Arabian Journal of Chemical and Environmental Researches
Vol. 03 Issue 1 (2016) 11–19
www.mocedes.org/ajcer

Treatment of liquid effluents from Hot dip galvanization by the couple lime/chitosan

H. Arroub[1]* A. Essamri[2] and A. EL Harfi[3]

Laboratory of Polymers, Radiation and Environment (LPRE), Team of Organic Chemistry and Macromolecular (ECOM), Department of Chemistry, Faculty of Science. Ibn Tofail University, BP133, 14000 Kenitra, Morocco.

Received 18 Dec 2015, Revised 26 Dec 2015, Accepted 26 Jan 2016

Abstract

During this work, we treated liquid effluents taken from the Galvacier Company neutralization station of Kenitra (Morocco) by a process of coagulation/flocculation using an assimilated system of Jar-test. The optimization of the process of the coagulation / flocculation shows that the optimized parameters (pH, time of floc formation, the dose of coagulant and flocculant used) have an important effect on the performance of this method. When treating water from various stages of the hot-dip galvanizing, we achieved significant returns on the disposal of the following pollutant: 98.43% for turbidity, 72.86% for conductivity, 96, 49% for suspended solids, 98.81% for the chemical oxygen demand and 98.83% for biochemical oxygen demand in comparison with the reference method used at the company's hot-dip galvanizing.

Keyword: coagulation / flocculation, hot galvanizing, turbidity, COD, TSS, BOD_5.

*Corresponding author.
E-mail address: arroubhana30@gmail.com

1. Introduction

Industrial liquid effluents from the hot galvanizing are in most cases handled by physicochemical processes which include the coagulation / flocculation process [1-2-3-4-5]. The latter having a wide use in the treatment of waste water loaded with inorganic micropollutants [6] organic [7] and organometallic [8-9] are harmful to health and the environment. These are suitable methods to reduce colloidal materials [1-2-10]. Coagulation is the first step in this process of treatment of industrial waste waters. It is to neutralize or reduce electric loads and thus promote the approximation of colloidal particles [1-2-10].

ISSN : 2458-6544

The most frequently used anti-coagulants are lime (Ca (OH) 2), aluminum salts (Al2 (SO4) 3 and AlCl 3) and iron salts (FeCl3, Fe2 (SO4) 3) [11], etc. Flocculation is the process which directly follows the coagulation and it promotes the contact between the destabilized colloid particles to form agglomerates requiring flocculants such as polyacrylamides [12], anionic polyacrylamides, cationic, polyacrylic acid and / or polyvinyl alcohol. [13]

The objective of this study is to treat waste water from industrial hot dip galvanizing to reduce pollutants in the coagulation / flocculation process. First, we have optimized the dose of the used flocculant, and secondly, we evaluated the purifying power of the flocculant.

2. Materials and Methods

2.1. Overview of the study area

The experimental study area was defined using the waste water from various stages of the hot dip galvanizing of Galvacier company (city of Kenitra, Morocco).

2.2. Samples

The sample was taken from the downstream and upstream of the neutralization station, in bottles whose capacity is one liter based on a high density of polyethylene (HDPE).

2.3. Coagulants / flocculants

Concerning the coagulation/flocculation process of reference, the initial coagulant used is lime ($Ca(OH)_2$) of 97% purity. The polyelectrolyte used for flocculation is ferrocryl®8723 powder with a purity of 98%,of the polyacrylamide family, whose chemical formula is ($C_3H_5NO.C_3H_4O_2$)n,of anionic character. As for the experimental couple coagulation/flocculation which we used and formed by the lime/chitosane , the latter is an cationic polymer which is obtainable by acetylation of chitin [13-14] whose chemical formula ($C_2H_4NO.C_6H_9O_4$) n.

2.4. Optimization of the process of the coagulation / flocculation

2.4.1. Optimization of samples' pH

The wastewater treatment by the coagulation / flocculation process was conducted using a Jar test (ISCO Model RPM / PMS). Aqueous solutions of the used coagulants and flocculants were successively prepared at a concentration of 40g/l for the lime and 3g/l for the ferrocryl®8723 flocculants and the chitosan. The samples were taken downstream and upstream of the neutralization station and filled into 4 beakers having a capacity of one liter after adjusting their pH to the values 6, 7, 8 and 9 with lime which is in this case the used coagulant. The obtained samples were subjected to oxidation with H_2O_2. The flocculation process was conducted for 3 min with a stirring speed estimated by 200tr/min, during which we added 10 ml of the flocculant previously prepared in each beaker, then reduced the stirring speed to 20TR/min for 5 min. Before measuring the pH of each preparation, we decanted it for 30min.

