Evaluation of Electro Coagulation Process Performances for Decolorization of Alizarin Saphirol Containing Solution

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Electro coagulation represents a good alternative to the conventional treatment techniques for dye containing wastewaters. In this paper, electrochemical coagulation efficiency (expressed in terms of colour removal degree) with aluminum and iron sacrificial anodes has been tested on an Alizarin Saphirol containing solution, an acid dye that belongs to antraquinone class. The influence of electrolysis time, operating current density, pH value and anodic material type on process performances was investigated. It has been concluded from experimental results analysis that the solution can be effectively treated using electro coagulation. The maximum removal efficiency, 99% was recorded at 200 A/m^2, pH=6, after 12 min.

Keywords: electro coagulation, sacrificial anode, Alizarin Saphirol, antraquinonic dye, wastewater treatment.

Water and energy have been identified by Smalley as two top challenges for 21st century [1]. Deteriorations in the quality of source and increased demand coupled with more stringent water quality regulations have resulted in an increase in the implementation of new treatment techniques [2].

Textile industries are considered as one of the most polluting in terms of volume and complexity of wastewater. Effluents from dyeing industry are not only colored but also contain high amounts of organic matter and dissolved solids [3]. Dyes are gradually emerged as a class of anthropogenic organic substances that pose a serious threat to the environment and human health. Furthermore, dye effluent may contain chemicals that are toxic, carcinogenic or mutagenic for microbes and fish species [4].

Residual dyestuffs, although only present in small amounts, are sources of aesthetic pollution and determine water eutrophication, interfere with light penetration that disturbs biological processes and thereby have to be removed from wastewater before being discharged [5].

At this moment, the dye effluents are treated by several biological, chemical and physical processes. Although biological degradation is one of the most economic processes, the disadvantages generated by pollutants characteristics (low biodegradability, molecules of refractive nature, high biochemical stability, relative high molecular weight) make this option impossible to take into account [6, 7].

In this context, electro coagulation (EC) usage appeared as a suitable alternative to classic treatment methods. Electro coagulation is an electrochemical method used for natural and wastewater treatment, based on metallic ions generation by electrolysis, which act as destabilization agents in the coagulation process. The most frequently used electrode materials are: iron, stainless steel, aluminum and graphite [8, 9].

When a direct current (DC) is applied from an external power source the following electrolysis reaction is expected to occur in the vicinity of the electrodes [10]:

Anode:

$$M_{(s)} \rightarrow M_{(aq)} + ne^- \quad (1)$$

$$2H_2O_{(l)} \rightarrow 4H^+ + O_{2(g)} + 4e^- \quad (2)$$

Cathode:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \quad (3)$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^- \quad (4)$$

If M = Al or Fe, the generated $Fe^{3+}_{(aq)}$ or $Al^{3+}_{(aq)}$ ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. For example, Al^{3+} ions on hydrolysis may generate: $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)^{2+}$, and the hydrolysis products may form many monomeric and polymeric species such as: $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)^-_4$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ over a wide range of *p*H. Similarly, ferric ions generated by electrochemical dissolution of iron anodes may form monomeric ions, $Fe(OH)_3$ and polymeric hydroxy complexes, namely: $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5OH^{2+}$; $Fe(H_2O)_4(OH)^+_2$, $Fe_2(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{4+}$ depending on the pH of the aqueous medium [11-13]. The dye containing solution decolourization by electro coagulation has become a very attractive method in recent years.

The influence of the operational parameters (current density, electrolysis time and initial *p*H) on the electro coagulation efficiency of treatment of textile wastewater containing reactive dyes was evaluated. The experiments were carried out using a 2^3 full factorial statistical analysis in order to establish the optimum current density and electrolysis time for achieving a 90-95% colour removal efficiency [14].

The removal of Acid yellow 36 from an aqueous solution by the electro coagulation method using iron electrodes has been investigated by Kashefialast et al. The authors established that the electro coagulation process has been

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influenced by the following parameters: current density, initial *p*H, electrolyte concentration and electrolysis time. The results showed that at 50 ppm initial dye concentration, the dye was effectively removed at *p*H range 7 – 9, time of electrolysis of approximately 6 min, 127,8 A/m^2 current density, achieving complete decolourization [15].

