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Decolourization of dye-containing solutions by electrocoagulation

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In the electrocoagulation of Drimarene Discharge X-3LG® (R12S) and Samaron Yellow 4® (D05H), the effects of sacrificial anodes, initial pH, rate of stirring and concentrations of dyes on the fraction of decolourization were tested. The experimental results revealed that the colour of dyes in the aqueous phase was effectively removed when iron and aluminium were used as sacrificial anodes and the concentration of the dyes was less than 100 p.p.m. When the concentration of R12S exceeded 300 p.p.m. iron was a more suitable sacrificial anode for electrocoagulation of R12S than aluminium. For the electrocoagulation of D05H in aqueous solution aluminium as a sacrificial anode was superior to iron when the concentration of D05H exceeded 300 p.p.m. Using iron as sacrificial anode, the residual concentration fraction of R12S was decreased below 10% when the initial concentration of R12S and charge passed were 500 p.p.m. and 120 C, respectively. The decolourization fraction of D05H was 99% when aluminium was used as sacrificial anode.

1. Introduction

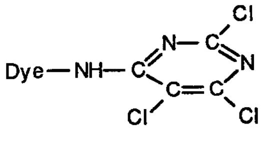
The characteristics of wastewater from textile dyeing are high or low pH, high temperature and a high concentration of colouring material. The methods of treatment of dyeing waste water are biological treatment, chemical coagulation, activated carbon adsorption, ultrafiltration and ozonization [1, 2]. Although the cost of biological treatment of dyeing waste water is less than that of other methods, the smaller efficiency of decolourization using this treatment is due to the toxicity of the dissolved or suspended matter [3]. The colouring matter of dyeing waste water can be effectively removed by methods of chemical coagulation, adsorption on activated carbon, ultrafiltration and ozonization. The costs of adsorption, ultrafiltration and ozonization exceed that of chemical coagulation.

Secondary pollution may be caused by chemical substance added at a high concentration when chemical coagulation is used to treat dyeing waste water. Excessively added coagulants can be avoided by electrocoagulation. The coagulant in this case is generated by electrooxidation of a sacrificial anode. The characteristics of electrocoagulation are simple equipment and easy operation, brief reactive retention period, decreased or negligible equipment for adding chemicals and decreased amount of sludge [4].

Therefore electrocoagulation has been widely used to treat waters containing food and protein wastes [5, 6], oil wastes [7–10], synthetic detergent effluents [11], mine wastes [12] and heavy metal-containing solutions [13–17]. Electrocoagulation can also be used to remove phosphate [18, 19], for the defluoridation of water [20], and to treat potable water [21] and textile waste waters [2]. The fraction of decolourization of textile waste water exceeded 90% [2]. Iron and aluminium are generally used as sacrificial anodes. The matter in dyeing waste water is coagulated by iron(II) and aluminium hydrates or hydroxides produced from the sacrificial anodes. In this paper the electrocoagulation of Drimarene Discharge X-3LG® (reactive dye) and Samaron Yellow 4® (dispersive dye) in aqueous solutions with iron and aluminium as sacrificial anodes is described.

2. Experimental details

Iron and aluminium were washed with acetone to remove surface grease. The impurities on the surfaces of iron and aluminium were removed by dipping for 20 min in a solution which was prepared by mixing HCl aqueous solution (35.0%, 25 ml) and hexamethylenetetramine ($(CH_2)_6N_4$) aqueous solution (2.8%, 50 ml). The dyes used in the experiments were R12S (Drimarene Discharge X-3GL®, Sandoz) and D05H (Samaron Yellow 4®, CAS). R12S is a reactive azo dye of structure



The hue and solubility of R12S are orange and $>100\,g\,dm^{-3}$, respectively. D05H is a dispersive azo dye. The hue of D05H is greenish yellow and D05H is suitable for polyester dyeing. The electrocoagulation current was 0.1 A and the sacrificial anode area

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was 5 cm^2. The distance between the sacrificial anode and the cathode was 1.5 cm. Electrocoagulation of dye-containing aqueous solution was carried out in a beaker (250 ml) with a magnetic stirrer to agitate the solution. At the beginning of a run, the desired concentration of dye in the aqueous solution (200 ml) was fed into the reactor, and the pH was adjusted to a desired value. The reaction was timed starting when the d.c. power supply was switched on. Samples were periodically taken from the reactor.

