N* for trials where pH is at the low level, i.e. trials 1–3 and 10–12. Similar calculations can be used for the second and the third level of pH. The effects of individual factors are shown in Table 2. Comparing the *S/N* for different factors shows that most of the variation of *S/N* is for pH and pressure.

In Table 2, a negative sign in column 4 and 5 shows that the effect declines while a positive

Table 2
Main effect of factors on *S/N*

Factors	Level 1	Level 2	Level 3	Level 2 – level 1	Level 3 – level 2
pH	41.9	42.1	46.8	0.12	4.69
Oil concentration	44.8	44.1	41.9	–0.72	–2.23
Pressure	42.5	43.7	44.6	1.25	0.89
Temperature	41.8	44.1	44.9	2.32	0.89
Flow velocity	41.7	43.9	45.2	2.29	1.20
$CaCl_2$	44.6	44.0	42.6	–1.5	–1.37
NaCl	44.1	43.4	43.3	–0.69	–0.72

sign means that the effect of the factor increases. In optimum conditions it is desired to have a positive and big value of *S/N*. Thus the best conditions achieved here are when pH is in the alkaline range, and pressure, temperature and flow velocity are at the highest level, and there is no salt in the feed. These conditions are very similar to trial 16.

The influence and relative importance of these factors are quantitatively given by the analysis of variance (ANOVA). The results of ANOVA are listed in Table 3. The row which is marked as Other/error indicates the errors which are caused by uncontrollable factors (noise), that is factors which are not included in the experiment and experimental error. In general, the value should be below 50%, otherwise the results are not reliable. Here, the calculated error is about 11% which is far enough from the limit. It means that almost all effective factors are taken into account and/or the error of the experiment is not significant.

The last column in Table 3, shows the percent contribution of each factor to the response. It is defined as the influence of one factor on the total observed variance in the experiment. A bigger value means that the factor contributes more to the final result. It can be seen that pH has the biggest contribution between the factors.

pH can affect by changing the emulsion properties and/or membrane surface charge. In a previous study [8] it was observed that regenerated

Table 3
Analysis of variance (ANOVA) for flux as response

Factors	DOF[a]	Sum of squares	Variance	*F*-ratio	Pure sum	Percent
pH	2	90.6	45.3	31.1	87.7	40.1
Oil concentration	2	28.4	14.2	9.75	25.5	11.6
Temperature	2	13.8	6.90	4.74	10.9	5.0
Pressure	2	32.8	16.4	11.2	29.9	13.7
Flow velocity	2	37.7	18.9	12.9	34.8	15.9
$CaCl_2$	2	8.37	4.18	2.87	5.4	2.5
NaCl	2	2.14	1.07	0.73	0.0	0.00
Other/error	3	4.37	1.45			11.2
Total	17	218.3				100.0

[a] DOF: Degree of freedom.

cellulose membranes had an almost constant and small negative charge within the studied pH range. Thus the observed variation in the response factor mostly comes from emulsion stability.

Emulsion stability can be explained by the zeta potential. A more negative value gives an emulsion with a higher stability. The influence and importance of pH, salt and operating conditions on the stability of the emulsion were examined by analysis of variance (Fig. 2). It was revealed that the most important factors were pH and $CaCl_2$ concentration.

In general, an increase in pH results in a more negative zeta potential. For example the measured zeta potential for cutting oil in this study at acidic conditions (pH = 5) was about −50 mV, while when the pH was increased to 7, it changed to −70 mV. Thus it can be said that the emulsion was more stable at pH = 7.

The stabilisation of emulsions by pH is a complex process. Adding NaOH which contains both a cation and an anion changes the charge of the oil drops. It seems that Na^+ acts as a bridge between drops and causes that the negative drops coalesce and a bigger drop forms. Drop size measurements showed that at higher pH the oil drop size increases (Fig. 3, trials 7–9 and 17, 18). The formation of a bigger drop reduces the free energy and thus the emulsion becomes more stable.

At acidic conditions the mixture contains H^+ ions. The attraction between the protons and the negative charge on the surface of drops can take place and consequently the drops could coalesce [9] but the drop size measurement shows a lack of bigger drops. It seems that the forces between the drops are not big enough to enlarge them, and therefore, repulsion forces by anions keep them far from each other.

The effect of salt may be explained by the DLVO theory [10,11]. According to this theory when salt is added to an emulsion the electrostatic interaction will be greater than the Van der Waals repulsion force and then the drops can attach. However, the interaction is influenced by the type of salt and the valance of the cations and the anions. For example, as can be seen in Fig. 2, the contribution of NaCl being a mono valent cation is about one third of the contribution from $CaCl_2$ with a double valency.