2.4.2. Optimization of the chitosan flocculant dose

On the one hand, the optimization of the flocculant dose of ferrocryl®8723 and that of chitosan was carried out at the pH optimized at 8 and at the increasing doses of the percentage weight flocculants from 0.1% to 0.5% with the method described by the data sheet of wastewater treatmant of the neutralization station. On the other hand, we diluted successively 1g/l, 2g/l, 3g/l, 4 g/l and 5g/l of ferrocryl®8723 and chitosan. In the end, we carried out the flocculation of our samples (in 5 beakers whose volume is 1 liter) with a speed of 200tr/min for 3 min. Next, 10ml of each dose of the flocculant solutions previously prepared were added sequentially to each beaker other than the control. After stirring for 5min with speed of 20tr/min, the samples were left to settle for 30 minutes to eliminate the float.

2.4.3. Comparative assessment of the power of the new couple coagulation/flocculation; lime/chitosan

In this part we evaluated the chitosan power. The demonstration of the effectiveness of the flocculant, in view of the reduction of the polluting load, was carried through a comparative study with the ferrocryl®8723 which is the reference to the flocculant station.To do this, we conducted the flocculation of our samples composed of a liter of wastewater taken downstream of the neutralization station whose pH was previously adjusted to 8 and subsequently oxidized by H_2O_2 using these two flocculants with a mass concentration of 3g/l. While the coagulant lime was added to the foregoing preparations with a mass concentration of 40g/l, the preparations obtained were then left to settle before making the measurements of the following parameters: pH, temperature, TSS, turbidity, electrical conductivity, COD and BOD_5.

3. Results and discussion

3.1. Evaluation of wastewater pollution parameters of the neutralization station

Table 1 summarizes the average of the physical, chemical and physico-chemical wastewater exploited in this study.

Table 1: Mean values of the physical, chemical and wastewater physicochemical taken at two different points.

Analysed parametrs	pH	T(°C)	Turbidity (NTU)	TSS (mg/l)	Conductivity (µs /cm).10)	COD (mg/l)	BO_5D (mg/l)	COD/BO_5 D
Measured values below neutralization station	1.02	17.5	560	570	184.3	2862	602	4.75
Values measured upstream neutralization station	4.01	25	65	515	107.12	2075	546	3.80

3.2. pH optimization through the used flocculant

The obtained measurements concerning the pH, the floc formation time, the form of flocs and the clarification and / or quality of the treated water are shown in Table 2.

Table 2: Water features processed by the couple lime/chitosan.

No of beakers	pH of the raw water	Time (min) of floc	pH treated water	Form of flocs	Quality of float
Beaker1	6	17	6.54	small	disorder
Beaker1	7	15	7.25	small	disorder
Beaker3	8	9	7.64	large	clear
Beaker4	9	11	8.02	large	clear

According to the results in Table 2, it shows us that the formation of flocs is very fast at the optimum pH to 8 and the combination of lime and chitosan is less advantageous at a pH higher or lower than this value.

3.3. Dose Optimization of the chitosan flocculant

The results of the analysis of the physical parameters (conductivity), chemical (MES) and physico-chemical of water samples processed according to the increasing doses of the chitosan flocculant are shown in figure 1:

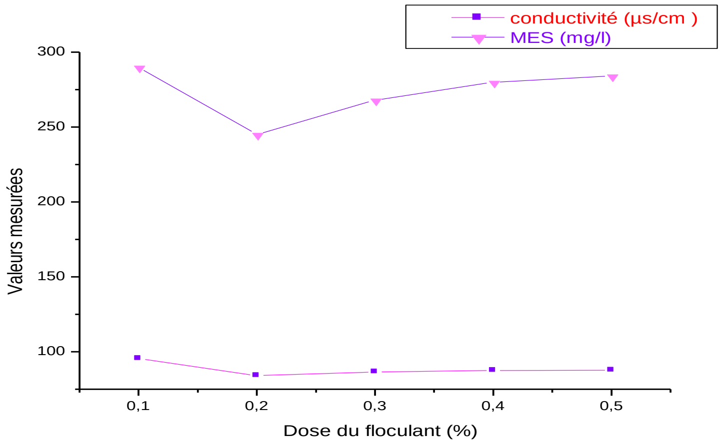

Figure 1: Change in the conductivity and MES following the dose of the flocculant.