The precipitate in the sample was centrifuged at 700 r.p.m. for 10 min and the filtrate was obtained. Filtrate (1 ml) was added into buffer solution (pH 7, 4 ml) and the residual concentrations of R12S and D05H were determined according to optical adsorption at 400 and 500 nm, respectively.

3. Results and discussion

3.1. *Aluminium as sacrificial anode*

3.1.1. Effect of initial pH on the electrocoagulation of R12S. With aluminium as sacrificial anode, the decolourization of R12S was significantly affected by the initial pH under acidic conditions. As shown in Fig. 1, the residual fraction of R12S decreased to 70.1% over fourteen minutes electrolysis with initial pH 2. In contrast, the residual fraction of R12S was decreased below 10% when the initial pH exceeded 3.

Using aluminium as sacrificial anode, the dominant species are cationic monomers such as Al^{3+} and $Al(OH)_2^+$ when a low initial pH is applied. The main mechanism for the coagulation of dyes is double-layer compression [22]. In this case, coagulant (Al^{3+}) at a high concentration is needed for effective removal of dyes in the aqueous solution [22]. Hence the coagulation efficiency to remove R12S at initial pH 2 was small within 14 min. When the pH was in the range 4.0–9.0, polymeric species (such as $Al_{13}O_4(OH)_{24}^{7+}$) and precipitate $Al(OH)_3(s)$ were formed. The dyes were effectively coagulated with the polymeric species and precipitated by the mechanisms of adsorption, charge neutralization and enmeshment [22]. Therefore, the residual fraction of R12S at the initial pH 2 was larger than that when the initial pH exceeded 3 in acidic solution.

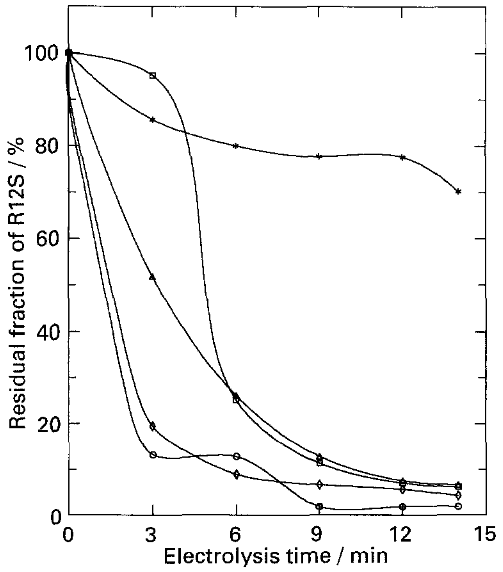

Fig. 1. Effect of electrolysis time on the residual fraction of R12S in acidic solution using aluminium as sacrificial anode. Conditions: [R12S] = 100 p.p.m., [NaCl] = 1000 p.p.m., room temperature, stirring rate: 200 r.p.m., sacrificial anode: Al, cathode: Al, anode–cathode distance: 15 mm, current density: 20 mA cm^{-2}, volume of solution: 200 ml. Initial pH: (∗) 2, (○) 3, (◇) 4, (□) 5 and (△) 6.

When the initial pH was less than 9 in the alkaline region and the electrolysis period was 14 min, the residual fraction of R12S effectively decreased to 4.0% (Fig. 2). The residual fraction was 60.0% when the initial pH was increased to 10. As described above, the coagulation efficiency was promoted by the enmeshment of R12S with $Al(OH)_3(s)$ in the neutral solution. When the initial pH increased to 10, the amount of $Al(OH)_3(s)$ decreased and the concentration of monomeric anion $Al(OH)_4^-$ increased. The efficiency of electrocoagulation of R12S then decreased with initial pH larger than 10.