A bipolar packed bed electrochemical reactor consisting of soluble electrodes was used in the batch mode to remove dye and 100% color removal was achieved in relatively short time (3-5 min) the corresponding power consumption being 2.24 kWh/m^3 [16].

An electro coagulation system with aluminium electrodes for decolourization of Remazol Red 133 dye solution was proposed. The results obtained showed that rising the *p*H from 5 to 9 lead to a decrease of the color removal efficiency from 90 to 70%, the same situation was found when the concentration increased from 100 to 1000 mg/L [17].

The main objectives of the study were: to establish the operational parameters (*p*H, current density, electrolysis time and anodic material type) influence on electro coagulation process efficiency, to find the best operating conditions and to evaluate the electro coagulation performances for decolourization an Alizarin Saphirol containing solution.

Experimental part

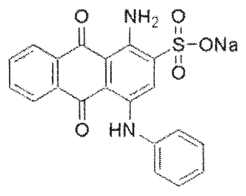
Alizarin Saphirol (acid blue 25) dye was provided by Sigma-Aldrich and used as received without further purification. Alizarin Saphirol is an antraquinonic acid dye, soluble in water, used to colour the nylon, cotton, woll fibers, in food industry, deteregents industry, cometics, ink industry. In cosmetics it is used in semi – permanent and temporary hair colouring products at concentrations up to 0.5% and as colorant in other cosmetic products which have short contact with the skin [18].

The electro coagulation unit used consisted of an electro coagulation reactor (a jar made of theromoresistent glass with 100 mm x 180 mm dimensions), four electrodes (two anodes and two cathodes) with identical dimensions 45 ×55 ×20 mm placed in parallel connection at 25 mm constant distance, a stabilized DC power supply and a magnetic stirrer. A short description of the electro coagulation principle is presented in figure1 [19].

Experiments were carried out with 10^{-4}M initial concentration of Alizarin Saphirol. At the begining of each run, 700 mL of solution was prepared and placed in the electrochemical cell, the electrodes were immersed in solution and connected to a Mastech HY3005D DC power supply. The *p*H was adjusted to desired value using 6% H_2SO_4 and respectively, 0.1N NaOH solutions and during the whole period of experiments was monitored using a Consort C380 pH-meter (0.01 *p*H resolution, Pt1000 sensor).

At the end of the electrocoagulation experiments, before analysis, samples were filtred using white ribbon filter paper. The dye concentration was determined at the wavelenght coresponding to the maximum absorbance (600 nm) using a UV-Vis double beam spectrophotometer Cintra 5 (spectral range 190-1100 nm).

Table 1
STRUCTURE AND GENERAL CHARACTERISTICS OF ALIZARIN SAPHIROL DYE

Chemical structure	
Chemical formula	$C_{20}H_{13}N_2NaO_5S$
Molecular Weight (g/mol)	416.39
Commercial name	Acid Blue 25
C.I Number.	62055
λ_{max} (nm)	600
Appearance	dark blue powder
Water solubility (g/L)	40
LC_{50} for fish (mg/L)	12 (96 hours)

Note: LC_{50} = lethal concentration 50

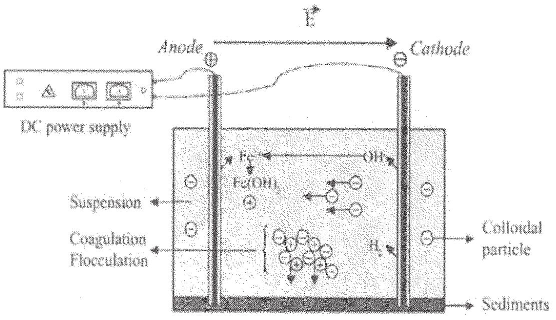


Fig.1. Schematic representation of the electro coagulation principle

The calculation of color removal eficiency after electrocoagulation treatment was performed using the folowing formula:

$$R(\%) = \frac{C_0 - C}{C_0}$$

where C_0 and C represent the concentrations of dye before and after electro coagulation in mg/L, respectively.