The optimum conditions are given by ANOVA. These conditions are determined according to the significances of the factors. This is expressed by the F-ratio which is defined as the ratio of variance due to the effect of a special factor on the variance compared to the error term. It means

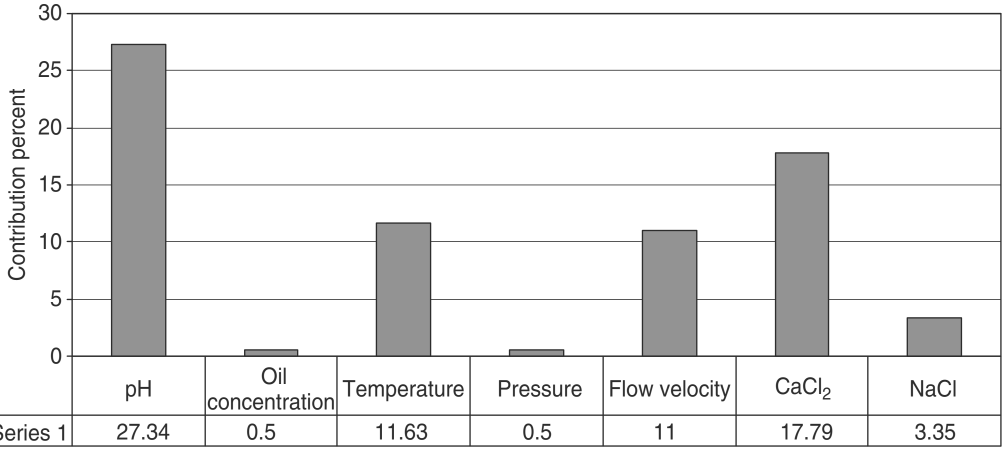

Fig. 2. Contribution percent of factors on zeta potential of emulsion.

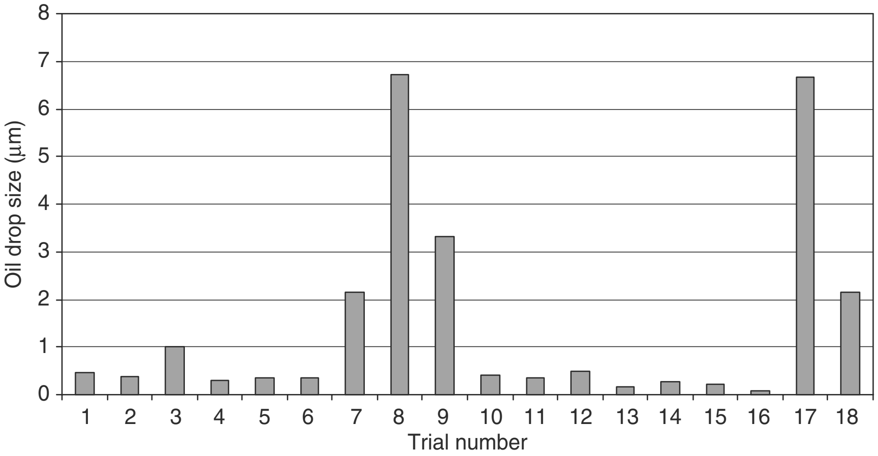

Fig. 3. Variation of oil drop size versus trial number (see Table 1).

that the factors with an F-ratio less than one have no significant effect compared to the error. In Table 3, the F-ratio for NaCl is less than 1, therefore, it was neglected.

Table 4 shows the optimum conditions. Since these conditions are not belonging to the trials which were presented in Table 1, a confirmation experiment should be done to verify the predicted results. If the average results (S/N) of this experiment is within the confidence limit then the prediction is acceptable. It was observed with the confidence limit 90% that the average of the measured permeate flux was within the range of flux which was predicted by the Taguchi approach. Table 4 indicates that the highest flux will be achieved when pH, temperature and flow velocity are at maximum level (highest value), the oil concentration is low and there are no salts in the solution.

It was mentioned above that the pH affects the response by changing the emulsion stability and it seems that in comparison with the effect on the membrane surface charge this effect is the dominant. However, adding salt influences emulsion stability but salt can also induce interaction between the surface of the membrane, which has a negative charge, and with the drops. This interaction causes a formation of an oil layer on the surface. The consequence of the formation of this layer is a decline in permeate flux.