3.1.2. Effect of initial pH on the electrocoagulation of D05H. Increasing the initial pH from 2 to 3 and keeping the electrolysis period at 15 min resulted in decreased residual fraction of D05H in the aqueous solution from 87.1 to 1.9% as shown in Fig. 3. Upon further increase of the initial pH to 10 the residual fraction of D05H remained constant. The final solution pH increased from 2.4 to 8.7 and remained constant when the initial pH was increased from 2 to 10. These results revealed that the pH of electrocoagulation of D05H with aluminium as sacrificial anode was in the range 2.0 to 2.4 with initial pH 2.0. The absence of adsorption, charge neutralization and enmeshment in the electrocoagulation of D05H resulted in the small coagulation efficiency at the initial pH 2. With aluminium as sacrificial anode, the disperse dye D05H was

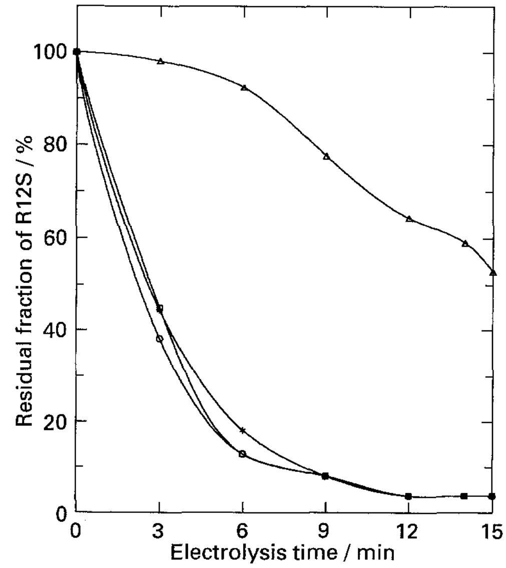

Fig. 2. Effect of electrolysis time on the residual fraction of R12S in alkaline solution using aluminium as sacrificial anode. Conditions: as for Fig. 1. Initial pH: (∗) 7, (○) 8, (□) 9 and (△) 10.

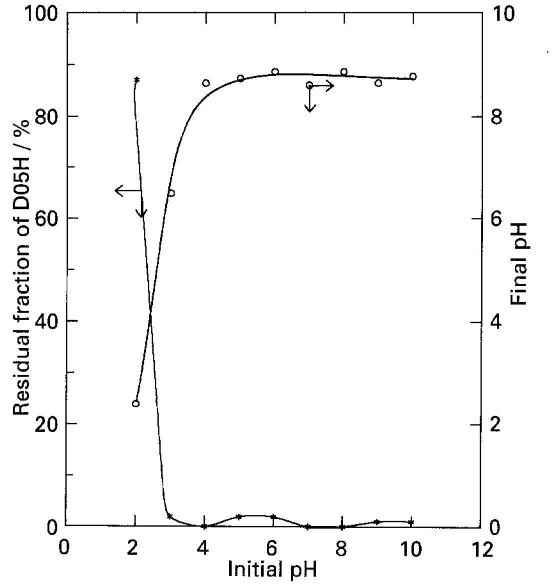

Fig. 3. Effect of initial pH value on the residual fraction of D05H and the final pH value using aluminium as sacrificial anode. Conditions: [D05H] = 100 p.p.m., [NaCl] = 1000 p.p.m. with electrocoagulation time: 15 min. Other conditions as for Fig. 1.

more readily removed and had a greater operational initial pH than that of the reactive dye R12S.

3.1.3. Effect of stirring rate on the electrocoagulation of R12S. With the stirring rate increased from 100 to 200 r.p.m., the residual fraction of R12S decreased from 51.9% to a minimum value 43.8% when the electrocoagulation period was kept at 3 min. Further increase of stirring rate to 400 r.p.m. increased the residual fraction of R12S to 70.0% as shown in Fig. 4. The effect of stirring rate on electrocoagulation of R12S decreased when the duration of electrolysis was increased. In the initial state of coagulation, rapid mixing of dye and coagulant species was required. After the initial state, gentle mixing was needed for the chemical precipitate to grow large enough for removal [22]. Therefore, increased stirring rate resulted in decreased electrocoagulation efficiency and increased residual fraction of R12S when the reaction time exceeded 12 min. The optimal rate of stirring for decolourization of R12S with aluminium as sacrificial anode was 200 r.p.m. (Fig. 4).