Results and discussion

The influence of initial pH value on color removal efficiency

The pH value represents an important parameter that influences the EC process performances because determines the species formed in the system [20]. In order to establish its influence on EC process, the samples were adjusted to the desired *p*H value for each experiment by using sulphuric acid or sodium hydroxide solutions. The influence of initial *p*H was studied within the range 2-10. Figure 2 shows the removal efficiency of Alizarin Saphirol as a function of initial *p*H. The experiments on aluminum electrodes were done in the following conditions: electrolysis time, (τ) = 90 min, $C_0 = 10^{-4}$M, interelectrode distance (d) = 2.5 cm, stirring rate = 200 rpm, current density (i) = 150 A/m^2 and are presented in figure 2 (a). From the figure it can be seen that for *p*H = 2 and 10 the color removal efficiency had an interesting behaviour. At *p*H = 2, after the first 10 min a 75% removal efficiency was recorded, after that, the curve had a constant increase until reached 95%, after 70 min . At *p*H = 10, in the first 45 min the curved showed a slow and uniform growth in the first 45 min, afterwards, at 60 min a suddently growth from 40 to 80% was observed, in the end, after 90 min the color removal efficiency being 90%.

The experiments on iron electrodes were done in the following conditions: τ = 12 min, $C_0 = 10^{-4}$M, d = 2.5 cm, stirring rate = 200 rpm, i = 150 A/m^2 and are presented in figure 2 (b). It can be observed that in the iron electrodes case, the time necessary to obtain 98% colour removal efficiency is much lower (almost 7 times) than in the case of aluminium electrodes. Besides this, in the *p*H range 2-8, after 8 min electrolysis time the color removal efficiency was 90%. For initial *p*H range 4 - 8, the curve look is similarly for both anodic materials used. From results analysis it can be concluded that for aluminum electrodes, the best results were obtained at *p*H = 2, and for iron in the range 6-8.

During the electro coagulation process, the initial *p*H value changes depending on the initial value and anodic material used [21]. The evolution of the *p*H during the electrochemical coagulation with aluminum electrodes, τ= 90 min, $C_0 = 10^{-4}$M, d = 2.5 cm, stirring rate = 200 rpm, i = 150 A/m^2 is represented in figure 3 (a).

As it can be seen, at initial *p*H values < 8, the final *p*H rises, while for initial *p*H > 8, final *p*H diminishes. The results obtained for iron electrodes, τ = 12 min, $C_0 = 10^{-4}$M, d = 2.5 cm, stirring rate = 200 rpm, i = 150 A/m^2, are presented in figure 3 (b). In the case of iron electrodes, the final pH it is always higher that the initial one, the difference between initial and final value is diminishing for *p*H > 8 [22].

The *p*H variation in the case of aluminum electrodes it is attributed to the fact that for initial *p*H values between 4 and 9, the solution stabilizes at nearly constant value around 9 due to buffering capacity of complex nature of aqua $Al^{3+}/Al(OH)_3$ system [23].

The influence of current density on color removal efficiency

Current density represents the most important parameter in the electro coagulation process because directly determines the reaction rate control in the reactor. Besides this, current density influences both coagulant dosage and bubble generation rates, as well as strongly influencing both solution mixing and mass transfer at the electrodes[24]. In order to evaluate the current density influence on color removal efficiency of Alizarin Saphirol, during the experiments, the current density was varied between 50-200A/m^2. The results obtained for aluminum

