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Treatment of effluents from cardboard industry by coagulation–electroflotation

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Abstract

The objective of the present study is to optimize the treatment of the cardboard industry wastewater generated in the process of machine washing. This type of effluent is usually treated by traditional physicochemical processes such as coagulation/flocculation and sedimentation. These processes give a limited purifying efficiency, particularly for the COD reduction. In this work, the treatment by coagulation–electroflotation process was adopted. In batch mode treatment, current density, pH and coagulant concentration are the operating parameters to optimize. The methodology of experimental research, with an orthogonal central composite plan was adopted. Good agreement between theoretical analysis and experimental results was obtained. Continuous mode was also studied in order to optimize the residence time. A physicochemical characterization including COD, BOD and suspended solids charge was done before and after the treatment in order to improve the efficiency of this process.

Keywords: Cardboard effluent; Coagulation; Electroflotation; Optimization

1. Introduction

Processes of wastewater treatment have been the objects of many recent studies. In addition to the traditional processes, new competitive treatment technologies are being used. Most of wastewaters contain generally large quantities of suspended solids and high charge of COD and BOD due to the presence of organic dye, which is hardly biodegradable. Conventional physicochemical treatment of this effluent consists of preliminary treatment such as coagulation/flocculation, sedimentation and sludge handling. Secondary and tertiary treatment such as biological filters or activated sludge can be also practised. Many studies were made to optimize the treatment of such effluents using these traditional processes [1–3]. These processes are not very efficient when the effluent contains low density of colloidal suspended solids and high charge of COD [4]. In case of cardboard industry effluent, the use of flotation technique can be efficient. In fact, separation by flotation is relatively faster compared to coagulation and sedimentation. Matis and co-workers [5] studied the effectiveness of different flotation techniques and they noted that for wastewaters containing colloidal particles, fine hydrogen and oxygen bubbles produced by electrolysis can effectively float these particles. Janssen and Koene [6] showed that electrochemical techniques are one of the competitive and interesting technologies in this field, since the generation of oxygen bubbles at the anode, led also to the reduction of the COD and BOD. Electroflotation techniques are highly versatile and competitive with settling tank techniques that require a large space of land. In fact, electroflotation supports the electrolysis of treated water due to the passage of electric current between insoluble electrodes [7,8]. The generation of fine oxygen and hydrogen bubbles is shown in the following reactions:

Anodic oxidation:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (1)$$

Cathodic reduction:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \quad (2)$$

This process is complex because of its dependence on several factors. Indeed, the current density influences directly the number and size of bubbles [9]. Chen [10] has demonstrated that current density and mass of bubbles produced are proportional. The pH is also a parameter which influences the mechanism of

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electroflotation owing to the fact that the hydrogen bubbles are the smallest with neutral pH and for the oxygen bubbles their sizes increase with pH [9]. Other than pH and current density there are several other parameters, which affect this process such as the state, the arrangement of the electrodes [11], the nature of water to be treated and processing duration.

The aim of this work is to optimize the treatment of cardboard industry effluent using the coagulation–electroflotation process. This study includes both the continuous and batch modes. The operating parameters to be optimized in batch mode are: current density, pH and coagulant concentration. In continuous mode, the parameter to be optimized is the processing time [8]. Considering the number of parameters, the scientific tool for analysis is the methodology of experiment planning which minimizes the number of experiments and allows the determination of a regression equation linking the efficiency of COD reduction with the operating parameters.

2. Materials and methods

2.1. Materials

2.1.1. Effluent characteristics

The effluent used in this study is the outcome of the washing of impression and pasting machines obtained from cardboard industry factory. Table 1 shows some physicochemical characteristics of the effluent, which was carried out before the treatment. It should be noted that this effluent presents a high charge of COD, BOD and suspended solids.