From the curves in Figure 1, we find that: for the optimum dose of flocculant equal to 0.2% we saw a low MES (245mg/l) on the one hand and a low presence of electrical conductivity (84 mg/l) on the other.

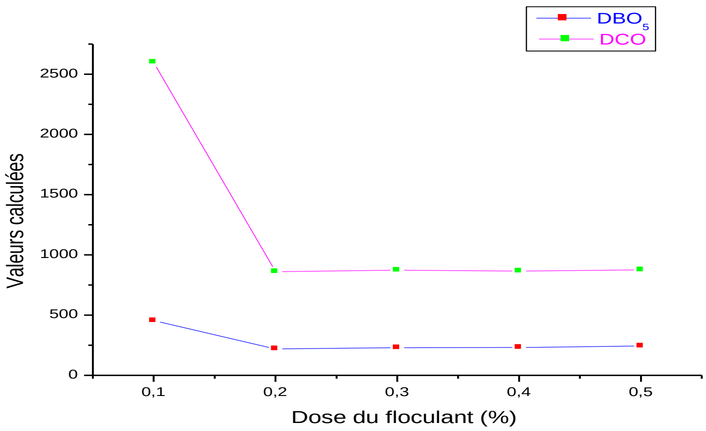

Figure 2: Change in BO_5D and COD depending on the dose of the flocculant.

From this figure, we find that:

The BO_5D has decreased by 602 mg/l to a minimum value which is of the order of 220 mg/l for an optimal dose of 0.2g/l of chitosan. The COD of the treated water decreases each time the flocculant concentration varies. In fact, the COD before treatment was significant in the order of 2862 mg/l. This is due to the too high load of raw water in oxidizable organic materials. After the treatment of waste water by the couple lime/chitosan, the COD decreases till the value of 860 mg/l for a dose of the flocculant which is 0.2 g/l.

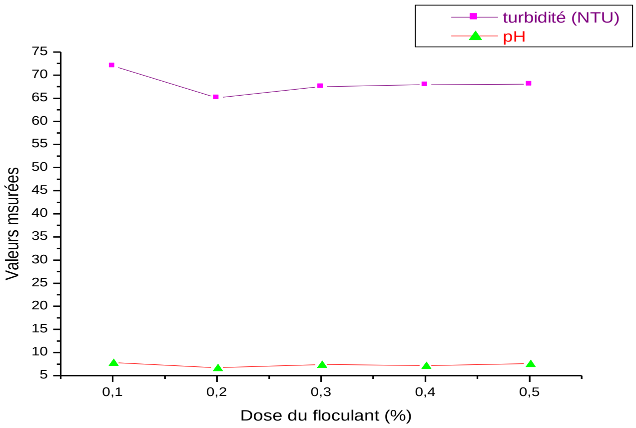

Figure 3: variation in turbidity and pH depending on the dose of the flocculant.

In figure 3 which represents the variation of the turbidity and the pH of the flocculant dose according to the obtained results we see a strong presence of turbidity in the wastewater after the treatment which decreases progressively as the concentration of the flocculant increases. The mass concentration of the stored turbidity is equal to 65.12 NTU for an optimum flocculant dose of 0.2%. However, the pH value is shown in the following values: 8; 7.8 -6.7-7.4-7.2-7.6.

3.4. Evaluation of the chitosan flocculation power

3.4.1. Results of treatment with chitosan

The water analysis results processed by the chitosan are summarized in Table 3.

Table 3: physical, chemical and physico-chemical characteristics of the water treated by the couple lime/chitosan.

Paramètres	pH	T (°C)	Turbidity (NTU)	Conductivity (µs /cm).10)	TSS (mg/l)	COD (mg/l)	BO_5D (mg/l)	COD/BO_5D
Initial values at the entry of the neutralization station.	1.02	17.5	560	184.3	570	2862	602	4.754
Measured values	7.6	16.2	8.76	50.01	20	34	7.04	4.82

- The pH

The registered pH of water treated by chitosan had the size (7.6).