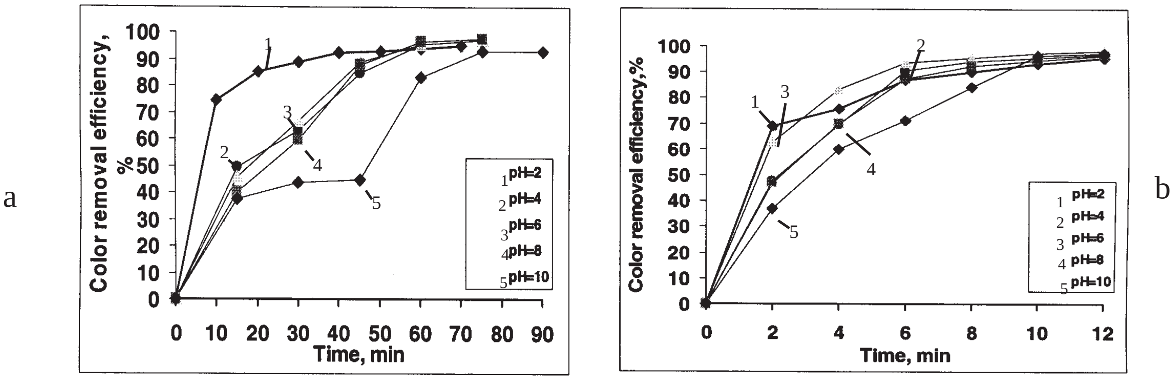


Fig.2. Effect of initial pH value on the removal efficiency of Alizarin Saphirol

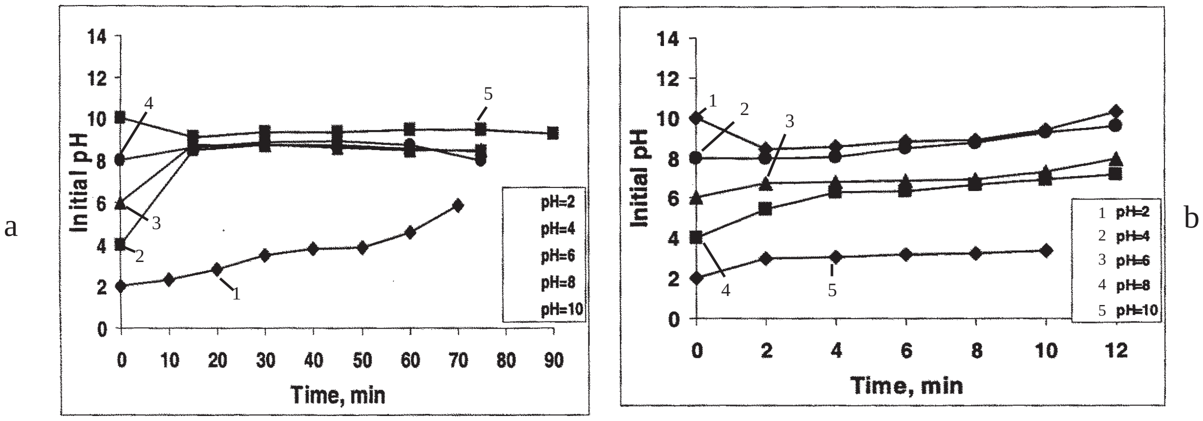


Fig.3. Evolution of pH during electro coagulation

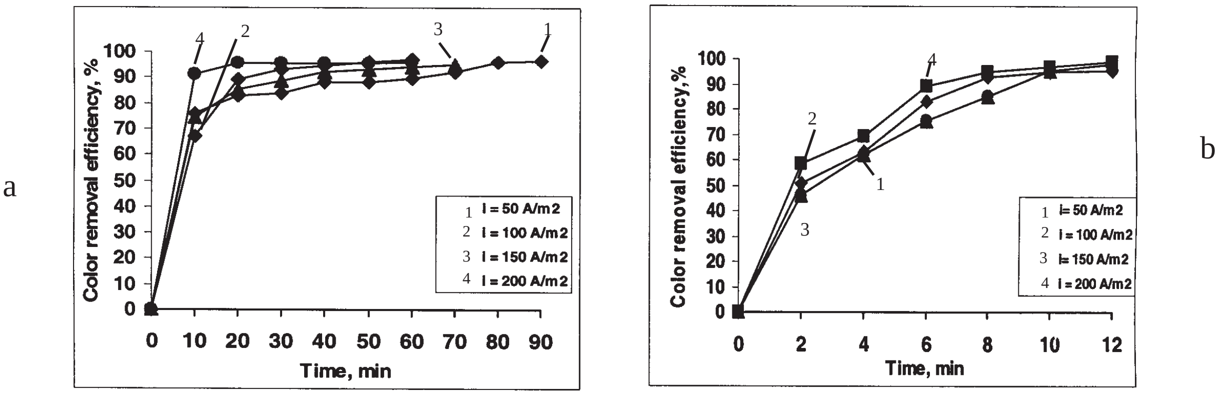


Fig.4. Effect of current density on removal efficiency of Alizarin Saphirol

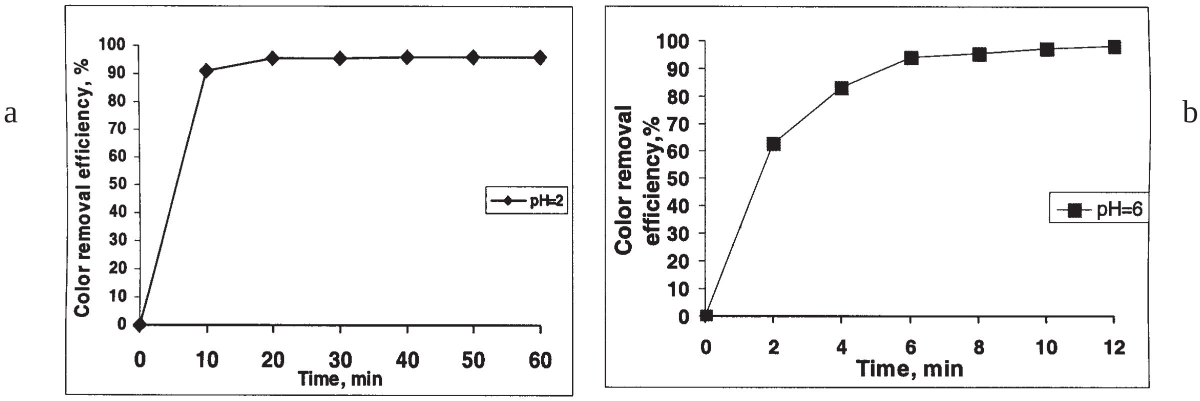


Fig.5. Effect of electrolysis time on color removal efficiency of Alizarin Saphirol

electrodes, τ = 90 min, C_0 = 10^{-4}M, d = 2.5 cm, stirring rate = 200 rpm, i = 150 A/m^2, pH_i = 2 are presented in figure 4 (a). From the graph it can be observed that in order to obtain 90% color removal efficiency in only 10 min it is necessary to apply a current density of 200 A/m^2, while for 50 A/m^2 the same color removal efficiency is obtained after 90 min.

The results obtained for iron electrodes, τ = 12 min, C_0 = 10^{-4}M, d = 2.5 cm, stirring rate = 200 rpm, i = 150 A/m^2, pH_i = 6 are presented in figure 4 (b). In this case, at current density 100 A/m^2, the color removal efficiency recorded after 8 min was 90%. Because current density applied to the electrolytic cell determines of Al^{3+} or Fe^{2+}/Fe^{3+} released during the anodic dissolution it can be concluded, that for iron electrodes it is not necessary to work at high current density values in order to obtain satisfactorily results. Anyway it is advisable to limit the current density in order to avoid excessive oxygen evolution as well as to eliminate other adverse effect like heat generation [25].

The influence of electrolysis time on colour removal efficiency

Reaction time is one of the parameters with high influence about electrochemical process efficiency. Electrolysis time determines generation rate and concentration of Fe^{2+} /Fe^{3+} respectively Al^{3+} ions and hydroxides released from anodes [26]. The ions generated in the system initiate particle charge neutralization and coagulation process. In order to be able to identify the influence of electrolysis time on EC performances, the current density and *p*H value were held constant [27].

The obtained results are showed in figure 5 (a) and (b) as dependence of colour removal efficiency on electro coagulation time. In figure 5 (a) are presented the results obtained with aluminum electrodes, τ = 60 min, C_0 = 10^{-4}M, d = 2.5 cm, stirring rate = 200 rpm, i = 200 A/m^2, pH_i = 2 and is obvious that after 10 min, the colour removal efficiency is 90%, in the following 50 min the graph displays an uniform and constant growth, after 60 min the colour removal being 98%.