Table 1
Characteristics of effluent samples before treatment

Parameter	Value
pH	7.2
COD (mg O_2/L)	3600
BOD_5 (mg O_2/L)	500
Suspended solids (mg/L)	266

2.1.2. Electroflotation cell

The electroflotation cell is a cylindrical column with a volume of 300 ml. It is provided with two electrodes: titanium coated with ruthenium oxide anode and a stainless steel cathode. These electrodes were superposed at the bottom of the cell and were connected to a dc generator. The distance between the electrodes is 5 mm. The electroflotation cell has two outputs. The first one is at the top of the cell and is used for the evacuation of sludge, while the second one is at the bottom and is used for treated water evacuation.

The electroflotation unit used in the continuous mode, shown in Fig. 1, has a total volume of 4.2 L. It is divided into three compartments. The first and the second ones are provided with two electrodes. The first one receives the effluent from a coagulation tank using a piston pump. The effluent then undergoes a primary treatment in which bubbles and effluent are in co-current movement. After that, the effluent goes through the second compartment by overflow and undergoes its final treatment. The bubbles and effluent are moved in counter current in the second compartment. The treated effluent is then evacuated to the third compartment and the formed sludge is eliminated at the top of the column. The agitation of the storing tank is ensured by a mechanical agitator necessary to avoid a possible sedimentation of sludge. A diagram of the process is given in Fig. 1.

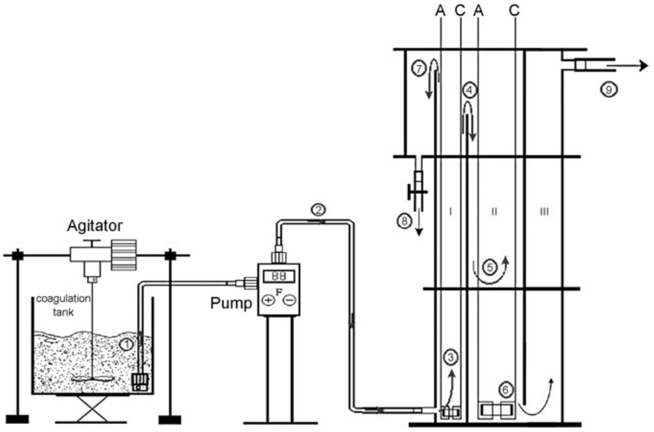

Fig. 1. Schematic diagram of the electroflotation unit in continuous mode. (I) First compartment; (II) second compartment and (III) third compartment. (A) Anode and (C) cathode, (1) effluent aspiration through the pump; (2) sending effluent to the unit; (3) effluent input to the first compartment; (4) effluent input to the second compartment by overflowing; (5) sludge ascent; (6) treated effluent penetration; (7) sludge recuperation by overflowing; (8) sludge evacuation and (9) treated effluent evacuation

2.2. Methods

2.2.1. Methodology of experiment planning

The methodology of experiment planning is an experimental research tool, which reduces the number of experiments and generates a regression equation, which relates all optimized parameters. In this study, this methodology was used to obtain a regression equation relating COD reducing efficiency as a function of the operating parameters, which are current density, pH and coagulant concentration.

The adopted methodology, with an orthogonal central composite design, requires in this case 14 experiments and four tests in center. The total number of experiments is calculated using the following equation [12]:

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

in which n_0 is the number of tests to be carried in the center of plan and K is the number of independent parameters.

2.2.2. Experimental conditions

In batch mode, the parameters to be optimized are current density, pH and coagulant concentration. The coagulant used is aluminium sulphate ($Al_2(SO_4)_3{\cdot}18H_2O$). Preliminary tests were performed to fix the intervals of variations of these variables as shown in Table 2.

The treatment duration was fixed at 30 min and during all experiments the voltage varied between 7 and 9 V due to the

Table 2
Intervals variation of parameters studied

Parameter	C_{coag} (mg/L)	pH	D (A/m^2)
Z_i^{min}	300	4	100
Z_i^{max}	1000	8	200
Z_i^0	650	6	150
ΔZ_i	350	2	50