- The conductivity, turbidity and TSS

According to the obtained results (Table 3), the physicochemical parameters such as, turbidity, conductivity and suspended solids showed a remarkable decrease after treatment of wastewater by the couple lime/chitosan. Indeed, turbidity stepped from the value 560 NTU in raw water to a 8.76 NTU value in the water treated with a registered abatement rate (98.43%). When the conductivity is past, we notice it goes from a 184.3µs.cm value in raw water to a value of 50.01 µs.cm registered with a reduction rate of (72.86%). In the end, the registered MES go from a value of 570mg / l in the untreated waters to values of 20 mg / l with a reduction rate recorded at (96.49%).

- The COD and BOD5

According to the treatment results by the couple lime/chitosan, we noticed a significant reduction in COD because the value of 2862 mg / l in the raw water dropped to 34 mg / l with significant abatement organic matter (98.81%). The BOD5 went from a value of 602 mg / l to a value of 7.04 / l with a significant reduction of the organic matter (98.83%).

3.4.2. Comparison of treatment performance of applied flocculant agents

The figure below shows the different treament performance of the couple lime/limestone and ferrocryl®8723 / chitosan.

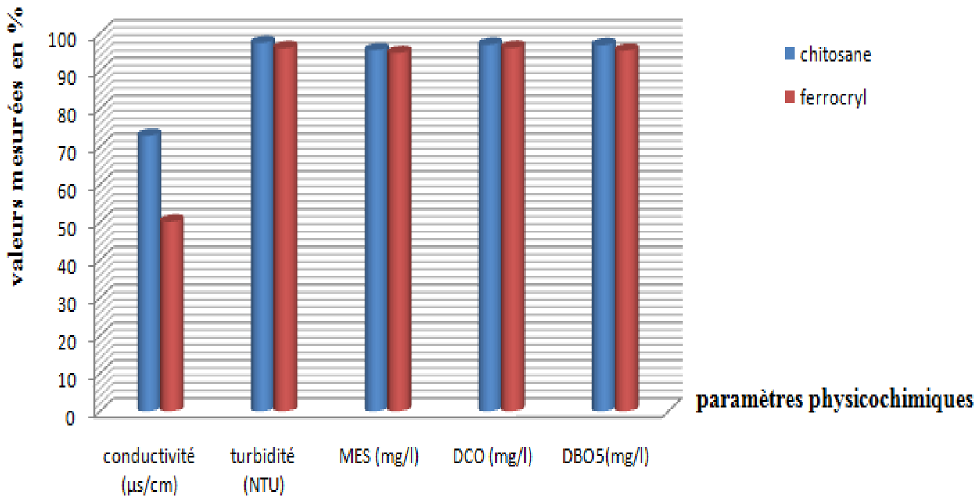

Figure 4: Performance of purifying ferrocryl®8723 flocculants and chitosan.

The comparison of the two flocculants showed us a very significant effect on the elimination of pollution loads by the chitosan over the ferrocryl®8723. Indeed, the treatment with the couple lime / chitosan, the rate abatement physicochemical parameters are: 72.86% of the conductivity, 98.43% of turbidity, 96.49% of suspended solids, 98.81% of the chemical oxygen demand and 98.83 % of the biochemical oxygen demand. However, the treatment with lime/ferrocryl®8723, we obtained only the removal of 72.86% of the conductivity, 96% of turbidity, 94.78% of suspended solids, 98.81% of the chemical oxygen demand, 98.83% of biochemical oxygen demand. According to the study which we conducted on the treatment of waste water from the hot dip galvanizing by coagulation/flocculation process according to the couple lime/chitosan is more effective and less costly in terms of floc formation time compared to the standard process performed at the station of the neutralization Galvacier society.

Conclusion

The solvent extracts of *I. Viscosa* were found to be effective antioxidants by in vitro assays, and can therefore be proposed as new potential sources of natural additives for the food and/or pharmaceutical industries. According to these results, there is a relationship between the total phenol content and antioxidant activity. Indeed, it is extremely important to point out that there is a positive correlation between the antioxidant activity potential and the amount of phenolic compounds in the extracts.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

[1] M. Sengul, H. Yildiz, N. Gungor, B. Cetin, Z. Eser and S. Ercisli., Total phenolic content, antioxidant and antimicrobial activities of some medicinal plants. *Pak. J. Pharm. Sci.* 22, 1: 102-106 (2009).

