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The Color Pollution Removal (Acid Red 88) of Industrial Waste Waters by Electrocoagulation Method

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Abstract- The aim of this study was to investigate the decolorization of Acid Red 88 (AR88) using electrocoagulation and photo electrocoagulation techniques. Chemical dyes have the most practical usage in different industries, having an essential role in most water industries, they have a high solubility in water, thus, water wastes contain a high level of these dyes. An effective way of eliminating these dyes is electrocoagulation The effect of operational parameters such as initial dye concentration, electrolysis time and electrolyte concentration was studied. The electrochemical cell comprised Al as cathode and Fe as anode which were placed inside a container having a low pressure mercury lamp at the top. 40 mg.L-1 of dye solution was withdrawn for each experiment and after adjusting the electrode distance to 15 mm, current density to 41.8 A m-2, different electrolytes at varying concentrations were added and the absorbance was measured at several reaction times. The results showed that electrocoagulation was more effective than photo electro-coagulation using NaBr, KBr, NaCl and KClaselectrolytes and decolorization rate increased with increasing electrolyte concentration. Also the coupled system with NaF electrolyte showed better decolorization rate than electrocoagulation, but the decolorization rate was higher at low concentrations of electrolyte. Therefore, it is concluded that electrocoagulation was more effective than coupled system in most cases and type of electrolyte plays an important role since employed NaCl/KCl would enhance the decolorization rate considerably.

Keywords: *red acid 88, electrocoagulation, industrial water wastes containing dyes, and elimination of industrial dyes, and dyes solved in water.*

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The Color Pollution Removal (Acid Red 88) of Industrial Waste Waters by Electrocoagulation Method

Hassan Zhian [α], Bahrooz Khezry [σ] & Chalak Azimi [ρ]

Abstract- The aim of this study was to investigate the decolorization of Acid Red 88 (AR88) using electrocoagulation and photo electrocoagulation techniques. Chemical dyes have the most practical usage in different industries, having an essential role in most water industries, they have a high solubility in water, thus, water wastes contain a high level of these dyes. An effective way of eliminating these dyes is electrocoagulation The effect of operational parameters such as initial dye concentration, electrolysis time and electrolyte concentration was studied. The electrochemical cell comprised Al as cathode and Fe as anode which were placed inside a container having a low pressure mercury lamp at the top. 40 mg.L^{-1} of dye solution was withdrawn for each experiment and after adjusting the electrode distance to 15 mm, current density to 41.8 A m^{-2}, different electrolytes at varying concentrations were added and the absorbance was measured at several reaction times. The results showed that electrocoagulation was more effective than photo electro-coagulation using NaBr, KBr, NaCl and KClaselectrolytes and decolorization rate increased with increasing electrolyte concentration. Also the coupled system with NaF electrolyte showed better decolorization rate than electrocoagulation, but the decolorization rate was higher at low concentrations of electrolyte. Therefore, it is concluded that electrocoagulation was more effective than coupled system in most cases and type of electrolyte plays an important role since employed NaCl/KCl would enhance the decolorization rate considerably.

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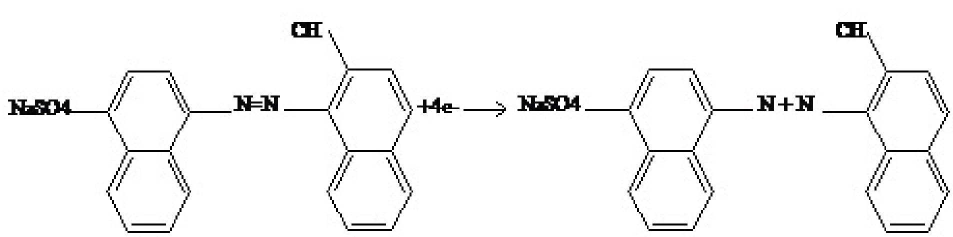
I. Introduction

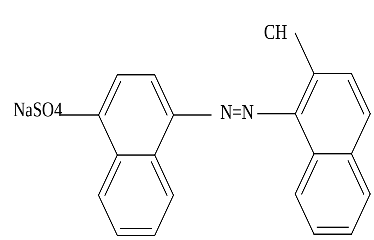
On group of water pollutants are synthesized compounds such as solvents, detergents, dyes, pesticides, food additives, and drugs.[1-2] Since the chemical compounds are increasingly being used, their effects on environment, the risk of their presence in the environment and the efficient methods of their eradication should be studied.[3]

