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Colour and Chloride Removal from Pulp Mill Effluent Using Ion-Exchange

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Giyeon Yun and Ian D. Buchanan

For copies of this or other SFM publications contact:

Sustainable Forest Management Network
G208 Biological Sciences Building
University of Alberta
Edmonton, Alberta, T6G 2E9
Ph: (780) 492 6659
Fax: (780) 492 8160
http://www.ualberta.ca/sfm

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Colour and Chloride Removal from Pulp Mill Effluent Using Ion-Exchange

SFM Network Project: Colour Removal from Kraft Mill Waters by Ion Exchange

by

Giyeon Yun and Ian D. Buchanan

Civil and Environmental Engineering

University of Alberta, Edmonton

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ABSTRACT

Pulp and paper mills face stringent effluent discharge regulations and have acknowledged that it is necessary to look into innovative technologies to recycle considerable amount of effluent rather than discharging into surface water. The pulp and paper industry has made efforts to reduce pollutants in effluents from mills and to approach zero effluent discharge.

Coloured effluents from mills give rise to aesthetic unpleasantness. To cope with more stringent effluent discharge regulations and to protect the ecosystem from harmful pollutants in the mill effluents, ion exchange was investigated on a bench scale to reduce colour and chloride in pulp mill effluents. Chloride is one of the non-process elements (NPE) in the mill systems, which are known to be harmful elements in pulping. Chloride was selected as surrogate measure of other NPEs.

The nine resins tested are weak basic anionic (WBA) resins including Amberlite® IRA67 and IRA92, and strong basic anionic (SBA) resins including Amberlite® IRA400, IRA402, IRA458, IRA900, IRA958, IRN78, and Amberjet® 4400OH. Batch testing has been conducted to select effective ion-exchange resins for colour and chloride removal and to determine effective regenerants for regeneration of exhausted resins.

The results from batch and column tests on decolourisation indicate that IRA958 has the potential to completely remove colour in the effluents. IRA458 and IRA900 also successfully removed colour. 1 *N* NaOH in combination with 1 *N* NaCl was found to regenerate the resins effectively to recover their original colour removal efficiency. The results of this study indicate that ion exchange technology may be applied to decolourise pulp mill effluents and aid in the drive toward progressive system closure.

IRN78 and 4400OH, which hold hydroxide ions as exchange groups, removed chloride in a modest removal efficiency up to 65%. Although this removal efficiency may not be sufficient, it implies a very important point that other NPEs, having higher affinity to the anionic resins than chloride, might be removed to greater degrees than was chloride. Regeneration of exhausted resins after chloride removal, using NaOH has been studied. However, it could not return the resins to their original chloride removal efficiencies.

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I would like to share the gladness with my husband, Jeongsik Jeong. Especially, I would like to return the glory to my parents, Kapju Yun and Euneam Won who enabled me to study in Canada and my siblings, Jihae Yun and Heonsuk Yun. I really want to express how deep I thank my true friends for their love and help. I thank the God who made it possible to achieve the Master's degree.

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INTRODUCTION

The pulp and paper industry accounts for more contaminant discharge (on a mass basis) than any other industrial sector in North America (EPA, 1995). Discharge requirements are becoming increasingly stringent in an attempt to reduce the impact of these effluents on the environment. In response, the industry has instituted several process modifications to reduce the contaminant loading in their effluent streams. Of these contaminants, colour has proven to be particularly difficult to remove in a cost efficient manner. The colour in pulp mill effluent is caused by lignin and its derivatives that are separated from the wood fibres during the pulping process. Among other effects, this colour gives rise to aesthetic unpleasantness when it is discharged into the receiving water. If this water is used as a drinking water source, the colour causing compounds also result in an increased chlorine demand during the disinfection process of water treatment plants.

Pulp mills are also major users of fresh water. The industry has sought to reduce its fresh water requirements in recent years by increasing the amount of process water recycled internally. This effort is termed progressive plant closure, with the goal being to attain a zero liquid effluent status. The main obstacle to recycling large amounts of process waters in kraft pulp mills is the build-up of dissolved non-process elements (NPE) in the recycled water that adversely affect the pulp quality and process infrastructure.

Of these NPEs, chloride and potassium ions are the most difficult to remove from waste streams. Their build-up is known to cause clogging and corrosion in the chemical recovery system of pulp mills (Jemma *et al.*, 1997; Melanson, 2000). These problems would force a mill to shut down several times a year to remove the deposits and flush the systems.

The most widely used treatment method for pulp mill effluent entails biological treatment followed by solids separation by sedimentation. This approach is very efficient for the removal of readily biodegradable organics and suspended solids, but has little effect on dissolved NPEs and colour. Therefore, more advanced technologies are needed to deal with these contaminants. Among the diverse removal technologies proposed for this purpose, advanced treatment using ion exchange resins offers an attractive alternative to remove both colour and other NPE to facilitate progressive plant closure.

The potential benefits of applying ion exchange technology to treat pulp mill effluents include:

- Selective removal of cations and anions;
- Regeneration and re-use of exhausted resins;
- Facilitation of progressive system closure in the mills; and
- Prevention of the corrosion of chemical recovery system.

Objectives

The objective of this study is to assess the ability of selected ion exchange resins to remove colour and chloride from pulp mill effluents as a step toward progressive system closure. The scope of the investigation includes:

- Determination of effective resins for colour removal;
- Determination of effective resins for chloride removal;
- Determination of effective regenerant for exhausted resins after colour removal;
- Determination of effective regenerant for exhausted resins after chloride removal;
- Verification of the results from batch testing in column testing via breakthrough and elution studies; and
- Determination of the optimal point within the mill to apply the treatment technology.

RESULTS AND DISCUSSION

Sample characterisation

Samples of kraft pulp mill effluent examined in this study were obtained from Weyerhaeuser Canada Ltd. in Grande Prairie, Alberta, Canada that uses no colour reduction technology except peroxide addition when high colour loadings occur. Samples were collected from the following locations within the plant:

(1) Influent to aerated lagoon;
(2) Effluent from aerated lagoon;
(3) Acidic sewer from the bleach plant; and
(4) Caustic sewer from the bleach plant.

The bleach plant operates with 100% chlorine dioxide bleaching (ECF bleaching). Samples were stored at 5°C.

The sample characterisation with respect to colour (TCU), chloride concentration (ppm), and pH is summarized in Table 3-2.

Table 1-2 Sample Characterisation

	Colour (TCU)	Cl^- (ppm)	pH
Lagoon influent	890-930	250	7.4
D stage effluent	2710	740	2.3
E_{op} stage effluent	2670	300	11.4
Blended bleach wastewater	1200	190	6.5
Final effluent	920-1330	200-290	7.9

D stage effluent (acidic) is produced from the brightening stage in which ClO_2 is the main chemical used. The pH value of the D stage effluent was very low at 2.3. On the other hand, E_{op} stage effluent (alkali) was collected from an extraction stage in the mill. The pH value of the E_{op} stage effluent was very high at 11.4. The chloride concentration of the D stage effluent was twice that of the E_{op} stage effluent while the colour concentration of the D stage effluent was comparable to the E_{op} stage effluent.

The flows of the acidic and alkali sewers are blended and mixed with wastewater from the wash stages and the flow from the general (sanitary) sewer before being introduced to an aerated lagoon. Therefore, it can be reasoned that the components in the lagoon influent are from the D and E_{op} stage effluents diluted by the many washing steps and general sewage prior to the biological treatment. Consequently colour and chloride concentrations of lagoon influent are much less than those of the D or E_{op} stage effluent. The pH values of both lagoon influent and final effluent are close to neutral. Aerated lagoon biological treatment is not able to remove colour other than by adsorption to floc particles. The differences in colour and chloride concentration may be caused by variation of sampling.

Colour Removal Batch Testing

Decolourisation with Different Resins

This testing was conducted to determine the effect of resin type and dose on colour removal. Colour removal from three types of samples including lagoon influent, D stage (acidic sewer) effluent, and E_{op} extraction stage (alkali sewer) effluent, was investigated using resin doses of 2, 10, and 30 g/L. The results of the colour removal tests for each effluent resin type and dose are shown in Figures 2-1, 2-2, and 2-3. No colour removal was observed in control vials containing effluent and no resin. Removal efficiency was calculated by equation (2-1).

$$\eta = \frac{C_o - C_e}{C_o} \times 100(\%) \qquad (2\text{-}1)$$

where:

η : Removal efficiency (%),

C_0 : Initial colour concentration in an effluent, and

C_e : Residual colour concentration after ion exchange.

Figure 2-1 illustrates that IRA958 treating lagoon influent showed approximately 97% colour removal at a resin dose of 2 g/L. IRA900 removed almost all of colour at 30 g/L. IRN67 also reached 90 % of colour removal at 10 g/L and IRA92 removed 85% at 30 g/L. IRN78, IRA400 and 4400OH removed less than 50% of initial colour concentration of lagoon influent at the highest resin dose of 30 g/L tested. IRA402 showed modest colour removal of around 60% from the lagoon influent at 2 g/L.

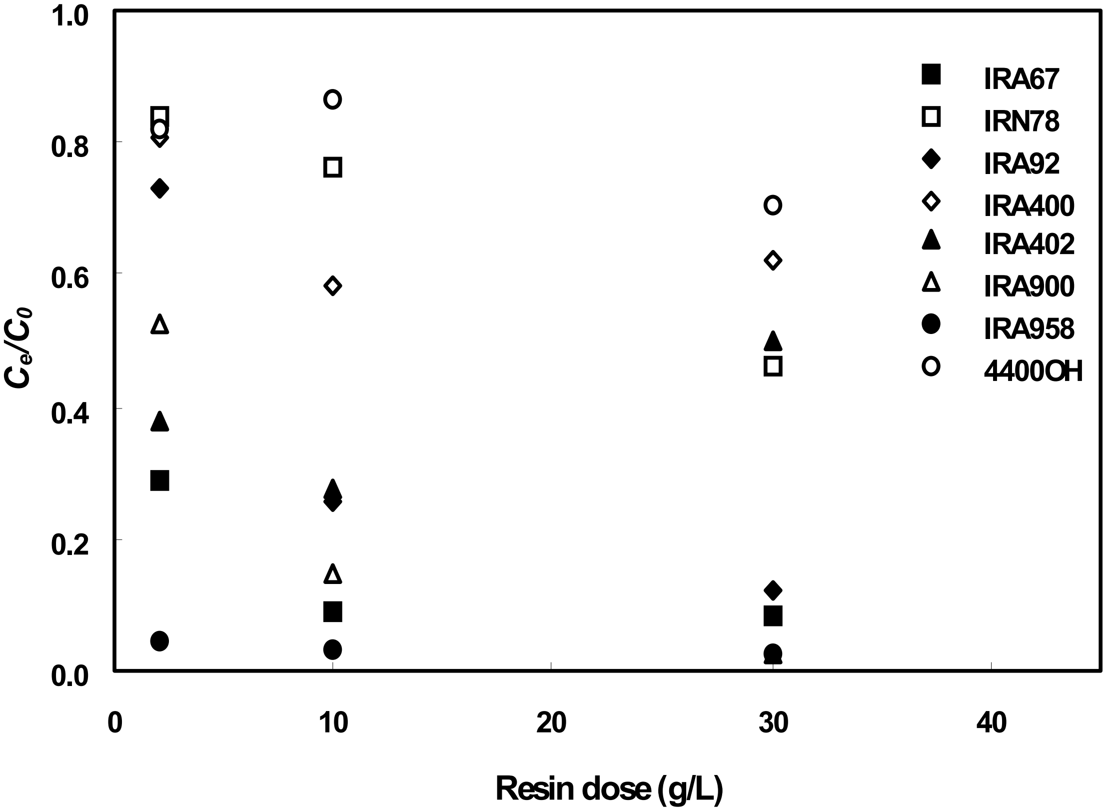

Figure 2-1 Decolourisation of lagoon influent by eight anionic resins (20°C, C_0 : 890 - 910 TCU, pH : 7.5 - 7.8, Contact time : 1 day)

Figure 2-2 shows that IRA958 achieved modest colour removal efficiency. IRA67, IRA92 and IRA900 showed better performance of colour removal than the others in treating the D stage effluent. As indicated in Figure 2-2, IRA400 and 4400OH did not have a good performance in removing colour from the D stage effluent. Removal with IRN78 and IRA402 improved with increasing resin dose but was not sufficient within the tested range.

