



## Solar energy integration in the treatment of industrial effluent by coagulation–electroflotation

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Received 15 November 2009; Accepted in revised form 5 February 2010

### ABSTRACT

This work presents the results of the solar energy integration in cardboard industry wastewater treatment generated in the process of machine washing. The treatment process used was coagulation–electroflotation. The effluent COD reduction rate was selected as the follow up parameter. A system of solar collector was also dimensioned in order to supply the insoluble electrodes of the electroflotation unit. In batch mode treatment, current density, pH and coagulant concentration was optimized while in continuous mode, residence time was optimized. A physicochemical characterization of the effluent was done before and after the treatment in order to improve the efficiency of the adopted process. The methodology of experimental research was selected as the experimental research tool.

*Keywords:* Optimization; Electroflotation; Solar collector; Experimental planification

### 1. Introduction

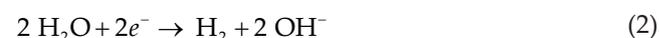
In front of the ecological universal issue and the high cost of traditional energy, industry is confronted nowadays with a real challenge which imposes the search of a new competitive treatment process and a new clean energy resource by respecting environment and natural reserves. In this context, we propose in this study to integrate solar energy in the treatment of wastewaters rich in adhesives and organic dyes, resulting from operation of washing machines of a cardboard manufacture. These effluents present a high rate of COD and suspend solids. In fact, many studies were carried out with an aim of treating industrial effluents charged with colouring and dissolved organic matter by biological way, adsorption on various materials and even by coagulation–flocculation [1–3]. These studies have demonstrated that such treat-

ment processes present major disadvantages [4]. On the other hand, Matis et al. [5] studied the effectiveness of several aeration techniques; they showed that fine bubbles of oxygen produced by electroflotation are very effective in the treatment of effluents presenting a high content COD. Janssen and Koene [6] also showed the effectiveness and the competitiveness of the electrochemical techniques in the treatment of such effluents. The electroflotation which is the electrochemical version of traditional flotation by dissolved air. It is characterized by its mechanism of oxygen and hydrogen bubble formation due to water electrolysis according to these reactions:

Anode reaction: water oxidation



Cathode reaction: water reduction



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This process is very complex because of interaction of several parameters. Indeed, the current density influences directly the number and the size of bubbles [7]. Chen [8] showed that the current density and the mass of bubbles formed are proportional. pH, electrodes arrangement [9], nature of water to be treated and several other parameters are also factors which influence the electroflotation mechanism.

The objective of this work is to optimize the treatment of wastewaters resulting from operation of washing machines of a cardboard manufacture. The selected process is coagulation–electroflotation. A system of solar energy was dimensioned in order to supply the insoluble electrodes of the electroflotation units. The study includes batch and continuous mode. Methodology of experimental research was adopted in order to minimize the number of experiments and to obtain a regression equation linking the COD abatement with operating parameters, which are current density, pH, coagulant concentration and treatment duration [10,11].

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Effluent characterization

The aqueous effluent, object of this study, results from the operation of washing machines of a cardboard manufacture. This effluent is rich in adhesive and organic dyes. A physicochemical characterization was established before the treatment (Table 1).

We note that this wastewater is close to neutrality, it presents high rate of COD and BOD<sub>5</sub> which makes effective an eventual treatment by coagulation–electroflotation.

#### 2.1.2. Electroflotation column

In batch mode, the electroflotation column, represented in Fig. 1, is a cylindrical Plexiglas column of 300 ml volume. It is provided with two insoluble electrodes, titanium coated with ruthenium oxide anode and a stainless steel cathode. The anode occupies the top position and presents perforations allowing the evacuation of bubbles. The gap between electrodes is 5 mm. We also note the presence of sludge and sample treated water

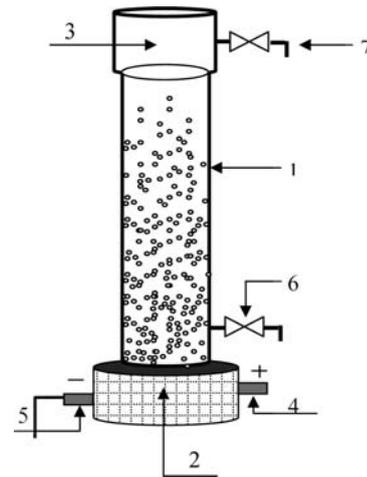


Fig. 1. Electroflotation column in batch mode. 1. Electroflotation column; 2. Base; 3. Sludge recuperator; 4. Anode; 5. Cathode; 6. Treated water recuperator; 7. Sludge evacuator.

recuperators, respectively at the top and the bottom of the column.