In textile industry where a lot of water is used in the process, water waste purification is a considerably important issue therefore, the plans are made to provide the chance for the industries to increasingly enjoy The science and researches regarding water purification solution, worthy to mention in Azonic.[4-5]

Dyes which contain Azo (-N=N-) if in any condition this factor breaks down, its dye is eliminated[6], as an example:



Red acid 88(AR88)is a mono azo dye and member of acidosis dyes in water solution with molecular formula of $C_2O\ H_{13}\ N_2\ O_4$ SNA and molecular mass of 400 g.mol^{-1}. This acid (C.I.No.15620) has the following formula structure:



Coagulation in which the colloidal particles are destabilized and ready to deposit, start sedimentation by complete coagulation of large particles produced by Vander Waals forces, coagulation is the best method to

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eliminate water waste colloidal particles which would be possible by using some specific chemicals.[7-8] The reduction of colloidal particles is due to the decrease of repulsive potential of electrical doubled layer and the electrical solution effect of iron or aluminum electrodes where releases iron or aluminum irons in anode, and hydrogen gas in cathode. Hydrogen helps flock particles float on the surface of water, a process called electrical congregation.[9] Coagulation is based on the addition of a coagulant to water to construct the nucleus of coagulation and deposit the impurities. Dye sediment process is essentially due to electro static attraction, for motion of unsolder dye complexes, and superficial physical absorption on the sediments produced by adding the coagulant.[10-11]

II. Ion Elimination Mechanism by Electrical Coagulation Process

In electrical coagulation, the sacrificial electrodes are mostly iron or aluminum and the reaction mechanism is summarized as follow,

$$Fe^{3+}{}_{(aq)} + H_2O_{(l)} \rightarrow Fe(OH)^{2+}{}_{(aq)} + H^+{}_{(aq)}$$

$$Fe^{3+}{}_{(aq)} + 2H_2O_{(l)} \rightarrow Fe(OH)^{+2} + 2H^+{}_{(aq)}$$

$$F^{3+}{}_{(aq)} + 3H_2O_{(l)} \rightarrow Fe(OH)_{3(s)} + 3H^+{}_{(aq)}$$

Ferric Ions, in alkali environment can also create $Fe_2(H_2O)_6$'$Fe(H_2O)_8(OH)_2{}^{4+}$, $Fe(H_2O)4(OH)^{+2}$, $Fe(H_2O)_5OH^{2+}$, $Fe(OH)^{-4}$‘ $Fe(OH)_2{}^{4+}$.

By hydroxide ions where consequently all convert to $Fe(OH)_3$.[12] ($CrO_4{}^{-2}$) Cr^{+6} Ions existing in water wastes can also be eliminated by electro coagulation using iron as sacrificial anode.[13] Fe^{2+}ion effected by electro oxidizations of iron anode in alkali environment would reduce Cr^{6+} to $Cr^{3+}$and would itself convert to Fe^{3+} as shown in the following reaction:

$$CrO^{2-}{}_{4(aq)} + 3Fe^{2+}{}_{(aq)} + 4H2O_{(l)} + 4OH^-{}_{(aq)} \rightarrow 3Fe(OH)_{3(s)} + Cr(OH)_{3(s)}$$

$$CrO_4{}^{2-}{}_{(aq)} + 3Fe^{2+}{}_{(aq)} + 4H_2O_{(l)} \rightarrow 3Fe^{3+}{}_{(aq)} + Cr^{3+}{}_{(aq)} + 8OH_{(aq)}$$

III. Dye Elimination Mechanism in Electro Coagulation

Depending on pH of the environments, and the type of ions existing in the solution there can be different mechanisms to explain bilateral effects between dye molecules and the dye produced by iron and aluminum ion water treatment for example $Fe(OH)_n$ gelatin suspensions which are produced due to electrochemical process can separate the pollutants from the water wastes by complexitizing and surface absorption as well as electrostatic attraction caused by coagulation and floatation.[14-15] In complexitizing it is assumed that the pollutant (ex.dye molecule) is attached to the metal Ion as a ling. Surface absorption mechanism in high ph environment and sediment mechanism in ph environment lower than 6.5 are considered.