Table 4
Optimal conditions according to ANOVA

	Factors	Level description	Level	Contribution
1	pH	11	3	3.17
2	Oil concentration	0.5 (V%)	1	1.22
3	Temperature	40 (°C)	3	1.00
3	Pressure	3.5 (bar)	3	1.36
4	Flow velocity	3.3 (m/s)	3	1.56
5	$CaCl_2$	0 (g/L)	1	0.55

Comparing the resistance of the membrane after filtration in each experiment (Fig. 4) as an evidence for the formation of a fouling layer, reveals that at acidic conditions fouling is very serious, i.e. fouling is facilitated by a low pH (trial 1–3 and 10–12).

As can be seen from Table 4, one of the predicted ways to get an optimum performance is to set the oil concentration at a low level. Reducing the amount of oil has a significant effect on concentration polarisation. The rejections of oil which were calculated by measuring the concentration of oil in feed and permeate was about 85%, it means that a small portion of oil can pass through the membrane and the rest will be retained by the membrane. Retention of oil causes that oil accumulates close to the surface and hence the resistance against the permeate flow increases (Fig. 4).

Moreover, the resistance is also affected by other operating conditions such as pressure and flow velocity. A high pressure can accelerate concentration polarisation. Increasing the pressure causes the bulk flow towards the membrane to get bigger than the back diffusion from the surface. But as can be seen in Fig. 5, which shows the estimated effect of factors at different pH, the flux up to 3.5 bar is still depending on pressure. However, the smaller increase in flux when pressure changes from 1.5 to 3.5 bar than from 0.5 to 1.5 bar, indicates that at even higher pressures flux will be independent of pressure.

Another operating condition which can affect concentration polarisation is the flow velocity. In order to get the highest flux it was predicted that the highest level of the velocity should be used. In a normal flow channel a high tangential flow increases turbulence close to the membrane surface which mitigates the formation of concentration polarisation. In a thin channel, such as the one used in this study, the flow is at a maximum in the transient region (Reynolds number varied between 2500 and 3000) and the velocity affects the flux by increasing the shear tension on the surface. The produced tension removes the oil from the surface and reduces the thickness of the oil layer. As can be seen in Fig. 5, flux improves with flow velocity. The bigger effect at high pH can be attributed to the bigger size of the oil drops which makes them easier to remove from the surface. The tangential force of the shear force is not big enough to overcome the Laplace pressure of the oil drops, and thus it can be said that the rupture of the oil drops and the formation of smaller drops is minimised.

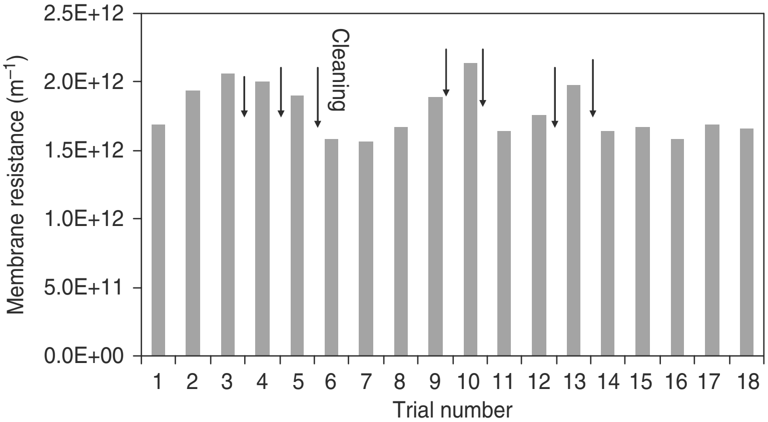

Fig. 4. The resistance of the membrane after filtration and after washing with water versus trial number. Arrows indicate cleaning with detergent.

Improving flux by increasing temperature is related to the decrease in the viscosity as well as in the possibility of the formation of bigger drops by accelerating the collision frequency between oil drops. The variation of flux with temperature is shown in Fig. 5.

One of the interesting points with the optimum conditions is that the optimum is achieved when no salt is in the mixture. The predicted condition is different from what was reported by Belkacem et al. [4]. They observed that adding a very low amount of $CaCl_2$ could improve the flux by reducing fouling. As can be seen in Fig. 5 adding salt up to 0.1 g/L has no effect on flux and a further increase results in a decline in flux. It seems that $CaCl_2$ has a positive effect when a proper ratio of salt per oil is used. The amount of oil which was used in this set of experiments was 50 times more than the concentration of salts. Therefore, there was not enough NaCl salt in the mixture to attach to all the drops and make bigger drops, or $CaCl_2$ was below its coagulation concentration and thus had no positive effect on flux. The current amount of salt just changed the zeta potential and the drop size and made the emulsion more unstable compared with the state where no salt was used.