In continuous mode, the electroflotation unit shown in Fig. 2 has a total volume of 4.2 L. It is divided into three compartments. The first and the second compartments are provided with two insoluble electrodes which are regularly cleaned. The first one receives the effluent from a tank of coagulation using a piston pump. The effluent then undergoes a primary treatment and it is in co-current movement with bubbles formed at electrodes. After that, the effluent gets through a second compartment by overflow and undergoes its final treatment. The bubbles formed at electrodes and effluent are now in counter current. The treated effluent is evacuated through the third compartment and the sludge formed is eliminated at the top of the unit. The agitation of the storing tank is ensured by a mechanical agitator necessary to avoid a possible decantation of sludge.

#### 2.1.3. Photovoltaic energy system

A photovoltaic system (Fig. 3) was dimensioned in order to supply the insoluble electrodes of the electroflotation columns in batch and continuous mode. This system is composed of a module (12 V, 3 A) made of 36 photovoltaic cells, a STECA SOLARIX regulator and an accumulation battery [12]. The modules are regularly cleaned to ensure maximum performance. This system was dimensioned to ensure a minimal operation duration of 8 h per days, i.e. a daily consumption of 8.8 Ah. The accumulation battery has a capacity 120 Ah; it can ensure endurance higher than 5 days if we fix a maximum discharge threshold of 40%. The level of its electrolytic solution is regularly verified. In order to control both current density and tension at the electrodes, a variator made of a transistor L200C, was conceived.

Table 1  
Physicochemical characterization of an effluent sample

Parameters	Characterization
pH	7.2
COD, mg O <sub>2</sub> /l	3600
BOD <sub>5</sub> , mg O <sub>2</sub> /l	500
Suspended solids, mg /l	266

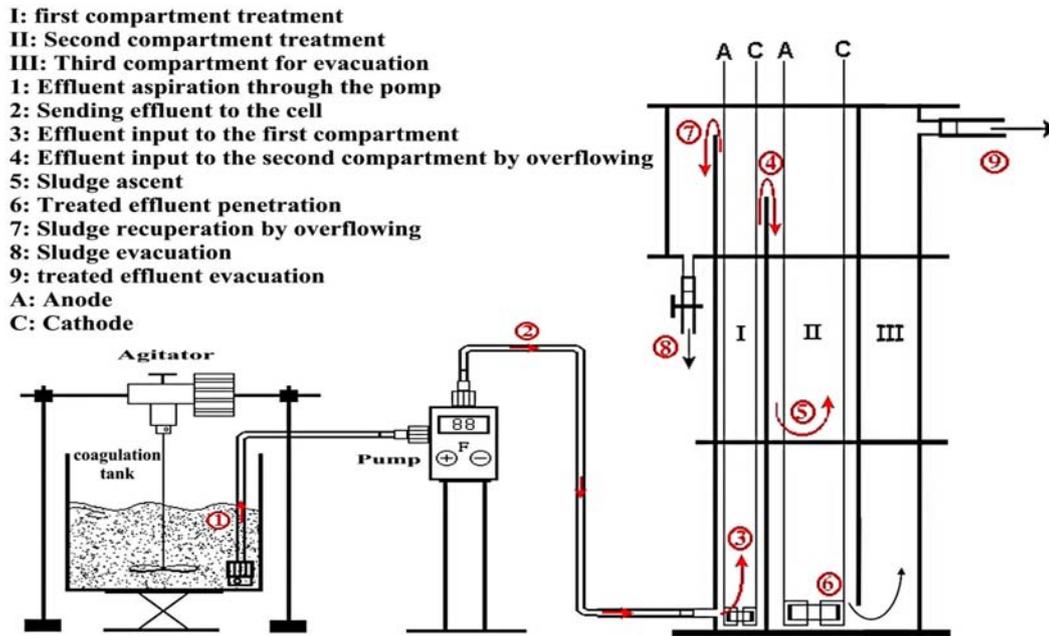


Fig. 2. Electroflotation unit in continuous mode.