a) Sedimentation Process

$$Dye + mono\ meric\ Fe \rightarrow [Dye\text{-}monomeric\ Fe]_S$$

$$Dye + poly\ meri\ Fe \rightarrow [Dye\text{-}poiymeric\ Fe]_S$$

b) Surface Absorption Process

$$DyE + Fe(OH)_{n(s)} \rightarrow\rightarrow [sludge]$$

$$[DyE\text{-}polymeric\ Fe]_{(s)} + Fe(OH)_{n(s)} \rightarrow\rightarrow\rightarrow [sludge]$$

IV. Methods

All experiments have been accomplished in none continues reactor at 297^0K in 500ml solution using iron and aluminum and graphite electrodes. Considering low conductivity of the sample ordinary salt was used to increase electrical conductivity of red acid 88 water solutions. In order to control the current and apply wattage a rectifier was used. In the experiment the reactors content was transferred to a scaled cylinder for the flocks to deposit. The produced clots were small at first and stayed at the top of the column, but after a while these clots joined each other and erected massive coagulations and started to deposit and the dying substance observed by coagulation was eliminated, then the solution in the upper part of cylinder was filtered and measured, in order to evaluate the efficiency of electro coagulation in dye elimination. Using before and after electrolyze absorption measure meant by UV/Vis photometer spectrum and remaining dye density calibration chart, cells have been observed in different forms.

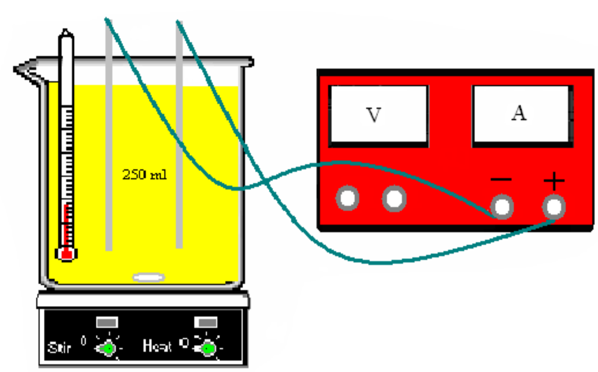

Figure 1 : Electrocoagulation apparatus

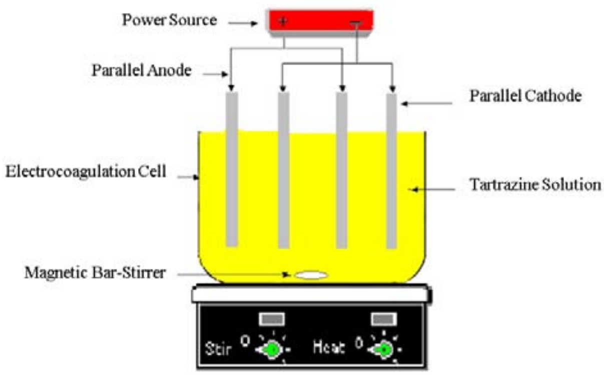

Figure 2 : Bench-scale EC reactor with monopolar electrodes in parallel connections

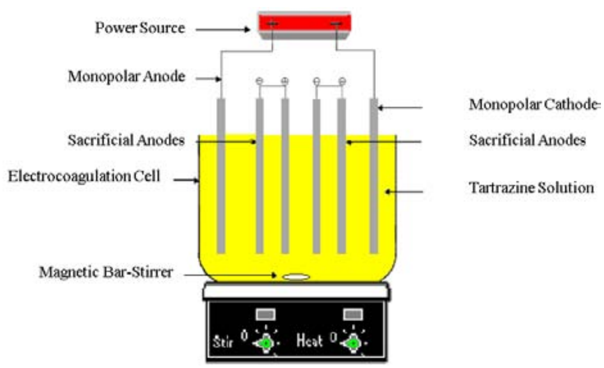

Figure 3 : Bench-scale EC reactor with monopolar electrodes in series connections