For iron electrodes, τ= 12 min, C_0 = 10^{-4}M, d = 2.5 cm, stirring rate = 200 rpm, i = 200 A/m^2, pH_i = 6 the results are presented in figure 5 (b). It can be observed that in the first 6 min the colour removal efficiency reaches 90%, afterwards, the graph exhibits a constant growth, after 12 min the maximum removal efficiency being 99.00%. In the end, after analyzing the results obtained for iron and aluminum electrodes, it can be concluded that in only 10 min for both materials was recorded a satisfactorily value (90%) for colour removal efficiency.

The influence of anodic material on colour removal efficiency

In any electrochemical process, the electrode material has significant influence on the treatment efficiency. Therefore, appropriate selection of the electrode material is important. The electrode material for treatment of water and wastewater should also be non-toxic to human health and environment. Aluminum and iron were chosen as electrode material because these are non-toxic and easily available [28].

In figure 6 is presented the influence of anodic material on colour removal efficiency for Alizarin Saphirol dye, C_0 = 10^{-4}M, d = 2.5 cm, stirring rate = 200 rpm, i = 200 A/m^2, pH_i = 6. The results clearly show that iron electrodes were more effective than aluminium electrodes. As it is seen, for iron electrodes after 5 min, the colour removal efficiency was 90%, while for aluminum, after 30 min the value was 80%. The plausible reason for lower colour removal efficiency in the case of aluminium electrodes in comparison with iron could be explained considering the insufficient ability of hydrous aluminium oxide to adsorb and interact with Alizarin Saphirol molecules.

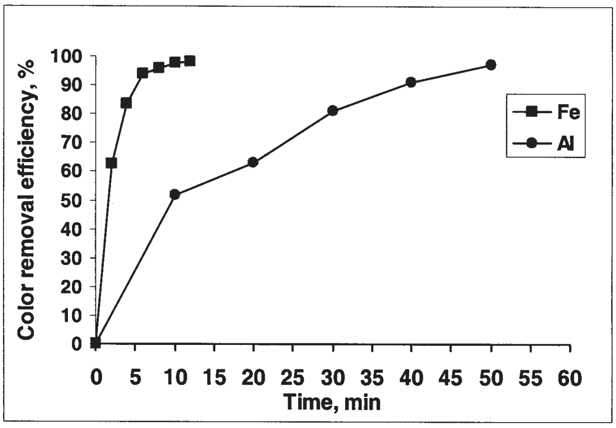


Fig.6 Effect of anodic material on color removal efficiency of Alizarin Saphirol

Conclusions

In this paper, electro coagulation process was used to remove colour from Alizarin Saphirol aqueous solution. The influence of various parameters such as: initial *p*H value, operating current density, time of electrolysis, anodic material on colour removal efficiency was studied.

Experimental results analysis revealed that It can be observed that in the iron electrodes case, the time necessary to obtain 98% colour removal efficiency is much lower (almost 7 times) than in the case of aluminium electrodes.

From results analysis it can be concluded that for aluminum electrodes, the best results were obtained at *p*H = 2, and for iron in the range 6-8. The results clearly show that iron electrodes were more effective than aluminium electrodes.

References

1.MOLLAH, Y.A, MORKOVSKY, P., GOMES, J.A.G., KESMEZ, M., PARGA, J., COCKE, D.L., J. Haz. Mat., 2004, **B114,** p 199

2.BAGGA, A., CHELLAM, S., CLIFFORD ,D.A., J.Mem.Sci., 2008, **309**, p 82

3.SANROMÁN, M.A., PAZOS, M., RICART, M.T., CAMESELLE, C., Chemosphere 2004, **57**, p. 233