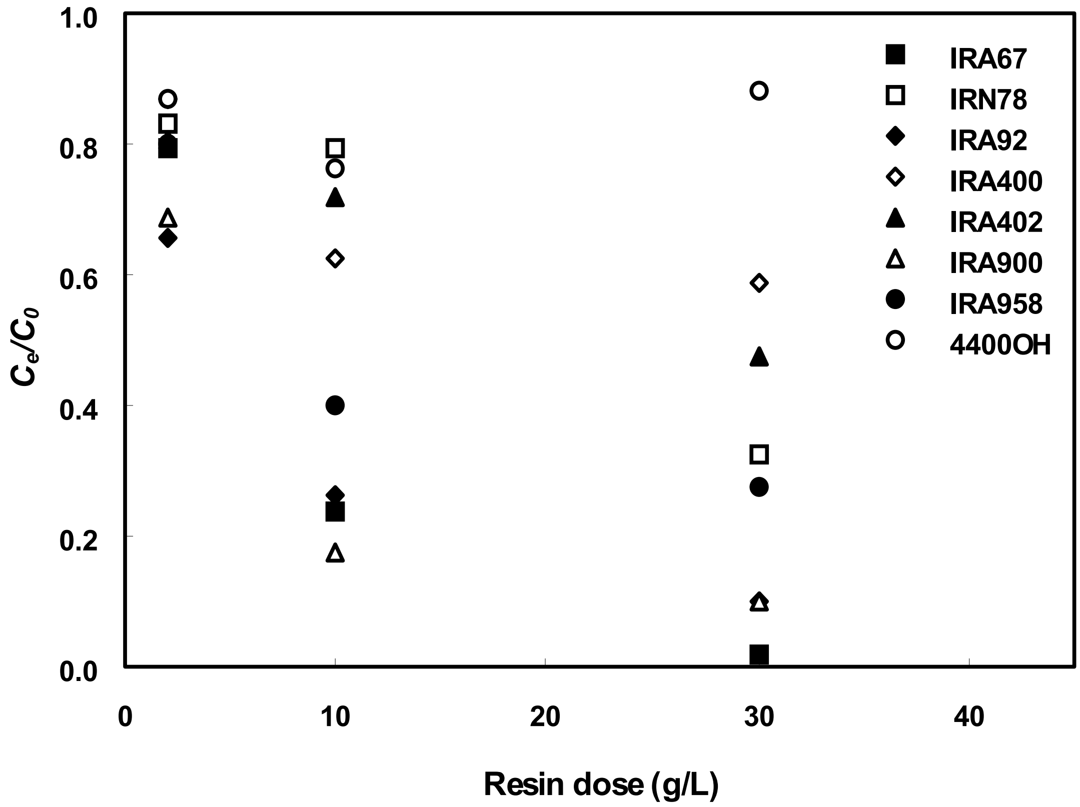

Figure 2-2 Decolourisation of D stage effluent by eight anionic resins (20°C, C_0 : 2550 - 2580 TCU, pH : 2.2 - 2.3, Contact time : 1 day)

In the decolourisation from the E_{op} stage effluent (see Figure 2-3), IRA900 and IRA958 had almost 90% removal efficiency at the resin dose of 30 g/L. IRN78, IRA92, IRA400, IRA402 and 4400OH performed fairly well. IRA67 could not remove any colour. Due to experimental error, the concentration after ion exchange seems higher than initial colour concentration of E_{op} stage effluent.

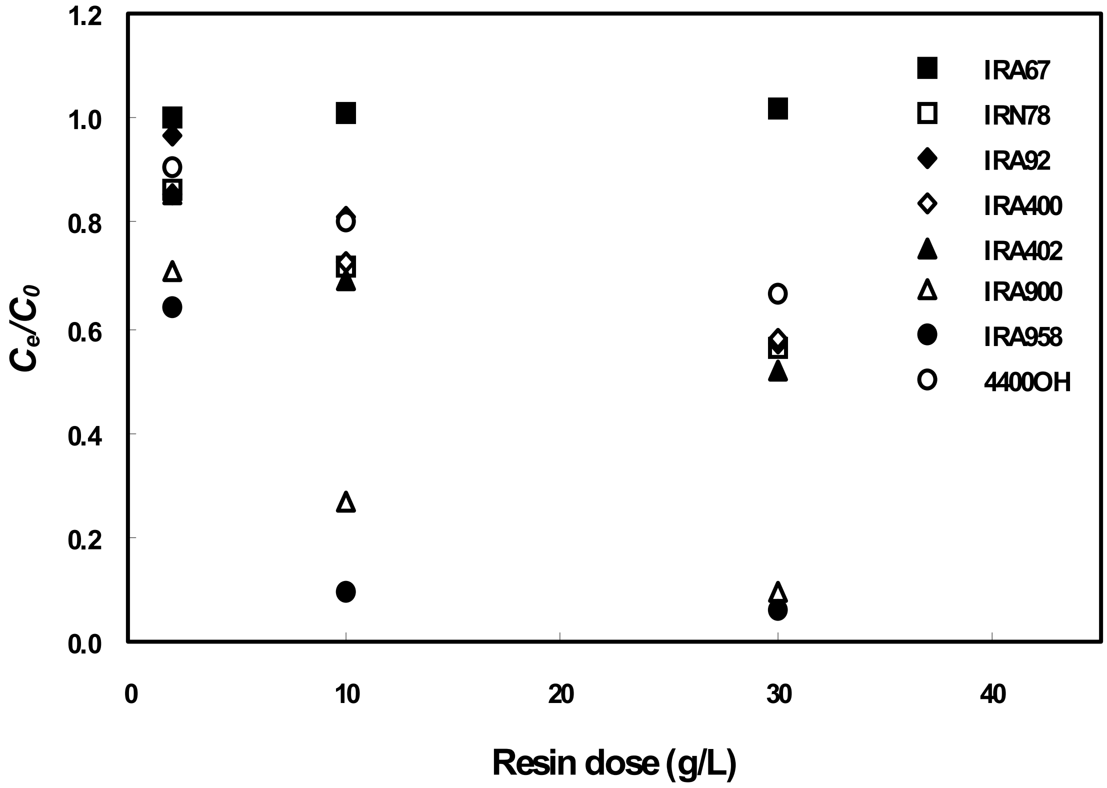

Figure 2-3 Decolourisation of E_{op} stage effluent by eight anionic resins (20°C, C_0 : 2620 - 2760 TCU, pH : 11.4, Contact time : 1 day)

Contrary to the results with lagoon influent (see Figure 2-1) and the E_{op} stage effluent (see Figure 2-3), IRA958 treating the D stage effluent (see Figure 2-2) did not produce the highest removal efficiency. The low pH of the D stage effluent might affect the ion exchange, or the stirrer used could not provide resins with enough mixing to let resins completely contact coloured effluent. Magnetic bars placed in vials broke some resin beads, particularly IRA900 which was being broken into fine powder in some vials. IRA900 did not seem to be resistant to the mechanical mixing.

Duplicates were prepared by placing the same amount of resin and effluent in two vials. Variation of colour removal between duplicates was quite considerable in cases where more resin breakage occurred in one vial than in the other. More colour removal was observed in the vials containing the broken resin beads than in the vials in which breakage did not occur. This may indicate that diffusion resistance due to the relative sizes of the colour causing compounds and resin pores is quite important. As indicated in Section of 2.2.2, the average molecular weight of colour causing compounds has been reported to be 5,600. Therefore, access of these large molecules to exchange sites located within the resin matrix may be limited by resin pore size.

Samples after decolourisation with IRN78 and 4400OH had high pH values. The final pHs of the three kinds of samples are shown in Tables A-1 to A-3 in Appendix A. These pH increases were due to the resins exchanging hydroxide ions for colour causing compounds.

The D stage and E_{op} stage effluent samples contained twice as much colour as the lagoon influent as shown in Table 3-2. Due to the difference in initial colour concentrations of the three samples tested, this may obscure the actual colour removal efficiencies of the resins. Therefore, it is instructive to review these data from the perspective of the number of TCU removed. The 2 g/L dose of IRA958 achieved almost the same removal from E_{op} stage effluent (35% of 2670 = 935 TCU) (see Figure 2-3) as it did from lagoon influent (97% of 910 = 883 TCU) (see Figure 2-1). The difference between the initial colour concentrations of the E_{op} stage and lagoon influent samples is due to dilution that the wastewater undergoes as waste streams from various points in the mill are blended. If this dilution can be calculated according to the difference in colour concentrations of the samples used in the present investigation, then a further reduction of (1 - 910/2670)*100% = 66% can be expected for the treated E_{op} stage effluent. Thus, if the E_{op} effluent were treated with 2 g IRA958/L and this treated effluent subsequently underwent the expected dilution, the resulting colour in the lagoon influent would be (2670 – 935)*(1 – 0.66) = 590 TCU. Therefore, it appears that application of colour removal by IRA 958 would be more efficient if applied to the lagoon influent which resulted in a final colour of approximately 27 TCU, and the representation of the results as fractional colour remaining is justified.

Regeneration Study

The objective of the regeneration study was to determine effective regenerants to release colour-causing compounds from the resins. In the regeneration study, two types of regenerants, NaOH alone and in combination with NaCl, were examined to regenerate exhausted resins. A regeneration study using NaOH was conducted on resins used to decolourise two types of effluents, final effluent from the aerated lagoon and blended (D-stage mixed with E_{op}) bleach plant wastewater. A regeneration study using the combined regenerant was conducted with resins that had been used to decolourise the final effluent.

Figure 2-4 represents the results from the regeneration study with 0.5 *N* NaOH at 10 g/L. The following six resins were tested: IRA67, IRN78, IRA92, IRA900, IRA958, and 4400OH. Three colour removal ion exchange cycles and two regenerations were conducted during this study. 1st in the graph stands for colour removal with virgin resins and 2nd or 3rd represents colour removal with resins which had undergone regeneration once or twice, respectively. Virgin IRA67, IRA900, and IRA958 achieved about 90% colour removal from final effluent. After exhausted resins were regenerated with 0.5 *N* NaOH, colour concentrations of the effluent after the 2nd and 3rd ion exchanges remained high, compared with that in the first colour removal cycle. Virgin IRA92 removed up to 50% of the colour, but removal efficiencies deteriorated with repeated regeneration trials. Virgin IRN78 and 4400OH achieved colour removal efficiencies of only 10 - 15%. In terms of regeneration efficiency, 0.5 *N* NaOH was not capable of regenerating resins sufficiently. Regeneration efficiency was calculated by equation 2-2.

$$\eta_R = \frac{C_0 - C_{R.e}}{C_0 - C_{e \cdot 1_{st}}} \times 100(\%) \tag{2-2}$$

where:

η_R : Regeneration efficiency (%),
C_0 : Initial colour concentration in an effluent,
$C_{R.e}$: Residual colour concentration using regenerated resins, and
$C_{e.1st}$: Residual colour concentration using virgin resins.

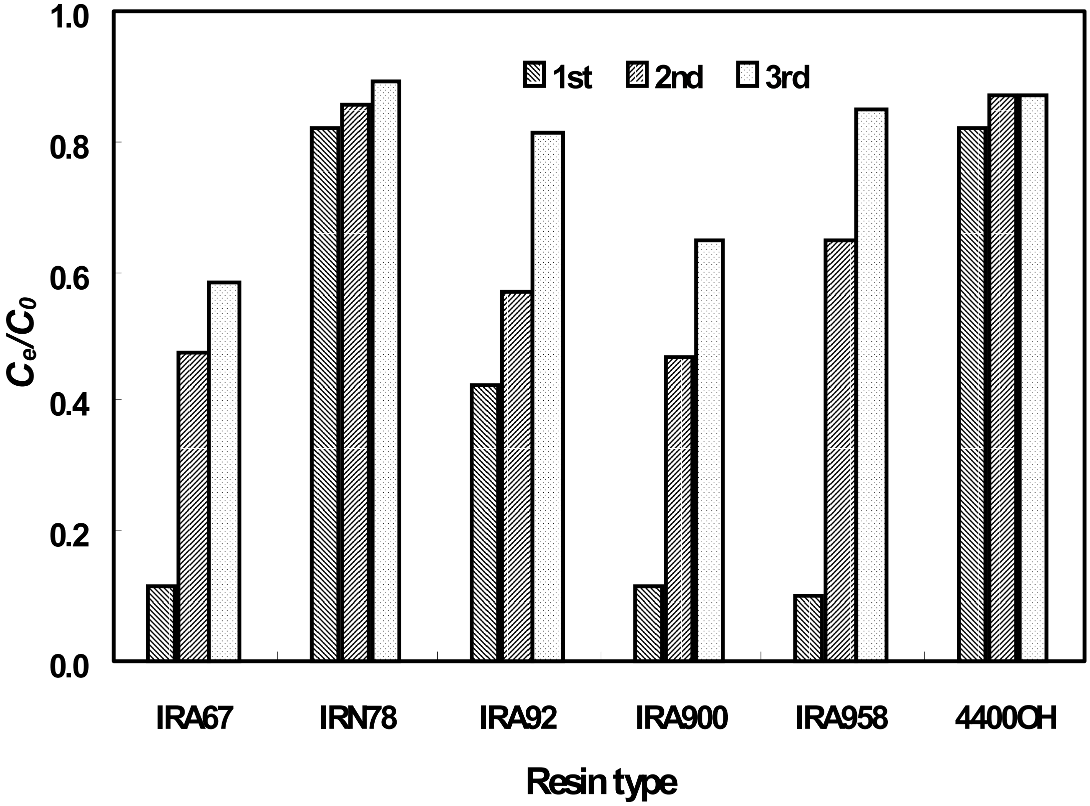

Figure 2-4 Regeneration using 0.5 *N* NaOH (21°C, Final effluent C_0 : 960 TCU, pH 7.9, Resin dose : 10 g/L, Contact time : 1 day)

Figure 2-5 contains results from the regeneration study which used the more concentrated regenerant of 1 *N* NaOH. The tests were conducted at the same resin dose of 10 g/L with the same sample (final effluent). IRA458 showed 80% of colour removal, but after regeneration the removal efficiency dropped to only 20%. Some resins experienced little improvement relative to regeneration efficiency obtained using 0.5 *N* NaOH. Data on colour removal with six virgin resins except IRA458 used from this study should be the same as in the previous trial (see Figure 2-4). However, the colour removal efficiency of IRA900 is remarkably different in Figures 2-4 and 2-5. This difference cannot easily be explained because both sets of tests were conducted under the same conditions (resin dose of 10 g/L, same kind of sample, and same temperature). Residual colour concentration after the first colour removal test with IRA900 in Figure 2-4 was 10% of the initial colour, but that in Figure 2-5 was almost 40% of initial colour concentration.

This difference may result from broken resins. As the colour removal testing summarized in Figure 2-4 was conducted, IRA900 was broken by a stirring bar and it may make IRA900 increase its available surface area and access to exchange sites.