Table 3
Experiments matrix

Experiment	$C=X_1$	$pH=X_2$	$D=X_3$	Y
1	1000	8	200	72.1
2	300	8	200	58
3	1000	4	200	64.3
4	300	4	200	65.3
5	1000	8	100	65
6	300	8	100	55.2
7	1000	4	100	54.2
8	300	4	100	55.1
9*	**650**	**6**	**150**	85.2
10	650	6	221	69.8
11	650	6	79	65.2
12	650	8.8	150	66
13	650	3.2	150	65
14	1145	6	150	80
15	155	6	150	72
16*	**650**	**6**	**150**	83.2
17*	**650**	**6**	**150**	86.5
18*	**650**	**6**	**150**	84

variation of current density. The experiment matrix is shown in Table 3 [13]:

Y is the COD reducing efficiency.

$$Y = \frac{COD_0 - COD_f}{COD_0} \times 100 \tag{4}$$

COD_0 is the value of COD before treatment and COD_f is the value of COD after treatment.

The use of this matrix leads to obtaining a second order regression equation, which relates Y with operating parameters:

$$\begin{aligned} Y = {} & a_0 + [a_1 \times X_1 + a_2 \times X_2 + a_3 \times X_3] + [a_{11} \times X_1^2 \\ & + a_{22} \times X_2^2 + a_{33} \times X_3^2] + [a_{12} \times X_1 \times X_2 + \cdots \\ & + a_{13} \times X_1 \times X_3 + a_{23} \times X_2 \times X_3], \end{aligned} \tag{5}$$

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

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

Table 5
Theoretical values of optimized parameters and a comparison between theoretical and experimental COD reduction efficiency

C_{coag} (mg/L)	pH	D (A/m^2)	Y_{the} (%)	Y_{exp} (%)
716.7	6.3	148.7	93.8	93.5

3. Results and discussion

3.1. Treatment in batch mode

Since the methodology of experiment planning is used, 18 experiments were conducted following the matrix of experiments. Table 3 presents the COD reducing effciency in each experiment. A representative volume of 300 ml was taken in each experiment.

The obtained regression equation coefficients, presented in Table 4, were validated by Student's *t*-test. The regression equation was also validated by Fisher test. The Newton method was used in order to maxmize Y [13]. The values of each parameter (i.e., pH, current density and coaguant concentration) after optimization are given in Table 5.

- Y_{the} is the value of COD reducing efficiency using the obtained regression equation.
- Y_{exp} is an experimental result using optimized parameter (i.e., $C = 716.7$ mg/L; pH 6.3 and $D = 148.7$ A/m^2).

It can be noted that all the first order terms exist, which confirm that pH, coagulant concentration and current density act directly on COD reduction efficiency. The second order terms of the regression equations exist, which explain that the optimum is in the fixed intervals. Furthermore, other interaction coefficients exist. In fact, an interaction exists between the coagulant concentration and pH because of the coagulant acid character. Another interaction exists between the coagulant concentration and current density. This can be explained by the fact that the current density acts directly on number and shape of the gas bubbles. Therefore, the number of bubbles increases when current density increases and the probability of collision between these bubbles and optimal coagulated floats increase. As a result, more particles will be eliminated.

3.2. Treatment in continuous mode

For an eventual extrapolation of the process on an industrial scale, the supply flow of treated effluent was optimized in continuous mode; it was varied and monitored by the corresponding

Table 4
Coefficients of regression equations obtained

Constant	C	pH	D	C^2	pH^2	D^2	CpH	CD
39.4	6.1×10^{-2}	2.9	−0.18	-4.7×10^{-5}	−0.159	9.3×10^{-4}	-4.3×10^{-4}	10^{-5}

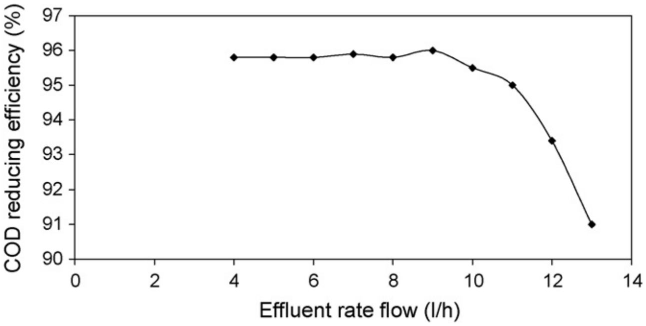

Fig. 2. Effect of effluent supply flow on the COD reduction efficiency.