4.MUTHUKUMAR, M., KARUPIAH ,M.T., RAJU ,G.B, Sep.Pur.Tech., 2007, **57**, p. 198

5.DUMITRU, M., SAMIDE, A., PREDA, M., MOANTA, A., Rev.Chim. (Bucharest), **60**, no.9, 2009, p. 957

6.PANIZZA ,M., BARBUCCI, A., RICOTTI, R., CERISOLA, G, Sep.Pur.Tech., 2007, **54,** p. 382

7.BOUSHER, A., SHEN, X., EDYVEAN, R., Removal of coloured organic matter by adsorptio on low-cost waste materials Water.Res., 1997, **31,** p. 2084

8.DEMIREV, A., NEMOV, V, Ozone:Sci.Eng., 2005, **27**, p. 475

9.CAPRARESCU, S., VAIREANU, D-I., COJOCARU, A., MAIOR, I., SARBU, A., Rev. Chim. (Bucharest), **60,** no.7, 2009, p.673

10.KABDAŞLI, I., VARDAR, B., ARSLAN-ALATON, I., TUNAY, O., Chem.Eng.J., 2009, **148**, p. 89

11.BAYRAMOGLU M., KOBYA, M., O.T.Can, M.Sözbir, Sep.Pur.Tech., 2004, **37**, p. 117

12.CAN, O.T., KOBYA, M., DEMIRBAS, E., BAYRAMO, LU M., Chemosphere, 2005, **62**, p. 181

13.MURUGANANTHAN, M., RAJU-BHASKAR, G., PRABHAKAR, S., Sep.Purif.Tech., 2004, **40,** p 69

14.ALINSAFI, A., KHEMIS, M., PONS M.,N., LECLERC, J.P., YAACOUBI, A., BENHAMMOU A., NEJMEDDINE A., Chem.Eng.Proces., 2005, **44**, p 461

15.KASHEFIALAST, M., KHOSRAVI, M., MARANDI, R., SEYYEDI, K., Int.J.Sci.Tech., 2006, **2,** p. 365

16.OGUTVEREN, U.B., GONEN, N., KOPARAL, S., J.Environ.Sci.Health., 1992, **A27**, p. 1237

17.CAN, O.T., BAYRAMOGLU, M., KOBYA, M., Ind.Eng.Chem.Res., 2003, **42**, p. 3391

18.*** European Comission, Health &Consumer Protection Directorate – General, Public Health and Risk Assesment, Scientific Committee on consumer products, Opinion on Acid Blue 62; 2005

19.LARUE, O., VOROBIEV ,E., Int.J.Miner.Process., 2003, **71**, p 1

20.EMAMJOMEH, M., SIVAKUMAR, M., J.Env.Man., 2009, **90** p. 1663

21.RAJESHWAR, K., IBANEZ, J., In: Tarr, Matthew A., (Ed.), Chemical Degradation Merhods for wastes and pollutants. Academ.USA Press, 1997, p. 720

22.NI'AM, M.F., OTHMAN, F., SOHAILI, J., FAUZIA, Z., Malays.J.Analy.Sci., 2007, **vol.11**, pp 198-205;

23.MATTESON, M.J, DOBSON, R.L., GLEEN, R.W., KUKNOOR, N.S., Waits W.H., Clayfield E.J., Colloids Surf., A Physicochem.Eng.Asp., 1995, **104**, p. 101

24.SONG, S., HE, Z., QIU ,J., XU, L., Chen J., Sep.Pur.Tech., 2007, **55**, p. 238

25.KOBYA, M., DEMIRBAS ,E., CAN O.T., BAYRAMOGLU, M., J. Haz. Mat. 2006, **B132,** p. 183

26.HOLT, P., BARTON, G., MITCHELL, C., Chemosphere, 2005, **59,** p. 355

27.MOLLAH M,.Y., PATHAK, S.R., PATIL, P.K., VAYUVEGUL,A M., AGRAWAL, T.S., GOMES, J.A.G., KESMEZ, M., .COKE, D.J, J.Haz.Mat., 2004, **B109**, p. 165

28.DANESHVAR. N., OLADEGARAGOZE. A., DJAFARZADEH. N., J.Haz.Mat. 2006, **B129,** p. 116

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