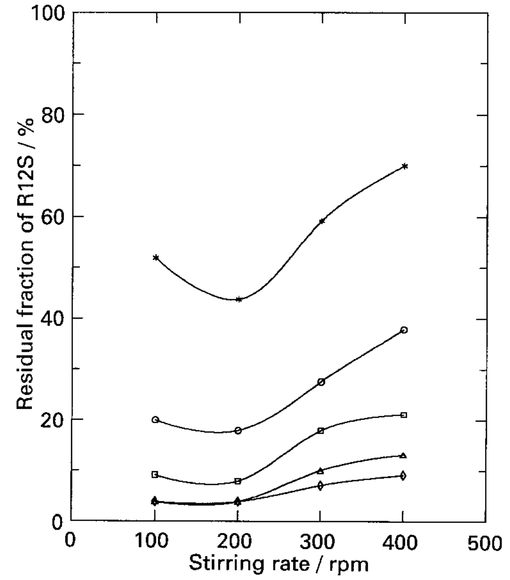

Fig. 4. Effect of stirring rate on the residual fraction of R12S using aluminium as sacrificial anode. Conditions: as for Fig. 1 with initial pH 7. Run time: (∗) 3, (○) 6, (□) 9, (△) 12 and (◇) 15 min.

*Table 1. Residual percentage of R12S in the aqueous solution**

Initial conc. of R12S/p.p.m.	*Electrolysis time*/min				
	6	*12*	*15*	*18*	*20*
100	17.6	3.8	3.8	—	—
300	67.6	48.1	35.7	28.6	25.2
400	74.8	51.9	43.8	36.7	30.0
500	74.8	57.4	51.9	43.3	39.0

* Conditions: initial pH: 7.0, [NaCl]: 1000 p.p.m., room temperature, stirring rate: 200 r.p.m., sacrificial anode: Al, cathode: Al, distance between anode and cathode: 15 mm, current density: 20 mA cm^{-2}, volume of solution: 200 ml.

3.1.4. Effect of concentration of dye in aqueous solution. Using aluminium as sacrificial anode and maintaining the initial pH at 7, with the concentration of R12S increased from 100 to 500 p.p.m., the residual fraction of R12S increased from 3.8 to 51.9% with an electrolysis time of 15 min (Table 1). Under the same conditions, the residual fraction of D05H increased from 0 to 34.3% when the initial concentration of D05H was increased from 100 to 500 p.p.m. as shown in Table 2. The amount of coagulant species for the coagulation of dyes needs to be increased when the dye concentration increases. Hence the increase in dye concentration subsequently caused an increase in the residual fraction when the electrolysis time was fixed. With the concentration of D05H increased from 250 to 500 p.p.m., the residual fraction of D05H was reduced to below 2.0% when the electrocoagulation time was 20 min (Table 2). At the same electrolysis time, the residual fraction of R12S increased from 25.2 to 39.0% when the concentration of R12S increased from 300 to 500 p.p.m. (Table 1). The results revealed that the removal of disperse dye D05H was easier than that of the reactive dye R12S with aluminium as sacrificial anode.

*Table 2. Residual percentage of D05H in the aqueous solution**

Initial conc. of D05H/p.p.m.	*Electrolysis time*/min				
	6	*12*	*15*	*18*	*20*
100	29.0	0.0	0.0	—	—
250	72.9	5.5	4.3	1.9	1.5
400	74.8	61.0	3.3	1.4	1.4
500	74.3	71.9	34.3	3.8	1.4

* Conditions: initial pH: 7.0, [NaCl]: 1000 p.p.m., room temperature, stirring rate: 200 r.p.m., sacrificial anode: Al, cathode: Al, distance between anode and cathode: 15 mm, current density: 20 mA cm^{-2}, volume of solution: 200 ml.

3.2. *Iron as sacrificial anode*

3.2.1. Effect of initial pH. As shown in Fig. 5, the residual fraction of R12S decreased significantly with time in the acidic range except for the condition of initial pH 2 where the residual fraction of R12S increased from 100.0 to 114.8% over 15 min (Fig. 5). At lower pH, the dominant species of coagulant generated from the iron sacrificial anode were cationic monomers such as Fe^{3+} and Fe^{2+} [22]. As described above, the efficiency of coagulation of dyes with cationic monomers was small. Furthermore, the increase of concentration of Fe^{3+} and Fe^{2+} might result in the increase of light absorption in the analytical process. The importance of coagulation of R12S due to adsorption, neutralization and enmeshment increased when the initial pH increased in the acid solution. Hence the electrocoagulation efficiency increased and the residual fraction of R12S decreased when the initial pH increased in the acidic range.