Table 6
Characteristics of effluent samples after the continuous mode treatment in optimal conditions

Parameter	Before treatment	After treatment	Efficiency (%)
pH	7.2	7.6	–
COD (mg O_2/L)	3600	144	96
BOD_5 (mg O_2/L)	500	45	91
Suspended solids (mg/L)	266	9.3	96.5

COD reduction. Current density, pH and coagulant concentration are fixed at optimized conditions in the batch mode study. The results are given in Fig. 2.

It is clear that the optimal flow which maximizes the COD charge reduction is reached at 9 L/h which corresponds to an optimal residence time of $t_r = 28$ min. It can be noted that the efficiency of COD reduction decreases at high supply effluent flows. A complete analysis of water treated in the optimum conditions was made as illustrated in Table 6.

This physicochemical characterization shows that COD charge reduction is better in continuous compared to batch mode. This can be explained by the fact that the effluents undergo two-stage treatment in continuous mode.

The obtained results show that suspended solids, COD and BOD charges were considerably reduced. The large reduction of COD may be explained by the oxidation of dissolved organic substances due to the presence of fine oxygen bubbles as a strong oxidizing agent in the medium. This confirms that coagulation–electroflotation process is effective in case of such effluent.

4. Conclusion

The coagulation–electroflotation process was used to treat cardboard industry effluents having a high COD, BOD and suspended solids charge. The methodology of experiments planning was used as an experimental research tool. The obtained regression equations were optimized to find the optimal conditions of treatment in batch mode. The optimized parameters are coagulant concentration, pH and current density. Physicochemical characterization was performed before and after treatment. The results show that coagulation–electroflotation technique can be successfully selected as an efficient process to treat this type of effluent since it leads to high purification efficiency.

Treatment tests in continuous mode were carried out successfully by determining the optimal residence time of effluents. COD charge was reduced to more than 95%.

References

[1] M. Bagane, S. Guiza, Removal of dye from textile effluents by adsorption, Ann. Chim. Sci. Mater. 25 (2000) 615–626.
[2] M.S. El Geundi, Colour removal from textile effluents by adsorption techniques, Water Res. 25 (1991) 271–273.
[3] M.R. Assalin, M.A. Rosa, N. Duran, Remediation of Kraft effluent by ozonation, Ozone: Sci. Eng. 26 (2004) 317–322.
[4] Ph. Sutarik, M. Hendou, Discoloration of dyes by electrochemical process, TSM 3 (1997) 61–68.
[5] A.I. Zouboulis, K.A. Matis, G.A. Stadilis, Innovations in flotation technology, in: P. Mavros, K.A. Matis (Eds.), Proceedings of the NATO Science Series, Greece, Kluwer Academic Publishers, The Netherlands, 1991, pp. 12–25.
[6] L.J. Janssen, L. Koene, The role of electrochemistry and electrochemical technology in environmental protection, Chem. Eng. 85 (2002) 137–146.
[7] C.C. Ho, C.Y. Chan, Application of lead dioxide-coated titanium anode in the electroflotation of palm oil mill effluent, Water Res. 20 (1986) 1523–1527.
[8] L. Ben Mansour, Y. Ben Abdou, S. Gabsi, Effects of some parameters on removal process of nickel by electroflotation, Water Waste Environ. Res. 2 (2001) 51–58.
[9] Y. Fukui, S. Yuu, Removal of colloidal particles in electroflotation, AIChE J. 31 (1985) 201–208.
[10] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.
[11] C. Llerena, J.C.K. Ho, D.L. Piron, Effect of pH on electroflotation of sphalerite, Chem. Eng. Commun. 155 (1996) 217–228.
[12] V. Kafarov, Méthodes Cybernétiques et Technologie Chimique, ed. Mir, Moscou, Moscou, 1992.
[13] J. Goupy, Plans d'expériences, Technique de l'Ingénieur, Traité analyse et caractérisation, P.230, Paris, 1997, pp. 1–24.