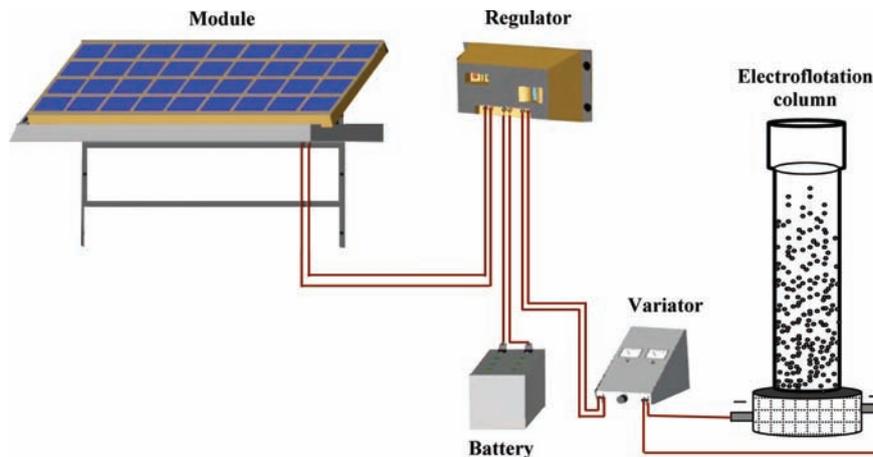


Fig. 3. Solar energy system.

2.2. Methods

2.2.1. Experiment planification

The methodology of experimental research was adopted in this study in order to reduce the number of experiments and to obtain a mathematical model linking the objective function with the operating parameters [13]. Indeed, we opted an orthogonal plan with two levels and four variables which are: current density, coagulant concentration, pH and treatment duration. This methodology leads to obtain a second order equation including variable interactions. The experiment number is given by:

$$N = 2^k + 2k + n_0 \tag{3}$$

in which  $k$  is the independent parameter numbers,  $n_0$  is the

experiment number in the center. So we obtain a matrix of 28 experiments with four experiments in the centre as shown in Table 3.

The exploitation of this matrix leads to obtaining a second order regression equation which connects the parameters with the COD abatement rate  $Y$ . This equation takes account of the interactions which can exist between these variables [14].

$$Y = a_0 + [a_1 \times X_1 + a_2 \times X_2 + a_3 \times X_3] + [a_{11} \times X_1^2 + a_{22} \times X_2^2 + a_{33} \times X_3^2] + [a_{12} \times X_1 \times X_2 + \dots + a_{13} \times X_1 \times X_3 + a_{23} \times X_2 \times X_3] \tag{4}$$

$a_0$ : constant term of the regression equation;  $a_i$  ( $i \in \{1,2,3\}$ ): linear effect coefficients;  $a_{ii}$  ( $i \in \{1,2,3\}$ ): quadratic effect

coefficients;  $a_{ij}$  ( $i, j \in \{1, 2, 3\}$ ): interaction effect coefficients.

It is also noted that these coefficients were obtained by matrix algebra and two tests of validity were made: a first test of Student which validates each coefficient and a second test of Fisher which validates the global model.

2.2.2. Experimental conditions

Preliminary treatment experiments of such effluents by coagulation–electroflotation were carried out in order to fix the parameter intervals influencing this process. Other studies also showed that the addition of a coagulant containing of  $Al^{3+}$  ions before the treatment by electroflotation contributes to the improvement of the purification rate [15]. Therefore, the addition of an adequate quantity of coagulant and the adjustment of pH by an acid or a base addition will promote the electroflotation process. Table 2 recapitulates these operating parameters intervals.

The COD abatement rate was selected as the parameter of follow-up ( $Y_{exp}$ ). Measurements of COD before and after the treatment were carried out in order to calculate this rate:

$$Y_{exp}(\%) = \frac{COD_0 - COD_f}{COD_0} \times 100 \tag{5}$$

in which  $COD_0$ : the initial COD value (before the treatment) (mg  $O_2/l$ );  $COD_f$ : the final COD value (after the treatment) (mg  $O_2/l$ ).

The experimental matrix is given in Table 3.