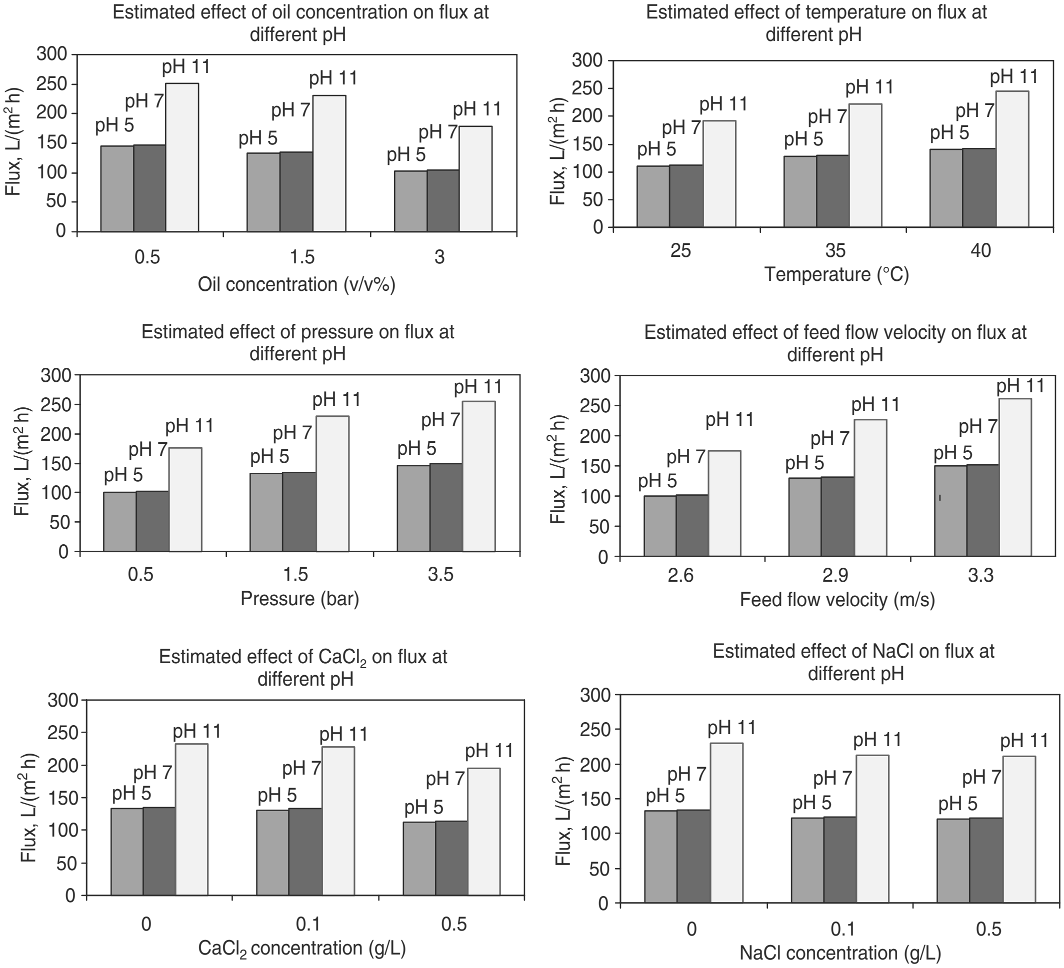

Fig. 5. Variation of flux at different pH and operating conditions.

Comparing permeate flux shows that most of the variation in flux due to NaCl can be seen when a low amount of salt was added (flux changed upon 0.1 g/L of NaCl and after that it was almost constant). This behaviour was different from what was observed for $CaCl_2$ (flux did not change upon addition of 0.5 g/L of salt) It seems that some interactions between NaCl and other substances of cutting oil occurred which make the response different from what is reported in the literature. Further studies should be made to recognise these reactions.

4. Conclusion

Considering different factors having influence on ultrafiltration in filtration of metal working fluids showed that the pH had the biggest influence. The effect of pH was attributed to the stability of the emulsion. The stability increased with pH. The oil drop size measurement showed that at higher pH the drops were bigger and, therefore, the free energy was lower and the emulsion became more stable.

When salt was added to the emulsion the zeta potential changed and the emulsion became more unstable. The effect of salt was very clear at low pH where flux remarkably decreased. The decline in flux could be attributed to the formation of an oil layer on the surface. The water flux after filtration confirmed that at acidic pH the fouling resistance increased significantly.

The best conditions which were predicted to get the highest flux are pH, pressure, temperature and flow velocity at the highest level and salts and oil at the lowest level.

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