The reactive dye R12S was effectively coagulated and the residual fraction was reduced below 13.8% in the initial range pH 7–10 over 15 min. Thus the effect of initial pH on the residual fraction of R12S in alkaline solution was smaller than that in acidic solution.

The residual fraction of D05H decreased to less than 10.0% with initial pH greater than 2 when the electrolysis time exceeded 12 min as shown in Fig. 6. The residual fraction of D05H decreased slightly to 90.0% at initial pH 2 over 15 min (Fig. 6). The small electrocoagulation efficiency of D05H with iron as sacrificial anode was due to the poor coagulation ability of cationic monomers as described above.

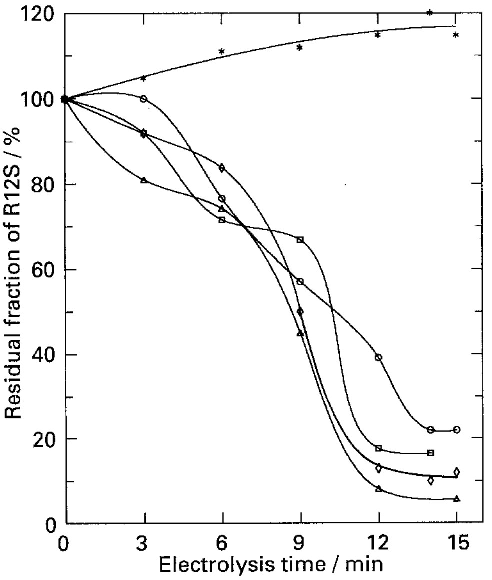

Fig. 5. Effect of electrolysis time on the residual fraction of R12S in the acidic solution using iron as sacrificial anode. Conditions: [R12S] = 100 p.p.m., [NaCl] = 1000 p.p.m., room temperature, stirring rate: 200 r.p.m., sacrificial anode: Fe, cathode: Fe, distance between anode and cathode: 15 mm, current density: 20 mA cm^{-2}, volume of solution: 200 ml. Initial pH: (∗) 2, (○) 3, (□) 4, (△) 5 and (◇) 6.

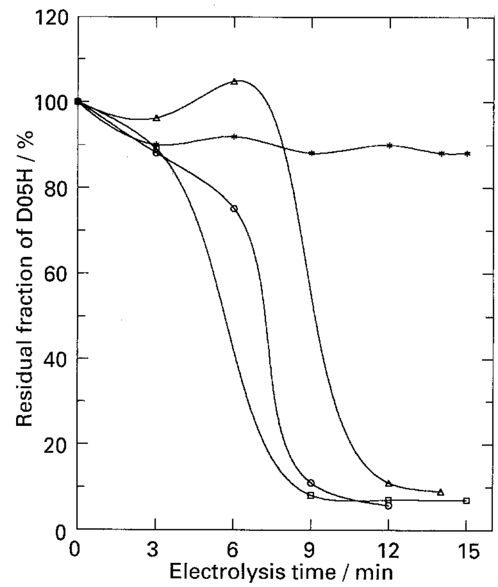

Fig. 6. Effect of electrolysis time on the residual fraction of D05H in the acidic solution using iron as sacrificial anode. [D05H] = 100 p.p.m., [NaCl] = 1000 p.p.m., with other conditions as in Fig. 5. Initial pH: (∗) 2, (○) 3, (□) 4 and (△) 5.

The residual fraction of D05H significantly decreased in the initial range pH 7–10 when the duration of electrocoagulation increased from 6 to 15 min as shown in Fig. 7. The residual fraction of D05H was reduced to less than 10.0% at 15 min (Fig. 7). The apparent slight increase of residual fraction of D05H in the initial stage of electrocoagulation was due to light absorption by ferrous and ferric ions generated from the sacrificial anode. The time for removal of D05H increased with initial pH increase in the alkaline range.