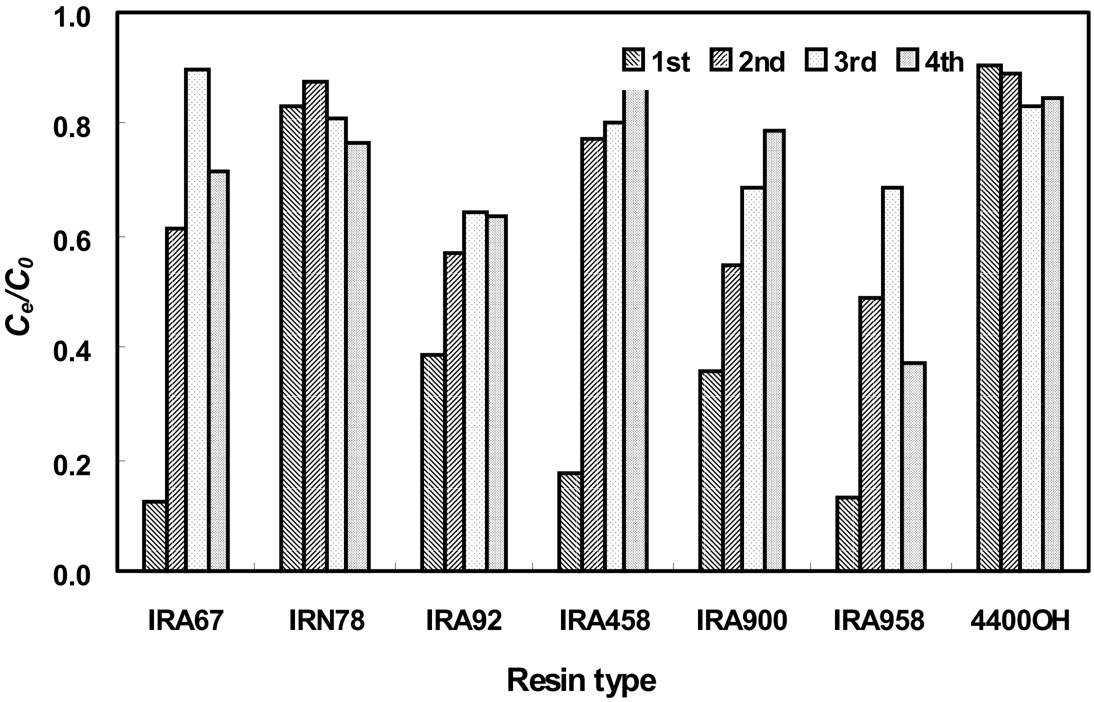

Figure 2-5 Regeneration using 1 *N* NaOH (21°C, Final effluent C_0 : 940 TCU, pH 7.8, Resin dose : 10 g/L, Contact time : 1 day)

Regeneration with either 0.5 *N* (see Figure 2-4) or 1 *N* NaOH (see Figure 2-5) could not show high regeneration efficiencies. Virgin IRA958, which performed best in the resin dose effect study and regeneration study had highest colour removal efficiency among resins tested. However, the removal stopped at around 50% after the first regeneration with 1 *N* NaOH compared to the 85% removal achieved by virgin IRA958 resin. These results indicate that NaOH alone is not an adequate regenerant for these resins (see Figure 2-5).

Figure 2-6 illustrates the results of the regeneration study with 1 *N* NaOH in terms of colour removal from blended bleach plant wastewater. Almost 98% of colour was removed by the virgin IRA458, IRA900, and IRA958 resins, but as was the case during the tests with final effluent (see Figure 2-5), residual colour concentration increased with increasing exchange-regeneration cycles. The WBA resins, IRA67 and IRA92 did not show good regeneration efficiencies. The regenerated IRA67 and IRA92 resins containing hydroxide ions on exchange sites might not easily lose the ions since the most preferred ion to WBA resins is hydroxide. Removal efficiency using the combined wastewater (see Figure 2-6) in IRN78 and 4400OH was better than that using final effluent (see Figure 2-5); yet, the two resins are not competitive with IRA900 and IRA958 in terms of colour removal efficiency.

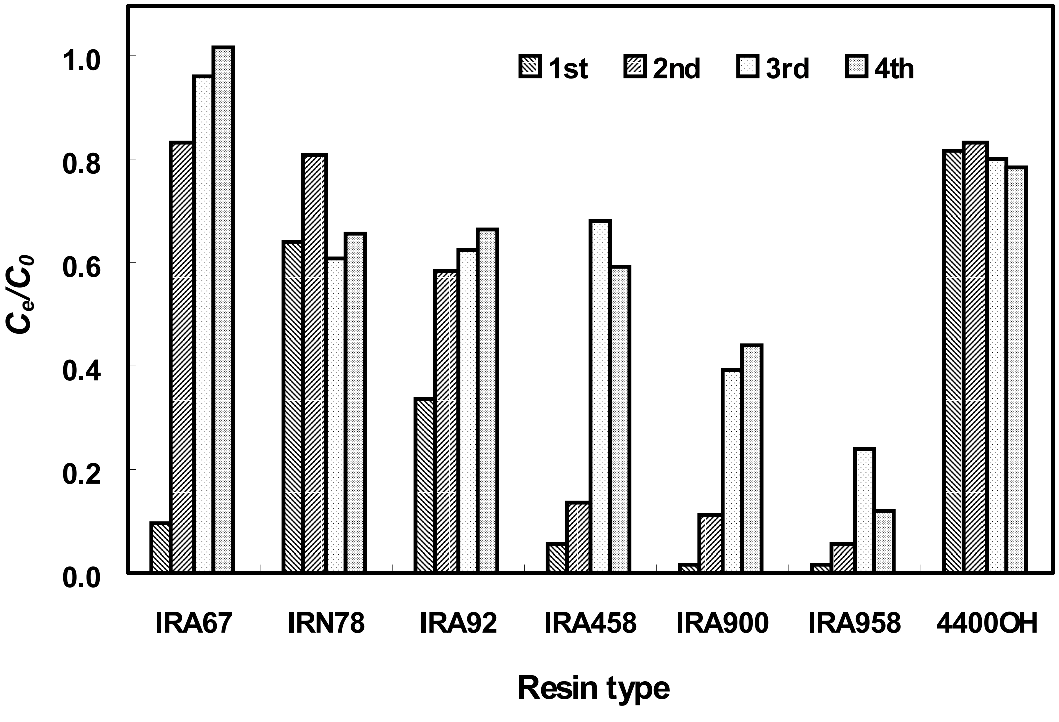

Figure 2-6 Regeneration using 1 *N* NaOH testing blended bleach wastewater (21°C, Blended bleach wastewater C_0 : 890 - 930 TCU, pH 6.5, Resin dose : 10 g/L, Contact time : 1 day)

At this point five types of samples had been tested for colour removal by ion exchange. These are: lagoon influent, final (lagoon) effluent, D stage effluent, E_{op} stage effluent, and the combined bleach plant effluent. The results indicate that the best colour removal was obtained from lagoon influent, final (lagoon) effluent, and the combined bleach plant effluent, when virgin IRA458, IRA900, or IRA958 were used. The amount of colour removed from D stage (pH 2.2) and E_{op} stage effluent (pH 11.4) per gram of resin supplied was somewhat less. This may be due to the effect of the extreme pH values of these two streams that reduce the resins' ion exchange abilities. Therefore, the process could be applied either to a blended bleach plant waste stream, just upstream of the lagoon inlet, or at its outlet using IRA458, IRA900, or IRA958 if a suitable regenerant were identified. Final effluent was chosen as the sole sample to be tested during the remaining colour removal tests in order to streamline the testing and because this wastestream is expected to require the least pre-treatment to render it amenable to treatment in ion exchange columns. Therefore, regeneration testing continued using final effluent and a regenerant consisting of 1 *N* NaOH and 1 *N* NaCl.

Figure 2-7 represents the results from using 1 *N* NaOH in combination with 1 *N* NaCl (40 g NaOH/L and 58.5 g NaCl/L of deionised water) to regenerate the three most effective resins: IRA458, IRA900, and IRA958 after colour removal from final effluent samples. The tests to remove colour from the final effluent were implemented at the three resin doses of 2, 10, and 30 g/L.

The results given in Figure 2-7 illustrate that IRA958 undergoing the first regeneration with the combined regenerant performed as well in terms of removal efficiencies as virgin resins and even slightly better. Virgin IRA958 removed more than 90% (±0.4%) of colour in final effluent at the resin dose of 10 g/L. IRA958 after the second regeneration achieved close to 100% (±0.5%) colour removal. IRA900 achieved a consistent removal efficiency of more than 90% through the three colour removal cycles at 10 g/L. IRA458 provided colour removal of approximately 70% in each colour removal period through all of three ion-exchange cycles at 10 g/L. It can be concluded that the ion exchange performance with all of the three resins after regenerations using 1 *N* NaOH in combination with 1 *N* NaCl did not decrease relative to virgin resin performance. In terms of regeneration efficiency, 1 *N* NaOH in combination with 1 *N* NaCl was very effective as a regenerant for all of three resins. IRA458, IRA900, and IRA958 were chosen to further investigate resin capacity in isotherm testing and column testing. More regeneration studies conducted using diverse ratios of NaOH and NaCl are given in Tables A-4 and A-5 in Appendix A.

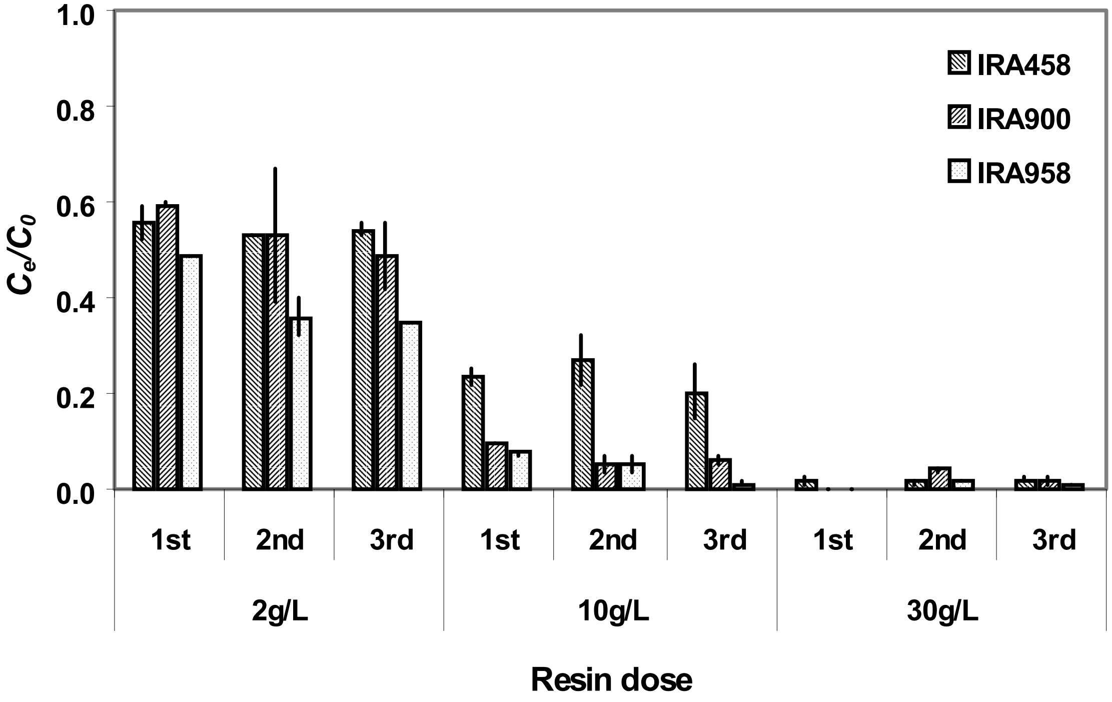

Figure 2-7 Regeneration using 1 *N* NaOH in combination with 1 *N* NaCl testing final effluent (18°C, Final effluent C_0 : 920 - 1230 TCU, pH 7.8 , Resin dose : 10 g/L, Contact time : 1 day). Note: 100% colour removal using IRA900 and IRA958 at the resin dose of 30 g/L.

Colour Isotherm Testing

The objective of the isotherm testing was to determine the best resin for colour removal based on resin exchange capacity. To obtain reliable results, a rotary shaker was substituted for the magnetic stirrer, which had caused resin beads to break during stirring. The colour isotherm tests were carried out at the resin doses of 2, 4, and 6 g/L, at a constant temperature of 20°C, and in duplicate.

Prior to the isotherm tests, preliminary equilibrium tests using IRA 900 for colour removal, and IRN78 for chloride removal, were conducted to determine the time required for equilibrium to be reached. Based on the observations shown in Table 2-1, equilibrium was reached after two and one days for colour and chloride removal, respectively.

Table 2-1 Results of equilibrium tests (Final effluent initial colour concentration: 1220 TCU, initial chloride concentration: 235 ppm, Shaker : 250 RPM, Resin dose : 10 g/L)

Test duration (Days)	Final colour (TCU)	Final chloride (ppm)
1	48	149
2	1	164
3	6	
Time to equilibrium	1 day	2 days

Residual raw data of colour isotherm testing shown in Table A-6 in Appendix A indicate IRA958 of the three outperformed the other two in terms of removal efficiency. Figure 2-8 represents Freundlich isotherm plots of three virgin resins including IRA458, IRA900, and IRA958. Freundlich isotherm graphs were linearised in logarithmic scale of residual colour concentration to a function of exchanged colour concentration divided by the quantity of resin for the ion exchange. It is reasonable to say that resins in lesser amounts removing more colour have high exchange capacities. Therefore, a high y intercept (log K_F) (see 2-6 in Section of 2.4.3) means that the resin possesses a high resin exchange capacity. Therefore, Figure 2-8 demonstrates that virgin IRA958 had the higher exchange capacity compared with virgin IRA458 and IRA900.