3. Results and discussion

3.1. Treatment in batch mode

Experiments were carried out following the experimental matrix, the calculus lead to a regression equation [14] linking the COD abatement rate with operating parameters already fixed, this equation is given below:

$$Y_{th} = -133.93 + 1.12 \times D + 26.38 \times pH + 0.05 \times C_{coag} + 3.05 \times t - 3.80 \cdot 10^{-3} \times D^2 - 2.13 \times pH^2 - 4.28 \cdot 10^{-5} \times C_{coag}^2 - 0.05 \times t^2 + 2.40 \cdot 10^{-3} \times D \times pH \tag{6}$$

Each coefficient of this equation was validated by Student test, the global model was validated by Fisher test. In fact, we can note through this equation that:

- all the linear effect coefficients exist which affirms that current density, pH, coagulant concentration and treatment duration influence directly on the COD abatement rate;
- all second order coefficients of the four operating parameters also exist, this means that the optimum of these parameters, which maximizes the COD abatement rate, is in the fixed interval [16];
- current density interacts with pH.

Table 2  
Operating parameter intervals

Factors	D (A/m <sup>2</sup> )	pH	C <sub>coag</sub> (mg/l)	t (min)
Z <sub>i</sub> <sup>max</sup> : maximum value	200	8	1000	40
Z <sub>i</sub> <sup>min</sup> : minimum value	100	4	300	10
Z <sub>i</sub> <sup>0</sup> : centre value	150	6	650	25

Table 3  
Experimental matrix

Test	D (A/m <sup>2</sup> )	pH	C <sub>coag</sub> (mg/l)	t (min)	Y <sub>exp</sub> (%)
1	200	8	1000	40	72.1
2	100	4	1000	40	73.5
3	200	4	300	40	64.3
4	100	8	300	40	65.3
5	200	4	1000	10	52.3
6	100	8	1000	10	55.2
7	200	8	300	10	54.2
8	100	4	300	10	55.1
9	200	4	1000	40	68.3
10	100	8	1000	40	69.8
11	200	8	300	40	65.2
12	100	4	300	40	62.8
13	200	8	1000	10	60.2
14	100	4	1000	10	52.1
15	200	4	300	10	50.6
16	100	8	300	10	52.7
17*	150	6	650	25	91.2
18	221	6	650	25	75.1
19	79	6	650	25	81.2
20	150	9	650	25	80.1
21	150	3	650	25	80.2
22	150	6	1145	25	91.1
23	150	6	155	25	82.3
24	150	6	650	46	90.8
25	150	6	650	4	57.4
26*	150	6	650	25	90.0
27*	150	6	650	25	89.1
28*	150	6	650	25	88.1

\*Tests in centre

In order to identify which factor most affect the COD abatement rate, explicative factor  $R^2$  of each parameter was calculated. The result shows that the current density is the most factor affecting the COD abatement rate ( $R^2 > 33\%$ ), while pH affect less this rate ( $R^2 \approx 23\%$ ). Treatment duration and coagulant concentration have almost the same explicative factor ( $R^2 \approx 28\%$ ).

After establishing this mathematical model which could predict the effluent COD abatement rate, we used the NELDER and MEAD method [13] to reveal the optimal operating conditions leading to a maximum purification rate. The optimal values of the operational parameters obtained are:

- Current density:  $D = 150 \text{ A m}^{-2}$
- pH = 6.5
- Coagulant concentration:  $C_{\text{coag}} = 656 \text{ mg l}^{-1}$
- Treatment duration:  $t = 28 \text{ min}$

Under these optimal conditions, the theoretical COD abatement rate calculated by the obtained model is 97%. Control tests were carried out, the average experimental output obtained is 96.6 %.

The characterization of the effluent after treatment and under these optimal conditions was made (Table 4).

### 3.2. Treatment in continuous mode

Treatment in continuous mode was also studied with an aim of an eventual extrapolating of this process on an industrial scale. Indeed, we carried out tests of treatment using optimal parameters already obtained in batch mode. Solar energy was also used as an electric current source for the electroflotation unit electrodes.

The result analysis of samples being treated show the COD abatement rate was 96 %. In fact, native oxygen bubbles produced by the electrolysis reaction lead to an effective COD reduction.

Analysis of treated wastewater by coagulation–electroflotation are illustrated in Table 5.

The results presented in Table 5 show that the electroflotation preceded by coagulation is a very effective process for wastewater resulting from the operation of washing machines of a cardboard manufacture. Indeed,

this process leads to very high COD abatement rate and also to reduce suspended solids more than 96%. We also note that the electroflotation process leads to a great suspended solid abatement rate. In fact, tiny hydrogen and oxygen bubbles produced by water electrolysis can float suspended solids to the top of the column and then sludge can be evacuated.