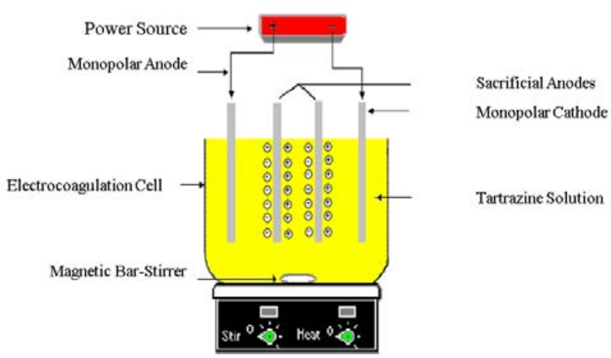

Figure 4 : Bench-scale EC reactor with bipolar electrodes in parallel connections

V. Method of Providing the Results

In all experiments, in order to measure the elimination percentage the following formula has been used:

$$CR\% = \frac{C_0 - C}{C_0} * 100$$

In which C_o is primary density C is the dye solution at the end of each experiment.

Study of the results would suggest the most efficient electro coagulation is achieved where in a cell containing mono polar electrodes in series formation with (sacrificial aluminum and iron anode and 304 steel cathode) iron is used as anode and aluminum as cathode or iron as anode and graphite as cathode the preference of iron anode over aluminum anode can be due following two reasons.

A: elimination process using aluminum anode is basically accomplished by electro coagulation, but with iron anode both electro coagulation and electro oxidization are involved.

B: the absorption capacity of pollutant on Aluminum hydroxide clots are less than iron hydroxide clots the result of experiment showing the effect of current density on AR88 elimination in an electrochemical cell in both series and parallel formations were compared and suggests that the series formation of monopolar electrodes is much more efficient in dye elimination and it can be because the series connected electrodes produce more resistance, thus, needs more potential difference to create current. More potential difference induces stronger field which consequently applies more power on the ions inside the field, as a result their velocity in reduction of oxidization and enhancement of AR88 ions will increase dye elimination efficiency.

In this formation of electrodes, more flocks are produced and aluminum hydroxide flocks are relatively large with less density and easily are floating and separated.

Table 1 : The effect of sodium chloride density on elimination efficiency

Time Density	0		2			4			6			8		
NaCl	A	C_{Dye}	A	C_{Dye}	CR%	A	C_{Dye}	CR%	A	C_{Dye}	CR%	A	C_{Dye}	CR%
100	1.296	42	0.795	20.78	52.75	0.452	9.40	78.09	0.045	0	100	0.02	0	100
200	1.274	41.33	0.515	12.30	72.98	0.428	8.70	79.45	0.052	0	100	0.015	0	100
300	1.281	41.54	0.741	19.15	56.22	0.621	14.52	65.20	0.15	0.25	99.50	0.019	0	100
400	1.251	40.63	0.849	42.42	46.95	0.427	8.64	79.22	0.052	0	100	0.008	0	100
500	1.249	40.60	0.799	20.90	50.74	0.539	12.11	70.62	0.047	0	100	0.016	0	100
600	1.280	41.51	0.766	19.90	54.34	0.466	9.92	76.78	0.063	0.36	99.20	0.013	0	100

Table 2 : the effect of current density on elimination efficiency

Density	A	C_{Dye}	CR%
40	0.754	22.51	47.54

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60	0.381	7.34	84
80	0.075	0.98	98.58
100	0.015	0	100
120	0.03	0	100
140	No transition		

Table 3 : The effect of solution temperature on elimination efficiency

T(K)	288		293		298		303		308	
Time Electrolyze	A	CR%	A	CR%	A	CR%	A	CR%	A	CR%
2	0.89	39.07	0.947	41.51	0.784	53.56	0.858	57.08	0.858	57.08
4	0.562	69.95	0.528	72.47	0.440	78.72	0.495	82.61	0.045	100
6	0.016	100	0.521	100	0.015	100	0.028	100	0.025	100
8	0.011	100	0.012	100	0.009	100	0.008	100	0.013	100

Table 4 : The effect of electrodes distance on elimination efficiency

Distance(cm)	A	C_{dye}	CR%
0.5	0.115	1.8	96.25
0.75	0.079	0.92	98.97
1	0.037	0	100
1.25	0.042	0	100
1.5	0.052	0	100
1.75	0.055	0.08	100

Table 5 : The effect of electrolyses time on elimination efficiency

Time Electrolyze (min)	A	$C_{day}(mgL^{-1})$	CR%
0	1.473	41.32	0
2	0.515	12.30	81.98
4	0.466	9.91	85.65
6	0.052	0	100
8	0.014	0	100
10	0.008	0	100