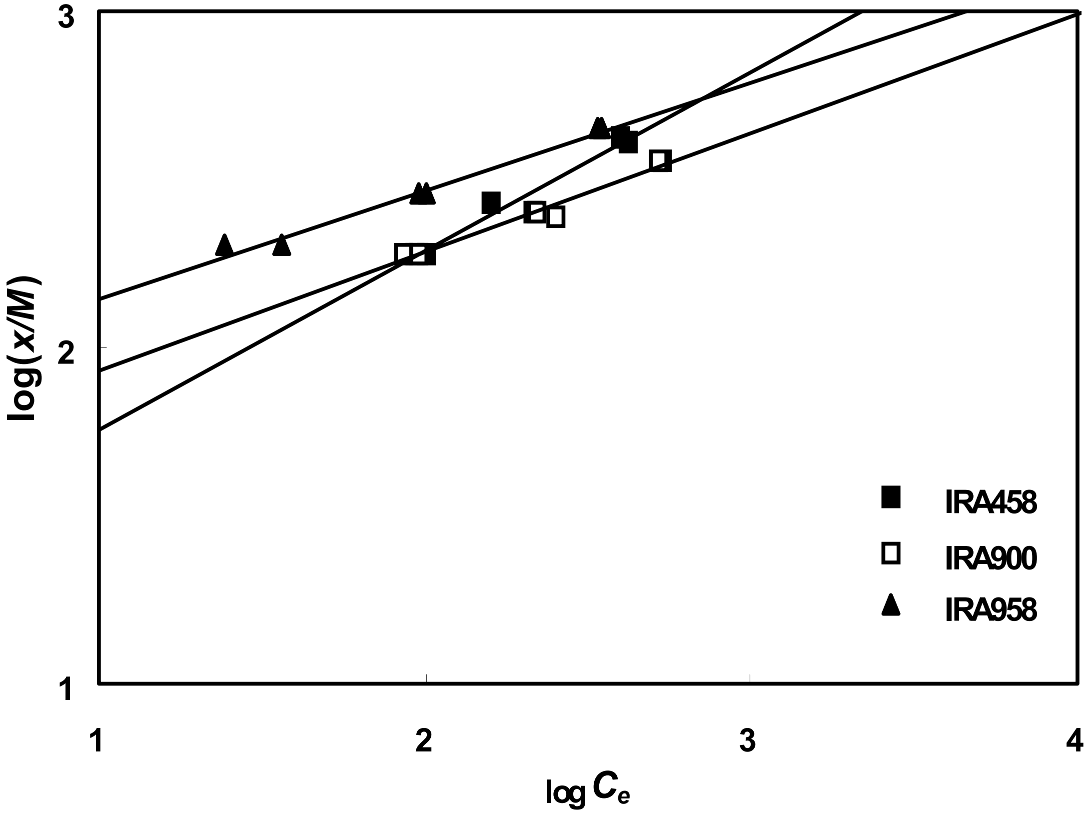

Figure 2-8 Linearised Freundlich isotherms for three virgin resins in colour removal (20°C, Final effluent C_0 : 1240 TCU, Shaker : 250 RPM, Resin dose : 2, 4, 6 g/L).

Figures 2-9 and 2-10 represent Freundlich isotherms of resins after one and two regenerations, respectively. After the first and second regeneration with 1 *N* NaOH in combination with 1 *N* NaCl, IRA958 still exhibited the higher exchange capacity of the resins tested. The Freundlich parameters (K_F and n) of virgin and regenerated resins were calculated and are shown in Table 2-3. Resin capacity, as characterized by the parameter K_F (see Table 2-2), has been lowered after the first regeneration for all resins at all resin doses except IRA900 and IRA958 undergoing two regenerations. This may indicate regeneration might not have been completed. Nevertheless, the regeneration efficiencies for IRA900 and IRA958 calculated in Table A-7 in Appendix A were remarkably high, indicating almost complete recovery of colour removal ability after regeneration. This suggests that an exchange capacity characterized by a high enough K_F is sufficient for excellent removal of colour from the sample tested. Even though the resin capacity of IRA458 decreased after the first regeneration (see Table 2-3), the regeneration recovered approximately 94% of removal efficiency (Table A-7 in Appendix A).

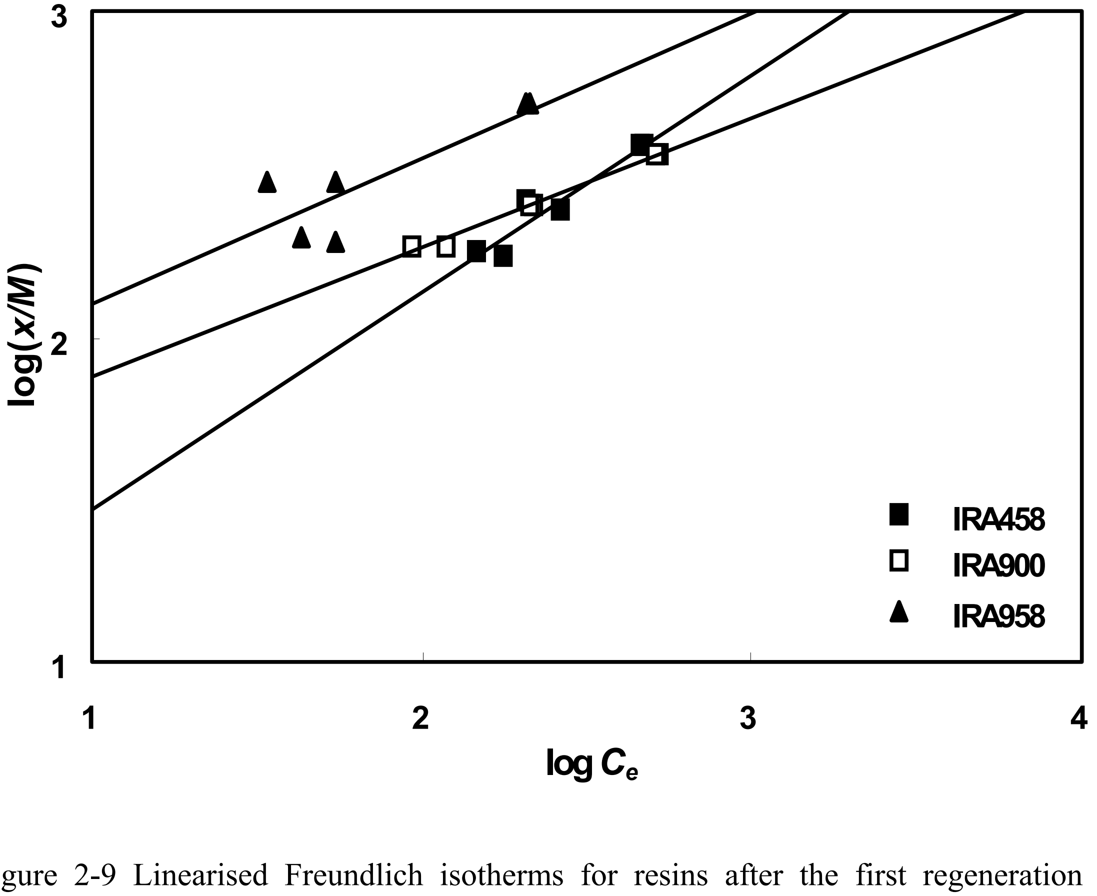

Figure 2-9 Linearised Freundlich isotherms for resins after the first regeneration in colour removal (25°C, Final effluent C_0 : 1240 TCU, Shaker : 250 RPM, Resin dose : 2, 4, 6 g/L).

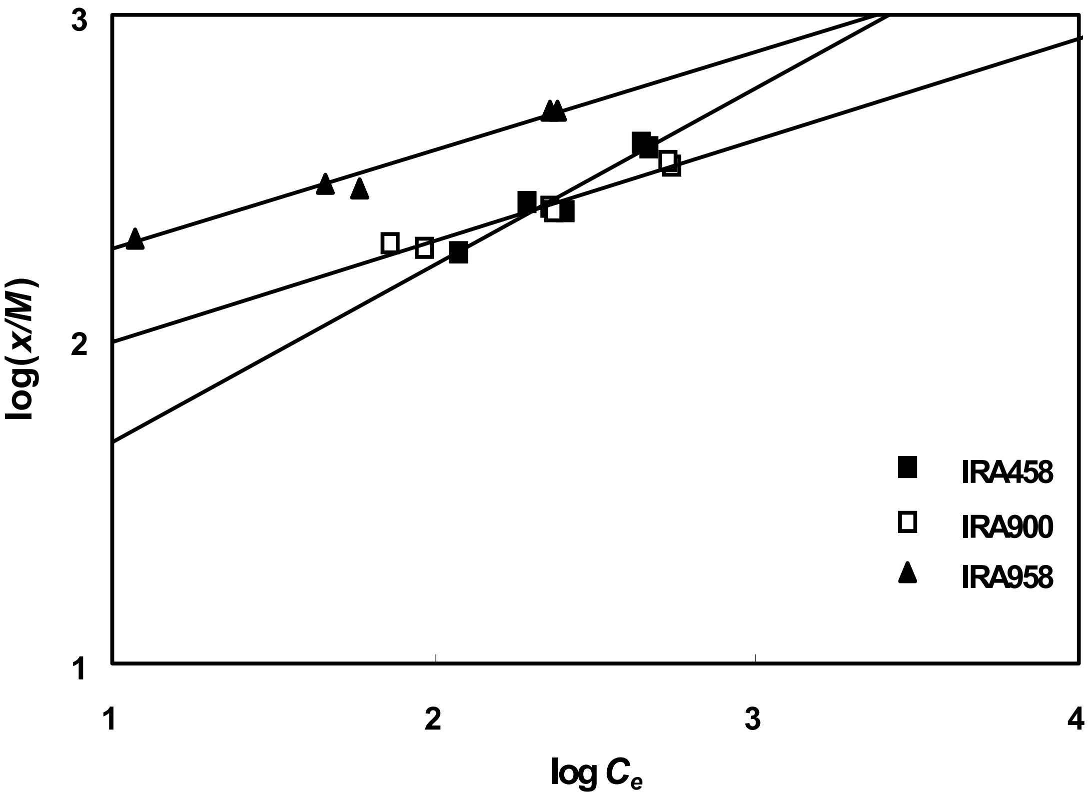

Figure 2-10 Linearised Freundlich isotherms for resins after the second regeneration in colour removal (25°C, Final effluent C_0 : 1240 TCU, Shaker : 250 RPM, Resin dose : 2, 4, 6 g/L).

Table 2-2 The Freundlich parameters for three effective resins on colour removal (20°C, Final effluent C_0 : 1240 TCU, Contact time : 2 days, Shaker : 250 RPM, Regenerant : 1 *N* NaOH in combination with 1 *N* NaCl).

	Resin	K_F (TCU-L/g)	n	Coefficient of Determination (r^2)
1st ion exchange	Amberlite IRA458	16.76	1.881	0.96
	Amberlite IRA900	38.34	2.837	0.97
	Amberlite IRA958	67.20	3.114	0.98
2nd ion exchange	Amberlite IRA458	6.368	1.498	0.93
	Amberlite IRA900	30.13	2.520	0.98
	Amberlite IRA958	44.44	2.220	0.72
3rd ion exchange	Amberlite IRA458	13.80	1.837	0.96
	Amberlite IRA900	48.17	3.209	0.97
	Amberlite IRA958	93.54	3.300	0.98

Colour Removal Column Testing

Breakthrough Studies

The batch studies showed that IRA458, IRA900, and IRA958 are effective to remove colour from the pulp mill final effluent. The following column breakthrough testing has been conducted to verify the results determined from the batch studies. In addition to the verification, the column testing could indicate optimum operating parameters and resin behaviour over time during runs for colour removal (breakthrough curves). Breakthrough point could indicate a proper point to initiate regenerating columns to prevent column effluent from seriously deteriorating.

Figure 2-11 contains the results of column breakthrough testing expressed as fractional colour remaining (residual colour divided by initial colour) versus the number of bed volumes (BV) of sample put through the column. Even though the raw water was filtered prior to being input to columns, clogging occurred in the column containing IRA458. While running the column, the top of resin bed was observed to subside. At the same time, the flowrate uncontrollably dropped regardless of opening the valve at the outlet. The clogging problem might be attributed to the reduction of available flow paths due to settlement of IRA458 or to the presence of air bubbles that had not been removed during the packing of resins. IRA458, unlike IRA900, is transparent which makes it hard to differentiate air bubbles from resins. The experimental error for packing might be overlooked. IRA458 is a gel type resin which tends to form aggregates of beads while IRA900 remains discrete. This aggregation might cause blockage of pores between resin beads and prevent the resins from evenly contacting effluent.