3.2.2. Effect of stirring rate. As shown in Fig. 8, with stirring rate increased from 100 to 500 r.p.m., the residual fraction of R12S increased from 9.0 to 45.2% at 12 min. Under the same conditions, the

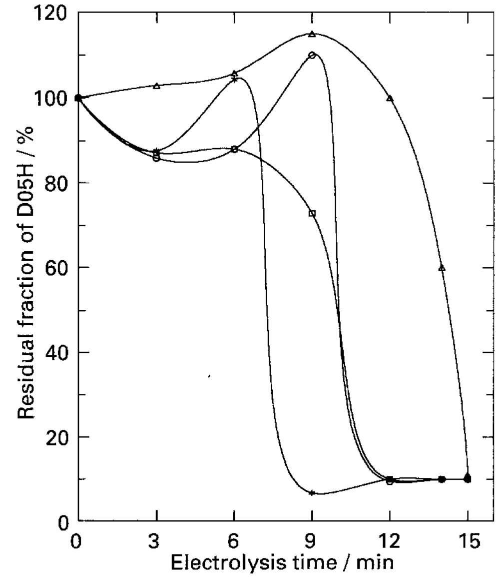

Fig. 7. Effect of electrolysis time on the residual fraction of D05H in the alkaline solution using iron as sacrificial anode. [D05H] = 100 p.p.m., [NaCl] = 1000 p.p.m., with other conditions as in Fig. 5. Initial pH: (∗) 7, (○) 8, (□) 9 and (△) 10.

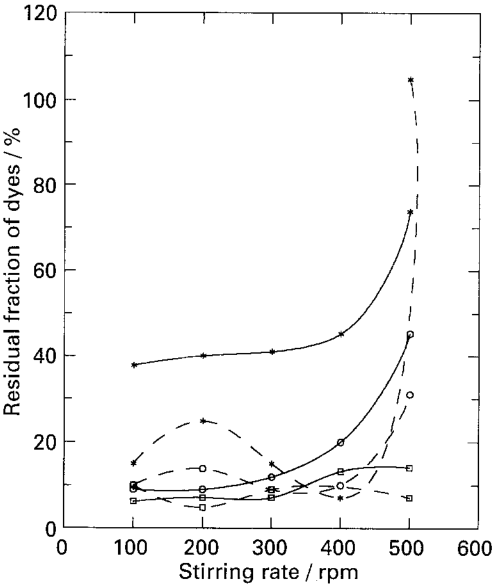

Fig. 8. Effect of stirring rate on the residual fraction of dyes using iron as sacrificial anode. [D05H] = [R12S] = 100 p.p.m., [NaCl] = 1000 p.p.m., with other conditions as in Fig. 5. Run time: (×) 9, (○) 12 and (□) 15 min. Curves: (—) R12S; (- - -) D05H.

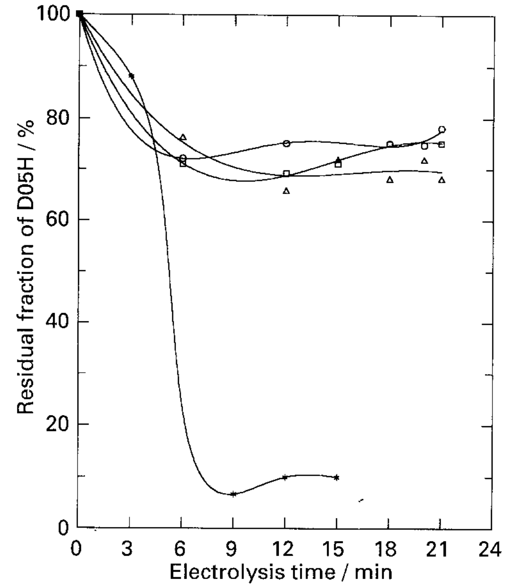

Fig. 10. Effect of electrolysis time on the residual fraction of D05H for various initial concentration of D05H using iron as sacrificial anode. [NaCl] = 1000 p.p.m. with initial pH 7.0. $[\text{D05H}]_i$: (*) 100, (○) 300, (□) 400 and (△) 500 p.p.m.

residual fraction of D05H increased from 10.0 to 31.0%. As described above, the rapid mixing inhibited the precipitate from growing large enough for removal, thus resulting in an increase in the residual fraction. With an electrolysis time of 15 min and increased stirring rate the residual fractions of R12S and D05H altered slightly (Fig. 8). The results indicated that the time for electrocoagulation increased with stirring rate.