## 4. Conclusion

The process of coagulation–electroflotation was adopted to treat effluents rich in adhesive and colouring resulting from the operation of washing machines of a cardboard manufacture. Solar energy was used to supply the insoluble electrodes of the electroflotation columns. The methodology of experimental research was used in batch mode treatment, a model linking the COD abatement rate with the operating parameters which are current density, coagulant concentration, pH and treatment duration was established. A physicochemical characterization at the optimal conditions was made and showed the effectiveness of the process used.

Continuous mode treatment was also carried out successfully. The outputs of purification obtained exceeded 96%.

## References

- [1] M. Bagane and S. Guiza, Elimination d'un colorant des effluents de l'industrie textile par adsorption, *Ann. Chim. Sci. Mat.*, 25 (2000) 615–625.
- [2] M.S. El-Geundi, Colour removal from textile effluents by adsorption techniques, *Wat. Res.*, 25 (1991) 271–273.
- [3] J. Perkowski, L. Kos and S. Ledakowicz, Application of ozone in textile wastewater treatment, *Ozone Sci. Eng.*, 18 (1996) 73–85.
- [4] Ph. Sutarik and M. Hendou, Discoloration of dyes by electrochemical process, *TSM*, 3 (1997) 61–68.

Table 4  
Effluent characterization in optimal condition in batch mode

Parameters	Before treatment	After treatment	COD abatement rate $Y_{\text{exp}}$ %
pH	7.2	7.6	—
COD, $\text{mg O}_2 \text{ l}^{-1}$	3600	121	96.6
$\text{DBO}_5$ , $\text{mg O}_2 \text{ l}^{-1}$	500	45	91
Suspended solids, $\text{mg l}^{-1}$	266	9.3	96.5

Table 5  
Effluent characterization in optimal condition in continuous mode

Parameters	Before treatment	After treatment	COD abatement rate $Y_{\text{exp}}$ %
pH	7.2	7.5	—
COD, $\text{mgO}_2 \text{ l}^{-1}$	3600	138	96.2
$\text{DBO}_5$ , $\text{mgO}_2 \text{ l}^{-1}$	500	61	88
Suspended solids, $\text{mg l}^{-1}$	266	8,8	96.7

- [5] A.I. Zouboulis, K.A. Matis and G.A. Stadilis, in: P. Mavros and K.A. Matis, eds., *Innovations in Flotation Technology*, Proc. NATO Science Series, Greece, Kluwer Academic, The Netherlands, 1991.
- [6] L.J. Janssen and L. Koene, The role of electrochemistry and electrochemical technology in environmental protection. *Chem. Eng. J.*, 85 (2002) 137–146.
- [7] Y. Fukui and S. Yuu, Removal of colloidal particles in electroflotation, *AIChE J.*, 31(2) (1985) 201–208.
- [8] G. Chen, Electrochemical technologies in waste water treatment. *Separ. Purif. Technol.*, 38 (2004) 11–41.
- [9] C. Llerena, J.C.K. Ho and D.L. Piron, Effect of pH on electroflotation of sphalerite, *Chem. Eng. Commun.*, 155 (1996) 217–228.
- [10] L. Ben Mansour, I. Ksentini and B. Elleuch, Treatment of wastewaters of paper industry by coagulation–electroflotation, *Desalination*, 208 (2007) 34–41.
- [11] L. Ben Mansour, Y. Ben Abdou and S. Gabsi, Effect of some parameters on removal process of nickel by electroflotation, *Water, Waste Environ. Res.*, 2 (2001) 51–58.
- [12] H. Yang, H. Wang, G. Chen and G. Wu, Influence of the charge regulator strategy on state of charge and lifetime of VRLA battery in household photovoltaic systems, *Solar Energy*, 80 (2006) 281–287.
- [13] V. Kafarov, *Méthodes Cybernétiques et Technologie Chimique*, Mir, Moscow, 1992, p. 230.
- [14] J. Goupy, *Plan d'expériences*, Technique de l'Ingénieur, Génie des Procédés, J2, 1981, p. 225.
- [15] A. Jarmany, A. Kheribech and M. Mountadar, Décoloration des rejets liquides de textile par électrocoagulation, *Phys. Chem. News*, 6 (2002) 101.
- [16] V. Kafarov, *Méthodes Cybernétiques et Technologie Chimique*, Mir, Moscow, 1974.