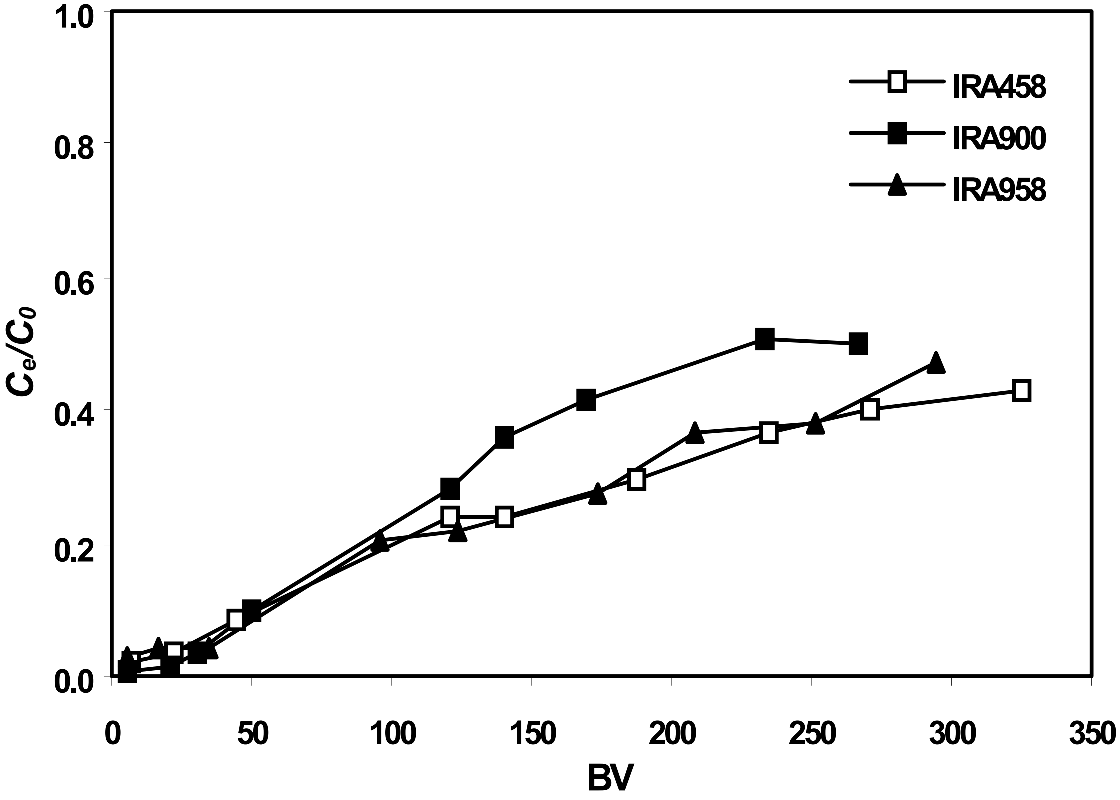

Figure 2-11 Breakthrough curves for selected resins during colour removal, expressed as fractional colour remaining (C_e/C_0) versus the number of bed volumes (BV) put through the column (18°C, Final effluent C_0 : 1240 TCU, 1 BV : 57 mL, EBCT : 12 mins).

The observed reduction of bed depth during the operation of the column could be explained by the aggregation of the IRA458 resin beads. This might increase the potential for the column to clog.

Preliminary column tests were conducted to optimise resin bed depth and bed contact time for subsequent column testing. The testing results established the resin bed depth of 20 centimetres and the bed contact time of 12 minutes. The results are given in Appendix B. While conducting these breakthrough studies, no sharp increase in effluent colour was observed. A point to regenerate columns could be selected referring to the studies up to colour discharge requirement.

The results indicated that the dynamic behaviour of the three resins was very similar from one resin to another. IRA458, a gel type resin, unlike IRA900 or IRA958, which is macroporous, seemed to be closely packed in the column through visual observation and approximate measurement of the used resin weight after the ion exchange. Of the three resins, IRA458 treated the greatest amount of the sample prior to approximately 50% colour breakthrough.

Elution Studies

The objective of the elution studies was to verify whether 1 *N* NaOH in combination with 1 *N* NaCl is also an effective regenerant in continuous flow mode, and to determine the effect of reagent flowrate on regeneration. This elution study could also show how much regenerant is needed to regenerate columns. During the elution studies, the colour released by the resins as they were regenerated was measured over time. The resins used in this study had previously been used in columns to remove colour from final effluent. Colour removal using continuous-flow ion-exchange columns was carried out until the colour concentration in the column effluent (C_e) reached 0.3 of the influent colour concentration (C_0). The columns were then taken out of service, rinsed thoroughly with deionised water, and regenerated. Figures 2-12 and 2-13 are the plots of the results of the elution of colour from ion exchange columns as a function of bed volumes of regenerant used at flowrates of 3.6 and 4.5 mL/min, respectively.

The results shown in Figures 2-12 and 2-13 indicate that 1 *N* NaOH in combination with 1 *N* NaCl released colour from the IRA 958 resin very efficiently in the continuous-flow mode, confirming the earlier batch test results. A comparison of Figure 2-12 to 2-13 shows that approximately the same volume of regenerant was required at each flow rate. These results indicate that the amount of regenerant required is relatively insensitive to the superficial velocity at which it is applied (within the range tested). For the size of column used in this study (1.9×10^{-2} m inner diameter), application of regenerant at a rate of 3.6 mL/min results in a superficial velocity of 12.7 mm/min. Increasing this velocity by approximately 25% to 15.9 mm/min (4.5 mL/min) had a negligible effect on the rate of colour elution from the resin bed. More elution studies with higher flowrates must be investigated since higher flowrates could save space for the ion-exchange set-up system or column capacity.

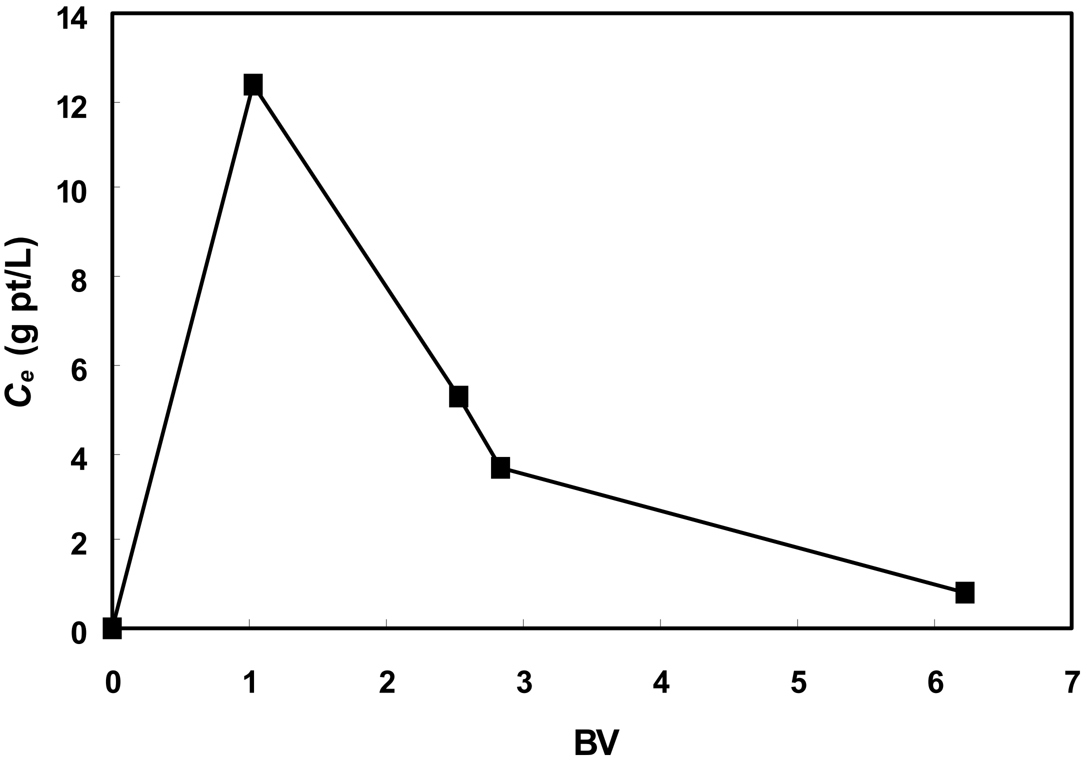

Figure 2-12 Colour elution curves during regeneration of IRA958 using the combination of 1*N* NaCl and 1*N* NaOH at 3.6 mL/min flowrate (18°C, 1 BV : 57 mL, EBCT : 16 mins)

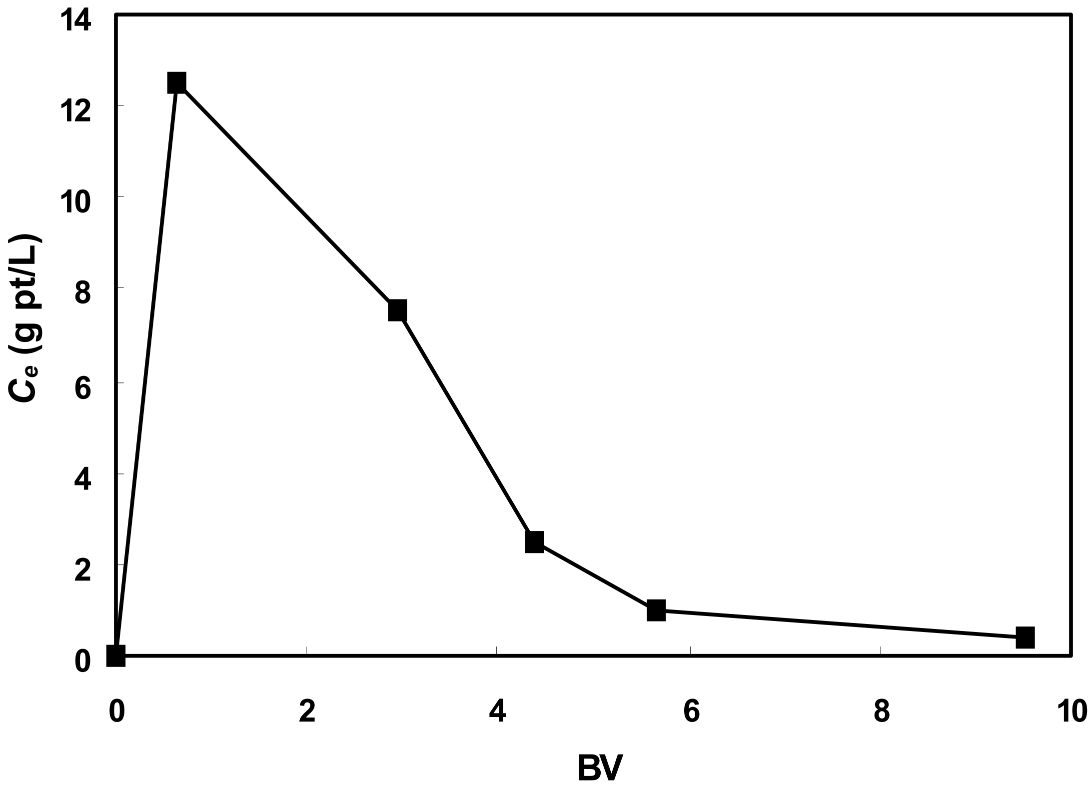

Figure 2-13 Colour elution curves during regeneration of exhausted IRA958 with the combination of 1 *N* NaCl and 1 *N* NaOH at 4.5 mL/min flowrate (18°C, 1 BV : 57 mL, EBCT : 13 mins)

Summary of Colour Removal Results

Based on all of the results of resin dose study with various effluents, the best resins for colour removal were IRA900 and IRA958. IRA458 also showed good colour removal ability during regeneration studies. While these resins were able to achieve good colour removal, they also released considerable amounts of chloride ion into solution during the exchange process. The chloride ions must therefore be removed in subsequent treatment if the treated wastewater is to be re-used in the pulping process.

The performance of WBA resins in the treatment of D and E_{op} stage effluents is of interest. Two WBA resins, IRA67 and IRA92, removed colour well from the D stage effluent and from the final effluent. However, they were not able to achieve good colour removal from the alkaline E_{op} stage effluent. This is because the WBA resins function best under acidic to neutral pH condition as mentioned in Section 2.4.3. Exchange with all of three types of effluents revealed that IRA900 and IRA958, which are both macroporous resins, were very effective to remove colour. IRA900 readily broke down by the stirring bars. This apparently improved its ability to remove colour. This may have been because this breakage allowed the colour causing compounds to interact with more of the resin exchange sites, which implies that the extent of colour removal may have been limited by access to exchange sites within intact resin beads due to the relative sizes of the resin pores and colour causing molecules. Therefore, larger pore size resins would be beneficial to decolourisation.

NaOH alone was not able to release colour-causing compounds captured on exchange sites of resins by exchange with hydroxide ions. However, 1 *N* NaOH in combination with 1 *N* NaCl achieved remarkably efficient regeneration.

Chloride Removal

Chloride Removal by Selected Resins

The study of resin dose effect on chloride removal was conducted to determine effective resins to remove chloride from pulp mill effluents. Figure 2-14 demonstrates the result of chloride removal batch tests using four resins including IRA67 and IRA92 in the free base form, and IRN78 and 4400OH in the hydroxide form. Raw lagoon influent sample was used for this study. Regardless of the resin dose applied, only the hydroxide form resins, IRN78 and 4400OH removed chloride. IRN78 and 4400OH at 10 g/L achieved removal of approximately 50% and 70%, respectively. These two resins showed that they have a potential to reduce chloride concentration in pulp mill effluents.

Regeneration Studies

Regeneration studies were conducted in the batch mode to determine effective reagents to regenerate exhausted resins after chloride removal. Raw final effluent was tested in this batch experiment. Figures 2-15 and 2-16 illustrate the results of testing NaOH as a regenerant.