Table 6 : The effect of AR88 primary density on the efficiency of elimination

Time electrode (min)	2			4			6			8		
Concentration mgL^{-1}	A	C_{Day}	CR%	A	C_{Day}	CR%	A	C_{Day}	CR%	A	C_{Day}	CR%
20	0.535	15.90	41.50	0.255	5.34	74.80	0.016	0	100	0.012	0	100
40	0.515	15.30	75.75	0.466	9.9	76.47	0.037	0	100	0.015	0	100
60	1.363	38	38.5	0.898	22.00	62.38	0.044	0	100	0.018	0	100
80	1.642	49.18	40.36	1.668	47.24	43.40	0.198	5.63	95.21	0.072	0.08	100

Table 7 : The effect of primary phone limitation efficiency

Electrolyze time(4 min)			6 min			8 min		
pH	A	CR%	pH	A	CR%	pH	A	CR%
2.4	0.038	12	2.35	0.005	100	2.64	0.005	100
2.41	0.193	89.65	3.4	0.084	96.98	3.68	0.011	100
4.55	0.288	84.43	4.85	0.208	79.97	5.69	0.023	100
5.65	0.496	68.75	5.85	0.329	78.28	6.69	0.015	100

Table 8 : The effect of electrodes on elimination efficiency

λ_{max}= 254		λ_{max}= 508			Cathode material	Anode material
A	A_0	CR%	$C_{Dye}(mg\ L^{-1})$	A		
1.223	0.841	69.17	13.33	0.449	Fe	Fe
0.398	0.778	95.02	3.39	0.122	Al	Al
0.448	0.848	98.8	0.89	0.072	Al	Fe
0.382	0.820	96.07	1.98	0.108	Fe	Al

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0.46	0.853	99.68	0.19	0.049	C	Fe
0.430	0.866	94.32	2.34	0.129	C	Al

Table 9 : The effect of electrolyze time on elimination efficiency regarding wave length 254 nm using iron a node and Aluminum cathode.

$$(C_o[Dye] = 40\ mg\ L^{-1}, C_{NaCl} = 200\ mg\ L^{-1},$$

$$[i] = 100\ Am^{-2}, d = 1.5\ cm, Fe/Al\ Anode/Cathode)$$

A	Electrolyze time(min)
0.873	0
0.307	5
0.303	10
0.303	15
0.319	30
0.339	45
0.430	60
0.314	75
0.333	90
0.348	105
0.398	120
0.391	135
0.381	150

VI. CONCLUSION

Considering the results obtained from the experiments of AR88 electro coagulation. The following outcomes can be achieved:

1. Electro coagulation, in comparison with other water treatment facilities is cheaper and more efficient in dye elimination of solutions containing dye eliminator AR88.
2. Electrocoagulation does not need much chemicals.
3. Dye elimination rate depends on factors such as current density, time of electrolyze, solution primary density, solution primary pH, experimented solution conductivity, time connection, distance between electrodes, solution temperature, stiring, type of electrodes and their formation.
4. In this method where 500ml solution containing.

Nacl 40mg AR88+200mg in electro coagulation by an electrochemical cell with iron anode and aluminum cathode in pH of about 6.7 and sediment time of 5 minutes and current density of 100 Am^{-2}, temperature of 298^0k (24^0C) and electrodes 1.5 centimeters apart and 6 minutes electrolyses time 100 dye is eliminated, looks to be an appropriate method of treatment of water wastes containing AR88.

1. In AR88 solution coagulation ordinary salt is to be the best electrolyte.
2. In AR88 electro coagulation maximum absorption reduction is at wave lengths of 245nm and 508nm,in an electro coagulation cell with iron anode and Aluminum cathode, and iron anode and graphite cathode.

   In an electrocoagulation cell with iron anode and cathode, and aluminum sacrificial electrodes, in series formation and an electro coagulation containing iron electrodes and aluminum sacrificial electrodes in parallel formation shows maximum absorption reduction too.
3. Considering high effects of different factors such as temperature, sediment stay time on AR88 elimination efficiency, it seems dye elimination is mostly done by physical surface absorption and complex formation is less involved.

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