3.2.3. Effect of concentration of dyes in the aqueous solution. Using iron as sacrificial anode, the residual fraction of reactive dye R12S was effectively reduced to less than 10.0% when the initial concentration of R12S was in the range 100–500 p.p.m. and the electrolysis period exceeded 20 min as shown in Fig. 9. When the initial concentration of R12S was 100 p.p.m., the residual concentration was decreased to 10 p.p.m. in 12 min. Increasing the initial concentration of R12S required increased electrolysis time for electrocoagulation of R12S. Under the same electrocoagulation conditions, the residual fraction of disperse dye D05H exceeded 70.0% when the initial concentration of D05H was larger than 300 p.p.m. and the time of electrocoagulation was 20 min as shown in Fig. 10. These results might be due to the high concentration of D05H causing an altered range of pH for removal of D05H with coagulant [22]. The residual fraction of D05H was reduced to 6.7% when the initial concentration was 100 p.p.m. These results showed that the removal of reactive dye R12S with iron as sacrificial anode was easier than that of disperse dye D05H, especially when the concentration of dye exceeded 300 p.p.m. In comparison with the results in Table 1, aluminium used as sacrificial anode for the electorcoagulation of disperse dye D05H was more suitable than iron. Comparing the results in Fig. 9 and Table 2, it is seen that the electrocoagulation of R12S with iron as sacrificial anode was superior to that with aluminium.

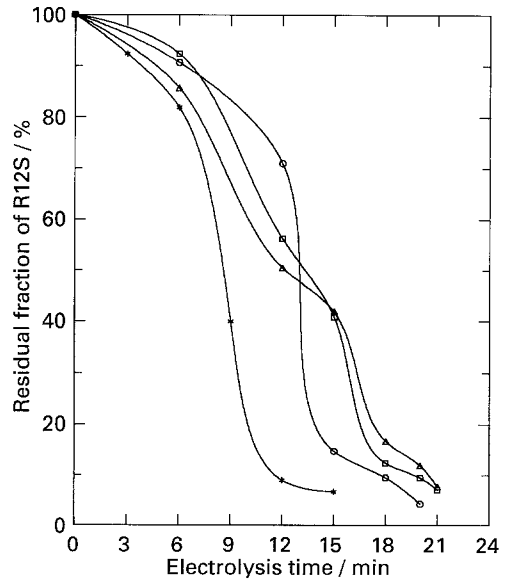

Fig. 9. Effect of electrolysis time on the residual fraction of R12S for various initial concentration of R12S using iron as sacrificial anode. [NaCl] = 1000 p.p.m. with initial pH 7.0. $[\text{R12S}]_i$: (*) 100, (○) 300, (□) 400 and (△) 500 p.p.m.

4. Conclusions

The decolourization of reactive and dispersive dyes (R12S and D05H) by means of electrocoagulation was affected by the nature of the sacrificial anode, initial pH, stirring rate, and dye concentration. The results showed that the dyes were effectively removed at initial pH 3–9 when the initial concentration of dye was 100 p.p.m. When the stirring rate exceeded 200 r.p.m. with increased rate of stirring, the decolourization time increased. The results also indicated that the residual fraction of R12S was reduced to below 10.0% when iron was used as sacrificial anode and the initial concentration of R12S exceeded 300 p.p.m. The residual fraction of R12S exceeded 25.0% when aluminium was used as sacrificial anode. Hence iron as sacrificial anode for decolourization of R12S (reactive dye) was superior to aluminium. With aluminium as sacrificial anode, the residual fraction of D05H was reduced less than 5.0% when the initial concentration of D05H exceeded 300 p.p.m. The residual fraction of D05H was larger than 70.0% when iron was used as sacrificial anode. This showed that aluminium was a suitable sacrificial anode for electrocoagulation of D05H (disperse dye).

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