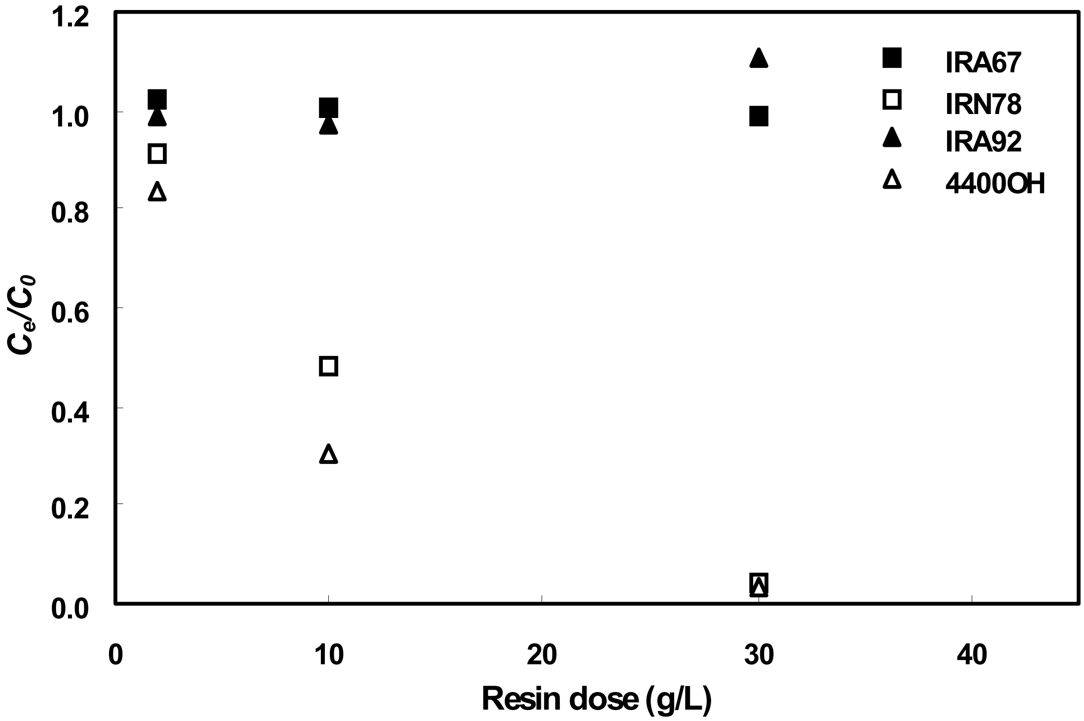

Figure 2-14 Chloride removal from lagoon influent using four anionic resins (21°C, C_0 : 240 ppm, Contact time : 1 day)

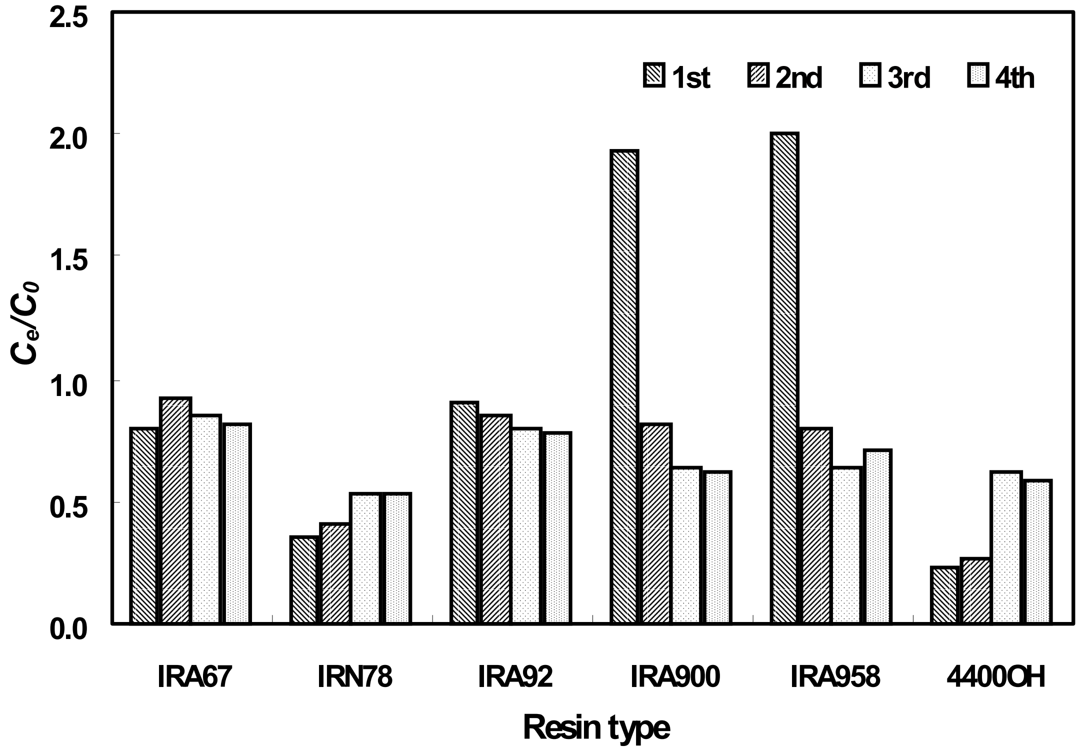

Figure 2-15 Regeneration of six anionic exchangers removing chloride from final effluent using 1 *N* NaOH (21°C, C_0: 240 ppm, Resin dose : 10 g/L, Contact time : 1 day).

Figure 2-15 is a plot of the data obtained from the regeneration study based on chloride removal from final effluent. Six anionic resins were tested over four chloride removal cycles and three regeneration cycles using 1 *N* NaOH. Of the resins tested, IRN78 and 4400OH performed much better than the others during the first two ion exchange cycles even though the chloride removal efficiency deteriorated with repeated regeneration. The chloride concentration in the samples actually increased when virgin IRA900 and IRA958 were used because of the exchange of Cl^- from the resin with colour causing compounds in the samples, as shown in Figure 2-15. After the regeneration with 1 *N* NaOH, the IRA900 and IRA958 can be assumed to possess hydroxide ions at many of the exchange sites. Therefore, after regeneration these resins accomplished removal of chloride comparable to the WBA resins, IRA67 and IRA92 (see Figure 2-15). Figure 2-16 is a plot of the data obtained from the regeneration study using blended bleach wastewater and six anionic resins for chloride removal and regeneration cycles using 1 *N* NaOH.

A comparison of Figure 2-16 to Figure 2-15 shows that IRN78 and 4400OH seemed to remove chloride more readily from the combined sample than from the final effluent. The chloride removal efficiency achieved by IRN78 and 4400OH regenerated with 1 *N* NaOH reached more than 70% chloride removal (see Figure 2-16). More concentrated NaOH solutions (2 *N* and 3 *N*) were studied as regenerants, but these could not improve the regeneration efficiency. The higher densities of these solutions caused the resins to float on the reagent liquid surface so that resins could make a proper contact with these higher normality regenerants. These results are given in Table A-9 in Appendix A.

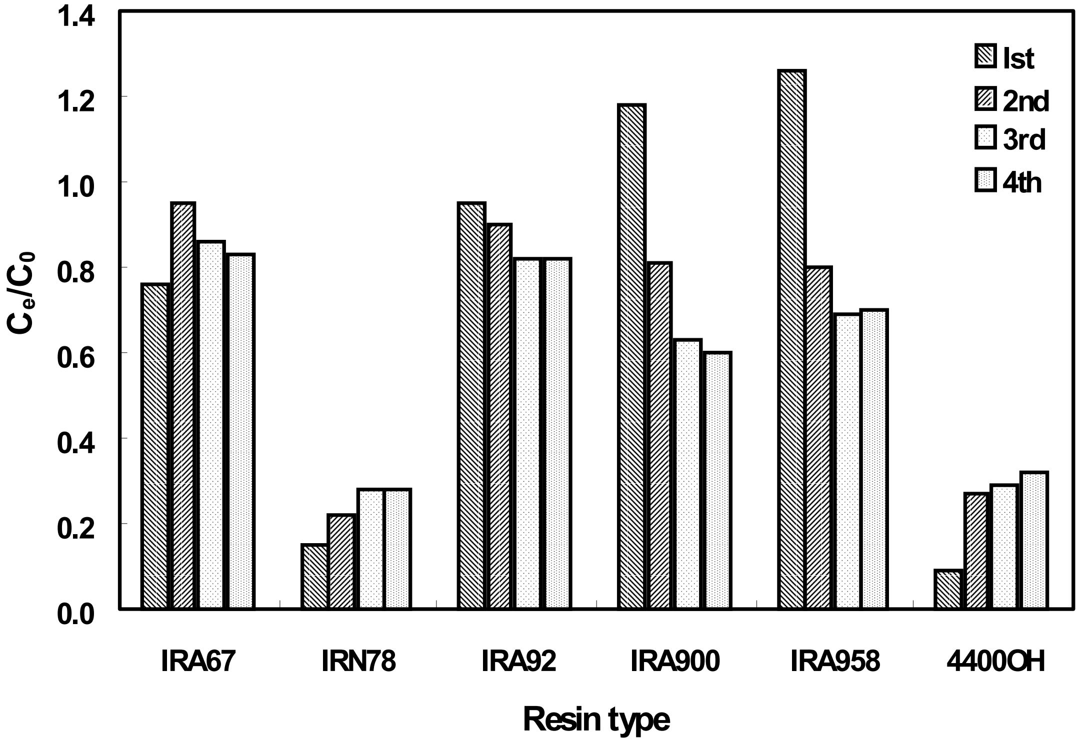

Figure 2-16 Regeneration of six anionic resins removing chloride from blended bleach wastewater using 1 *N* NaOH (21°C, C_0 : 190 ppm, Resin dose : 10 g/L, Contact time : 1 day).

Chloride Isotherm Testing

Isotherm tests were conducted in duplicate at the resin doses of 4, 10, and 25 g/L. The objective of the isotherm testing using IRN78 and 4400OH was to determine their relative exchange capacities during chloride removal from raw final effluent. Raw data expressed as residual chloride concentration divided by initial chloride of chloride isotherm testing are given in Table A-10. Table 2-3 lists the Freundlich parameters from the isotherm tests using virgin and regenerated IRN78 and 4400OH. Based on the K_F values from tests, virgin 4400OH was found to have higher exchange capacity than virgin IRN78. On the other hand, the K_F values of regenerated IRN78 resins were slightly higher than regenerated 4400OH, but the coefficients of determination (r^2) associated with this model calibration were rather low, indicating that the linearised Freundlich model did not represent the data adequately.

The Langmuir model was also applied to determine whether it could provide a better fit to the data from the chloride isotherm studies. The resulting model parameter values and coefficients of determination (r^2) are given in Table 2-4. The fit of the Langmuir model to the data from tests using 4400OH for both the second and the third ion exchange (see Table 2-4) was better than that of the Freundlich model (see Table 2-3). However, the r^2 values associated with the Langmuir model fit (see Table 2-4) for the data from the IRN78 isotherm tests were still very low. This suggests that the resins (particularly IRN78) were not evenly regenerated.

Table 2-3 The Freundlich parameters for two effective resins on chloride removal (20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 *N* NaOH, Resin dose : 4, 10, and 25 g/L)

	Resin	K_F (ppm-L/g)	n	Coefficient of Determination (r^2)
1st ion exchange	Amberlite IRN78	3.76	3.31	0.9
	Amberjet 4400OH	5.09	4.26	0.83
2nd ion exchange	Amberlite IRN78	5.33	8.21	0.28
	Amberjet 4400OH	1.17	2.64	0.56
3rd ion exchange	Amberlite IRN78	2.19	3.66	0.31
	Amberjet 4400OH	0.30	1.71	0.91

A possible cause for this may have been poor contact between the resin and the regenerant. It was observed that some of both IRN78 and 4400OH stuck to the flask wall during the test. To transfer the sticky beads, a spatula was used to draw them out. During ion exchanges, some resins sticking to the flasks might not sufficiently contact samples. The possible reason for quite low r^2 of model fits to data from the second or third ion-exchange might be attributed to some bead loss during transfer of resins from flasks to flasks. Nevertheless, based on the prior regeneration studies, it can be stated that IRN78 and 4400OH were able to remove more chloride per unit mass of resin than the other resins tested. The parameter of $(x/M)_{max}$ is related to resin capacity. This might show performance of resins. The parameters from ion exchanges using the two virgin resins indicate that IRN78 is a little better than 4400OH in the maximum surface concentration at resins. This Langmuir equation unlike Freundlich isotherm requires homogeneous nature of resins. Empirical Freundlich parameters are believed to give data better representation. Chloride isotherm tests could not show which resin of the two is better to remove chloride.

Table 2-4 Langmuir parameters for IRN78 and 4400OH on chloride removal (20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 *N* NaOH)

	Resin	$(x/M)_{max}$	b	Coefficient of Determination (r^2)
1st ion exchange	Amberlite IRN78	20	0.040	0.89
	Amberjet 4400OH	18	0.066	0.82
2nd ion exchange	Amberlite IRN78	11	0.081	0.22
	Amberjet 4400OH	14	0.008	0.69
3rd ion exchange	Amberlite IRN78	11	0.024	0.26
	Amberjet 4400OH	16	0.003	0.95

Chloride Removal Column Testing

The column for chloride removal was designed to follow that for colour removal since substantial increases in chloride concentration were observed during decolourisation.

Breakthrough Study

Based on the effective resin study and regeneration study for chloride removal, breakthrough study was investigated to verify chloride removal with the best effective resins tested, IRN78 and 4400OH in a continuous flow and examine the resin behaviour with run time.

Figure 2-17 is a plot of data of breakthrough studies using IRN78 and 4400OH in operating design parameters shown in Table 2-5. Sharp increase in chloride concentration at the output of the column containing each resin initiated after 25 BVs of final effluent put through (see Figure 2-17).

Table 2-5 Design parameters operated in columns with each IRN78 and 4400OH

	IRN78	4400OH
BV (mL)	26.1	25.5
EBCT (min)	6.3	7.0
Flowrate (mL/min)	4.1	3.6

For the determination of breakthrough point, it is needed to frequently measure the output chloride concentration between 20 and 40 in BV. The difference (see Figure 2-17) of the steepness while developing breakthrough curves using IRN78 and 4400OH were possibly made by the variation of parameters given in Table 2-5.

The breakthrough test of a little deeper bed and lower flowrate in a column with IRN78 than that containing 4400OH might produce the more favourable curve, which is in proportional to steepness of the curve after the breakthrough point (see Figure 2-17). These sharp increases in released chloride concentration (see Figure 2-17) occurring after the breakthrough points are useful for designing optimum operating parameters, especially a point to regenerate columns.

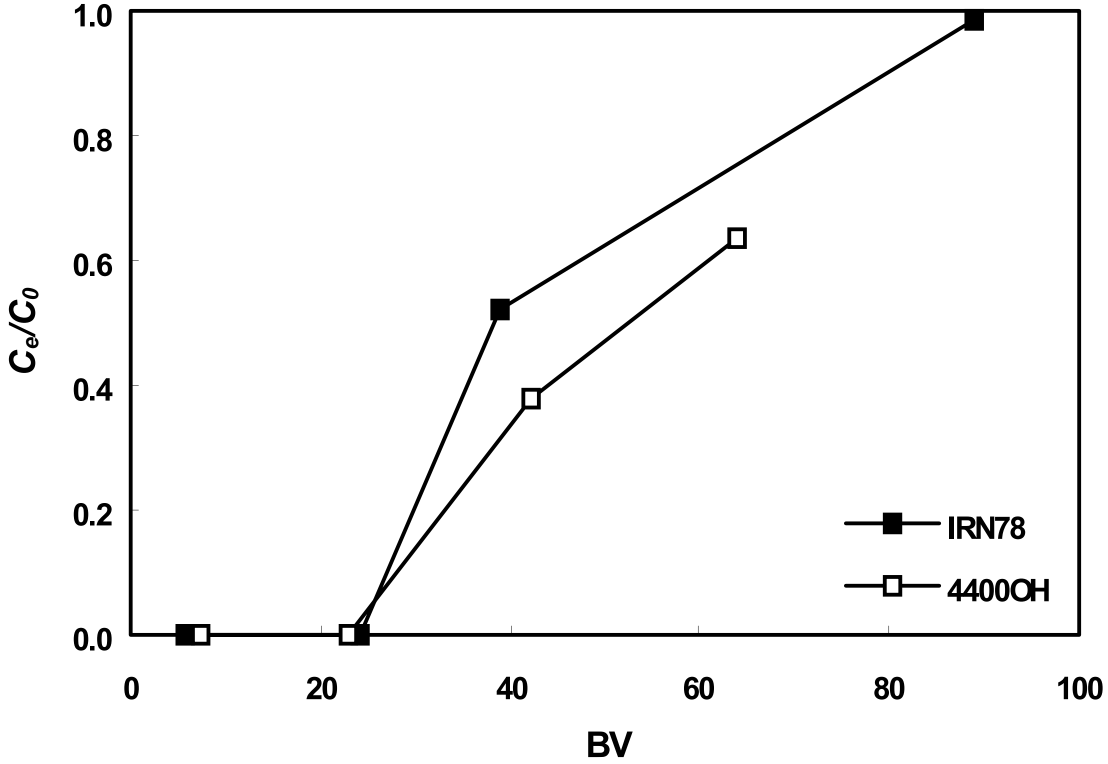

Figure 2-17 Chloride breakthrough curves with IRN78 and 4400OH at 18°C (Initial input water C_0 : 510 ppm).

Elution Study

The elution study was aimed at verifying the results obtained from batch testing that IRN78 is an effective resin for chloride removal and that 1 *N* NaOH is an effective regenerant. The results of the chloride elution study using IRN78 are shown in Figure 2-18. The design parameters for the elution study are given in Table 2-6. Final effluent was fed into a colour removal column containing IRA958 and then the column effluent, retaining little or no colour but having a high concentration of chloride, was pumped into the chloride removal column. The influent to the chloride removal column contained 510 ppm of chloride due to the chloride initially contained in the sample of final effluent (290 ppm) and the release of chloride into the sample during decolourisation with IRA958. The column containing IRN78 was run until the chloride concentration in the column effluent (C_e) reached 0.3 of the influent chloride concentration (C_0). The column was then taken out of service, rinsed thoroughly with deionised water and regenerated with 1 *N* NaOH. The results of the elution study are shown in Figure 2-18. These results indicate relatively slow and incomplete release of chloride from the resin during regeneration, even at the low superficial flowrate of 7.0 mm/min chosen for this elution study. More concentrated NaOH might improve the chloride release in columns. The use of deeper resin beds should also be investigated.

Table 2-6 Operating parameters for chloride removal and then elution (18°C, 1 BV : 28 mL).

	Chloride removal tests	Chloride elution tests
Cl^- in influent, C_0 (ppm)	510	0
Flowrate (mL/min)	4	2
EBCT (min)	7	14
Throughput (BV)	189*	17**

* final effluent sample
** regenerant (1 *N* NaOH)

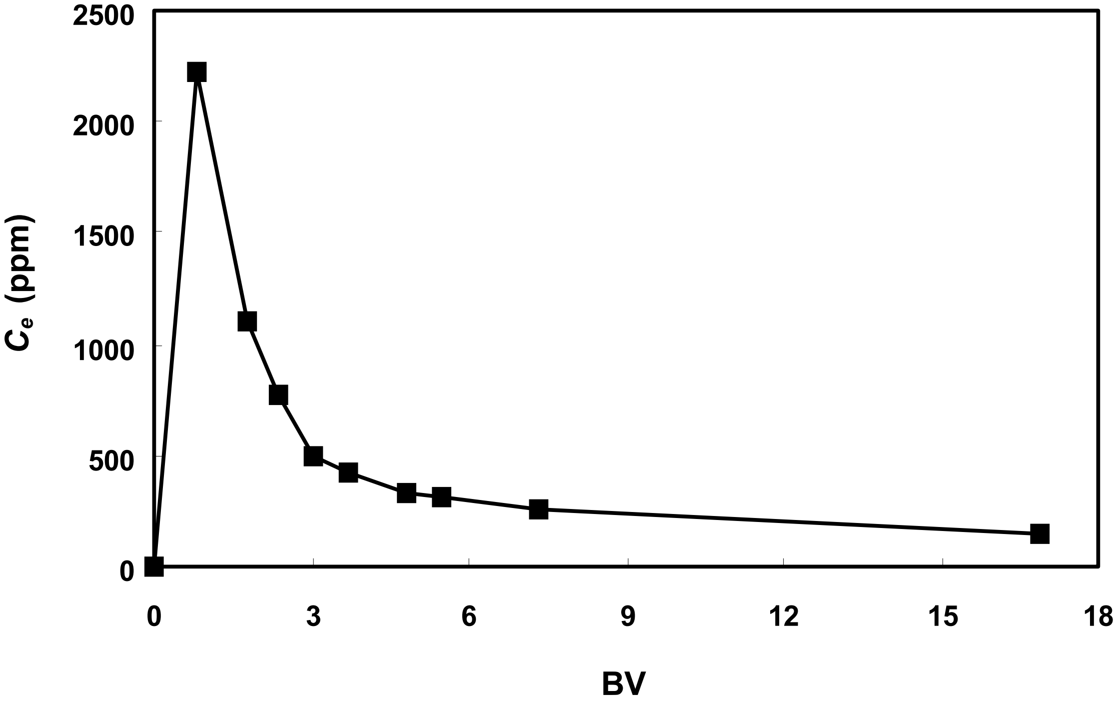

Figure 2-18 Chloride elution curve during regeneration of exhausted IRN78 with 1 *N* NaOH.

CONCLUSIONS

Colour removal

Out of all of the ion exchange resins tested through resin doses, regeneration, and isotherm studies, IRA958 proved to be the best resin for colour removal from lagoon influent and E_{op} stage effluent. IRA900 and IRA67 were best to remove colour of D stage effluent. IRA458 also showed a good ability to remove colour from final effluent and was well regenerated. The key concern for ion exchange is how well exhausted resins can be regenerated and reused in the system. 1 *N* NaOH in combination with 1 *N* NaCl tested as a regenerant was remarkably capable of regenerating IRA458, IRA900, and IRA958 having completely captured colour-causing compounds.

IRA67 and IRA92 can be also promisingly used for decolourisation with an advantage of no chloride addition proven in resin dose effect study on chloride removal. IRA67 and IRA92 are in the form of free base, which means no base (anion) on the exchange site. IRA67 removed a large amount of colour from lagoon influent during batch tests with 10 g IRA67/L and almost all of the colour of D stage effluent at 30 g IRA67/L. IRA92 removed colour very well from both lagoon influent and D stage effluent at 30 g IRA92/L. These resins showed remarkable colour removal efficiency and sufficient application feasibility to remove colour causing compounds in a proper range of pH (0 – 7).

IRA67 and IRA92 can be also promisingly used for decolourisation with an advantage of no chloride addition proven in resin dose effect study on chloride removal. IRA67 and IRA92 are in the form of free base, which means no base (anion) on the exchange site. IRA67 removed considerable amounts of colour from lagoon influent during batch tests with 10 g IRA67/L and almost all of the colour of D stage effluent at 30 g IRA67/L. IRA92 achieved excellent colour removal from both lagoon influent and D stage effluent at 30 g IRA92/L. These resins showed remarkable colour removal efficiency and sufficient application feasibility to remove colour causing compounds in a proper range of pH (0 – 7).

Chloride removal

Resin dose and regeneration studies on chloride removal in the batch mode showed IRN78 and 4400OH were the best among the resins tested, but had a modest chloride removal of approximately 65%. As expected, chloride ions were not removed very readily. In spite of this result, it implies that ions with ion exchange affinities to anionic resin that are greater than that of chloride could be removed to greater degrees than chloride. This might account for the relatively low chloride removal due to a lack of available exchange sites since most of exchange sites might be occupied by these other anions.

Optimal point of combined colour and chloride removal within a kraft pulp mill

One of goals of this study was to determine the optimal point of ion exchange application within a pulp mill. The results of this investigation indicate that the process could be applied either to a blended bleach plant waste stream, just upstream of the lagoon inlet, or at its outlet using either IRA459, IRA900, or IRA958. For the determination of optimal point for the chloride removal column, further chloride removal study is required. However, based on the results of the colour removal studies, the best point to apply the chloride removal may well be following the colour removal columns.

Combined colour and chloride removal

Even though the three best resins (IRA458, IRA900, and IRA958) for decolourisation have a potential for complete colour removal, they release chloride ions, replaced by colour-causing compounds. To avoid the addition of chloride to the wastewaters during decolourisation, IRN78 or 4400OH could be used for colour and chloride removal at the same time since the two resins showed a modest colour and chloride removal efficiency.

IRN78 showed modest colour removal ability although it was not as great as that achieved by IRA458, IRA900, and IRA958. Batch tests using IRN78 at 30 g/L achieved approximately 70% colour removal from D stage effluent and around 50% from lagoon influent and E_{op} stage effluent. This removal could undoubtedly be improved by using a higher resin dose. In order to improve the removal efficiency, a series of columns or one deep bed column packed with IRN78 or 4400OH can be employed.

RECOMMENDATIONS

The following recommendations are suggested to improve chloride removal:

- to determine more effective resins than IRN78 or 4400OH;
- to test a series of columns for chloride removal; and
- to treat the effluents with deeper bed columns.

The high feasibility of application of the ion exchange technology to the pulp mill systems was sufficiently shown by determining effective resin and regenerant for decolourisation. Further pilot scale study is recommended to establish ion exchange advantages and disadvantages for treatment of pulp mill effluents and what optimum operating parameters are for a full scale plant. In the meantime, the pilot scale study is needed to fully prove how well the ion exchange contributes to the development of progressive system closure.

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APPENDICES

Appendix A

Table A-1 Sample pH after decolourisation of lagoon influent (initial pH 7.5-7.8) (Referred to Figure 4-1).

	Resin dose (g/L)			
	0	2	10	30
IRA67	7.8	8.3	8.7	9.0
IRN78	7.8	8.8	11.3	11.6
IRA92	7.8	7.8	7.8	8.2
IRA400	7.8	8.0	9.7	11.3
IRA402	7.5	7.6	7.7	7.7
IRA900	7.5	8.0	7.3	7.4
IRA958	7.5	7.8	7.3	7.2
4400OH	7.8	8.8	11.1	11.5

Table A-2 Sample pH after decolourisation from D stage effluent (initial pH 2.2-2.3) (Data used to prepare Figure 4-2).

	Resin dose (g/L)			
	0	2	10	30
IRA67	2.2	2.3	4.2	7.4
IRN78	2.2	2.4	3.8	11.1
IRA92	2.2	2.4	4.1	6.1
IRA400	2.2	2.2	2.5	4.0
IRA402	2.3	2.3	2.3	2.5
IRA900	2.3	2.3	2.2	2.2
IRA958	2.3	2.2	2.2	2.2
4400OH	2.2	2.2	3.4	11.2

Table A-3 Sample pH after decolourisation from E_{op} stage effluent (initial pH 11.4) (Data used to prepare Figure 4-3).

	Resin dose (g/L)			
	0	2	10	30
IRA67	11.4	11.3	11.3	11.3
IRN78	11.4	11.4	11.8	12.1
IRA92	11.4	11.3	11.4	11.3
IRA400	11.4	11.5	11.7	11.9
IRA402	11.4	11.4	11.4	11.3
IRA900	11.4	11.4	11.4	11.4
IRA958	11.4	11.4	11.2	10.5
4400OH	11.4	11.5	11.9	12.1

Table A-4 Regeneration studies with reagents in diverse ratios of NaOH to NaCl expressed as C_e/C_0 (Final effluent colour concentration C_0 : 910 - 1220 TCU, 21°C, Resin dose : 10 g/L, Contact time : 1 day).

NaOH (N)	NaCl (N)	Resin type	1st	2nd	3rd
1	0.01	IRA458	0.22	0.76	0.88
		IRA900	0.17	0.45	0.71
		IRA958	0.11	0.70	0.90
1	0.1	IRA458	0.22	0.71	0.81
		IRA900	0.04	0.32	0.35
		IRA958	0.24	0.54	0.70
1	1	IRA458	0.23	0.27	0.20
		IRA900	0.10	0.05	0.06
		IRA958	0.08	0.05	0.01
1.7	0.5	IRA458	0.25	0.21	0.21
		IRA900	0.11	0.09	0.10
		IRA958	0.09	0.19	0.03

Table A-5 Regeneration studies with reagents in diverse ratios of NaOH to NaCl expressed as C_e/C_0. (Lagoon influent colour concentration C_0 : 860 TCU, 21°C, Resin dose : 30 g/L, Contact time : 1 day).

	0.475 N NaOH + 0.085 N NaCl		0.495 N NaOH + 0.017 N NaCl	
C_e/C_0	1st	2nd	1st	2nd
IRA67	0.06	0.99	0.09	0.96
IRN78	0.47	0.60	0.48	0.72
IRA92	0.07	0.19	0.08	0.65
IRA900	0.01	0.02	0.03	0.19
IRA958	0.02	0.00	0.02	0.17
4400OH	0.63	0.85	0.65	0.93

Table A-6 Colour isotherm data expressed as C_e/C_0 (Final effluent C_0 : 1240 TCU, 20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 *N* NaOH in combination with 1 *N* NaCl) (Data used to prepare Figures 4-8 through 4-10).

C_e/C_0	Resin dose (g/L)	IRA458	IRA900	IRA958
1st	2	0.33	0.43	0.28
	4	0.15	0.19	0.08
	6	0.08	0.07	0.02
2nd	2	0.38	0.43	0.17
	4	0.19	0.18	0.04
	6	0.13	0.09	0.04
3rd	2	0.37	0.44	0.19
	4	0.18	0.19	0.04
	6	0.10	0.07	0.00

Table A-7 Colour isotherm data expressed as regeneration efficiency (% of colour removal achieved after regeneration relative to that achieved by virgin resin) (Final effluent C_0 : 1240 TCU, 20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 *N* NaOH in combination with 1 *N* NaCl) (Data used to prepare Figures 4-8 through 4-10).

Regeneration	Resin dose (g/L)	IRA458	IRA900	IRA958
1st	2	93	101	115
	4	95	102	105
	6	95	99	98
2nd	2	95	98	112
	4	96	101	104
	6	98	101	102

Table A-8 Regeneration using 0.5 N NaOH expressed as C_e/C_0 (Final effluent C_0 : 230 ppm, 21°C, Resin dose : 10 g/L, Contact time : 1 day)

C_e/C_0	1st	2nd	3rd
IRA67	1.01	1.02	0.97
IRN78	0.59	0.77	0.72
IRA92	1.15	0.94	0.93
IRA900	2.29	0.80	0.84
IRA958	2.29	0.75	0.87
4400OH	0.59	0.82	0.81

Table A-9 Regeneration using 1, 2, and 3 *N* NaOH expressed as C_e/C_0 (18°C, Final effluent C_0 : 290 ppm, Resin dose : 10g/L, contact time : 1 day, Regenerant conc. : 1, 2, & 3 *N* NaOH, shaker : 250 RPM).

NaOH (N)		1st	2nd	3rd
1	IRN78	0.42	0.47	0.61
	4400OH	0.27	0.30	0.73
2	IRN78	0.61	0.84	0.90
	4400OH	0.66	0.92	0.97
3	IRN78	0.59	0.88	0.89
	4400OH	0.65	1.03	1.00

Table A-10 Chloride isotherm tests expressed as C_e/C_0 (Final effluent C_0 : 290 ppm, 20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 *N* NaOH) (Data used to prepare Tables 4-3 and 4-4).

Resin dose (g/L)	1st		2nd		3rd	
	IRN78	4400OH	IRN78	4400OH	IRN78	4400OH
4	0.71	0.72	0.83	0.87	0.83	0.89
10	0.48	0.50	0.69	0.65	0.73	0.74
25	0.09	0.07	0.22	0.41	0.32	0.52

Table A-11 Chloride isotherm tests expressed as regeneration efficiency in % (Final effluent C_0 : 290 ppm, 20°C, Contact time : 1 day, Shaker : 250 RPM, Regenerant : 1 *N* NaOH) (Data used to prepare Tables 4-3 and 4-4).

Resin dose (g/L)	1st		2nd	
	IRN78	4400OH	IRN78	4400OH
4	57	44	57	36
10	58	70	51	52
25	86	63	74	51

Appendix B

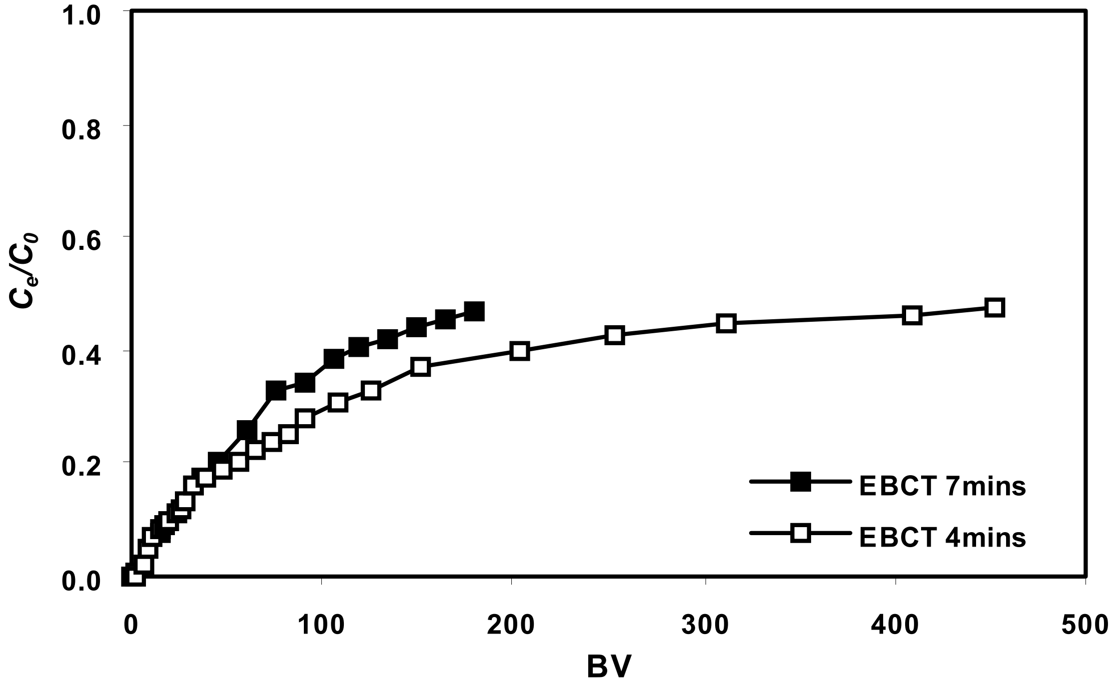

Figure B-1 Breakthrough study on colour removal using IRA900 at 4 and 7 minutes of EBCT (Final effluent C_0 : 1240 TCU, Resin bed depth : 10 cm, 1 BV : 28 mL)

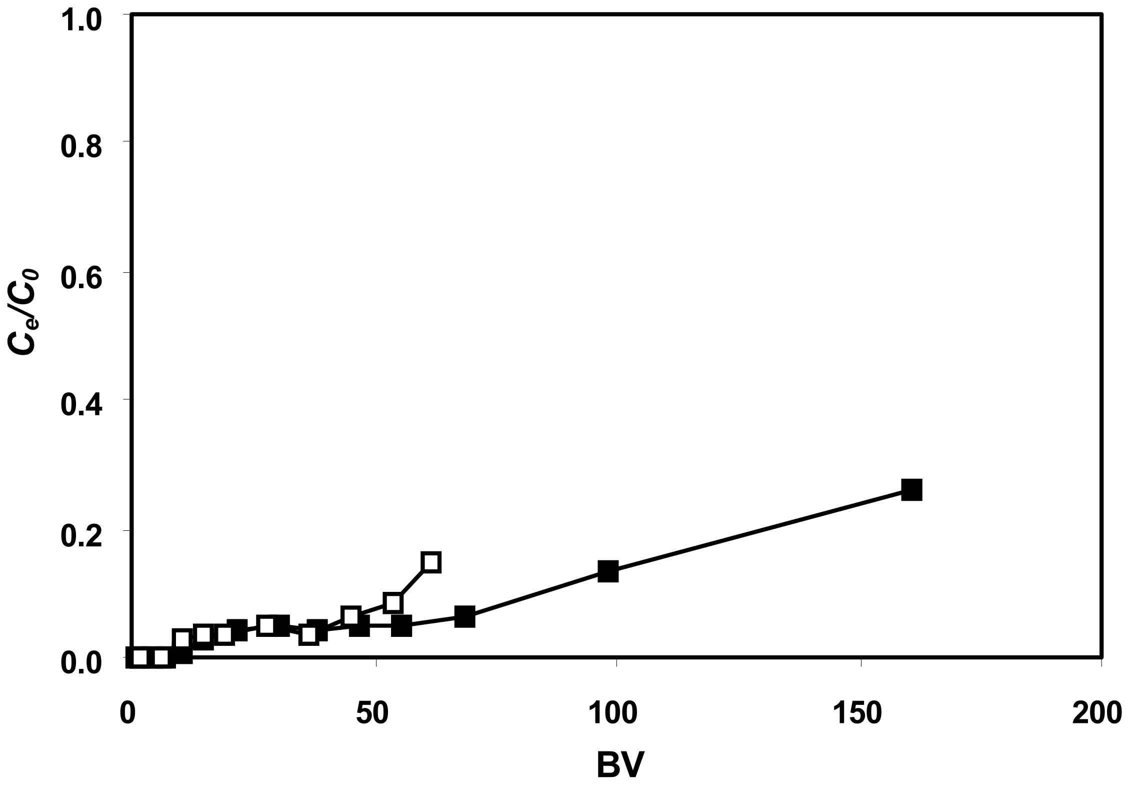

Figure B-2 Breakthrough study on colour removal using IRA900 at 14 minutes of EBCT in duplicate (Final effluent C_0 : 920 TCU, Resin bed depth : 23 cm, 1 BV : 64 mL).

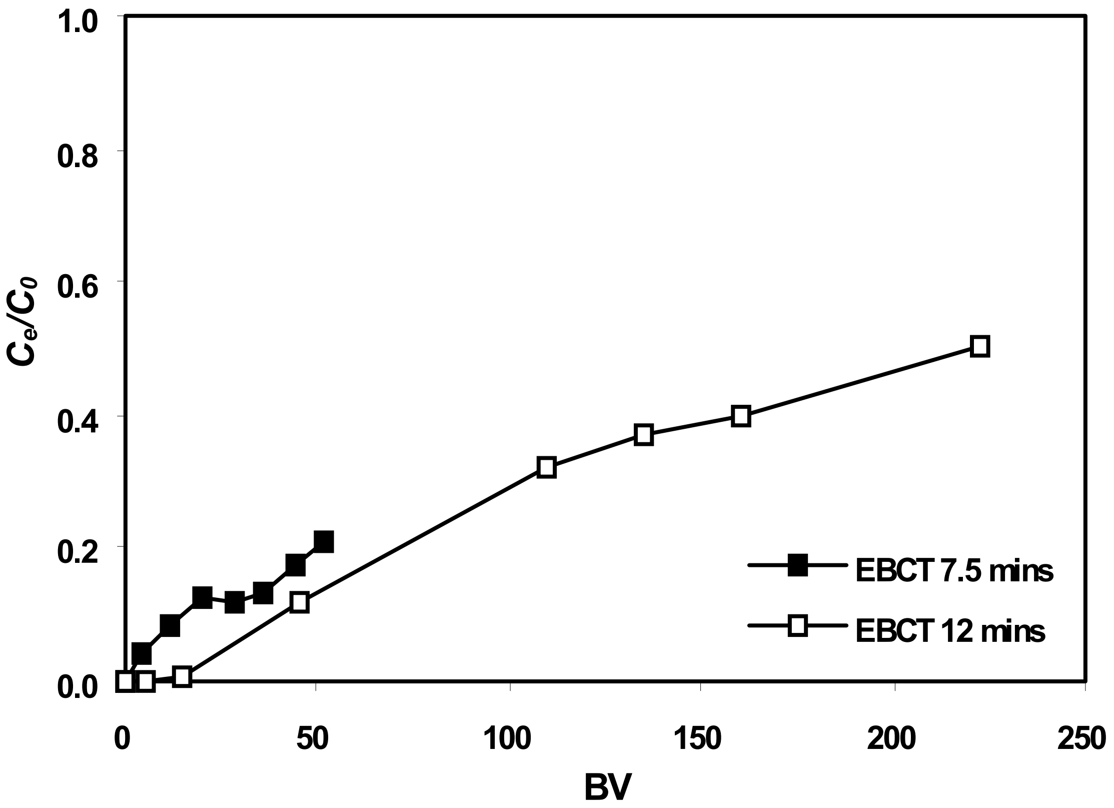

Figure B-3 Breakthrough study on colour removal with IRA900 at 7.5 and 12 minutes of EBCT (Final effluent C_0 : 1190 - 1330 TCU, Resin bed depth : 20 cm, 1BV : 57 mL)