[2] P. Veeru, M. P. Kishor and M. Meenakshi, Screening of medicinal plant extracts for antioxidant Activity. *Plants Research.* 3, 8: 608-612 (2009).

[3] A. D. Sathisha, H. B. Lingaraju and K., Sham prasad. Evaluation of Antioxidant Activity of Medicinal Plant Extracts Produced for Commercial Purpose. *E-Journal of Chemistry,* 8, 2: 882-886 (2011).

[4] D. S. Kumar, A. K. Muthu, A. A. Smith and R. Manavalan, In vitro Antioxidant Activity of Various Extracts of whole Plant of Mucuna pruriens (Linn). *PharmTech Research*. 2: 2063-2070 (2010).

[5] J. E. Wood, S. T. Senthilmohan, A. V. Peskin., Antioxidant activity of procyanidin-containing plant extracts at different pHs. *Food Chemistry*. 77: 155–161 (2002).

[6] S. Y. Qusti, A. N. Abo-khatwa and M. A. Bin Lahwa., 2010. Screening of antioxidant activity and phenolic content of selected food items cited in the Holly Quran. *EJBS.* 2, 1: 40-51 (2010).

[7] N. Wu, K. Fu, Y-J. Fu, Y-G. Zu, F-R. Chang, Y-H. Chen, X-L. Liu, Y. Kong, W. Liu and C-B. Gu., 2009. Antioxidant Activities of Extracts and Main Components of Pigeonpea [*Cajanus cajan* (L.) Millsp.] Leaves. *Molecules*. 14: 1032-1043 (2009).

[8] N. de laurentis, V. Losacco, M. Milillo, O. Lai., Chemical investigations of volatile constituents of *Inula viscosa* (L.) Aiton (Asteraceae) from different areas of Apulia, *Southern Italy*. *Delpinoa, n.s.* 44: 115-119 (2002).

[9] J. Kattouf, M. Belmoukhtar, H. Harnafi, H. Mekhfi, A. Ziyyat, M. Aziz, M. Bnouham and A. Legssyer., Effect of an aqueous extract of *Inula viscosa* leaves. *Phytothérapie.* 7: 309-312 (2009).

[10] M. Grande, F. Piera, A. Cuenca, P. Torres, X. Bellido., Flavonoids from *Inula viscosa. Planta Medica.* 24, 9: 414-419 (1985).

[11] C. Cafarchia, N. De Laurentis, M.A. Milillo, V. Losacco, V. Puccini, Antifungal activity of essential oils from leaves and flawers of *Inula viscosa* (Asteraceae) by Apulian region. *Parassitogia.* 44 : 153-156 (2002).

[12] V. Hernández, M. C. Recio, S. Máñez, R. M. Giner, J-L. Ríos., 2007. Effects of naturally

occurring dihydroflavonols from *Inula viscosa* on inflammation and enzymes involved in the arachidonic acid metabolism. *Life Sciences.* 81: 480-488 (2007).

[13] G. R. Schinella, H. A. Tournier, J. M. Prieto, D. Mordujovich, J. L. Rios, 2002. Antioxidant activity of anti-inflammatory plant extracts. *Life Sciences.* 70, 9: 1023-33 (2002).

[14] P. Barbetti, I. Chiappini, G. Fardella, A. Menghini, A new eudesmane acid from Dittrichia (Inula) viscosa. *Planta Med.* 51: 471 (1985).

[15] L, Lauro, C. Rolih, Observations and research on an extract of Inula viscose Ait. *Boll. Soc. Ital. Biol. Sper.* 66: 829–834 (1990).

[16] E. Lev, Z. Amar, Ethnopharmacological survey of traditional drugs sold in Israel at the end of the 20th century. *J. Ethnopharmacol.* 72: 191–205 (2000).

[17] J. Qasem, A. Al-Abed, M. Abu-Blan, Antifungal activity of clammy inula (Inula viscosa) on Helminthrosporium sativum and Fusarium oxysporum f. sp. Lycopersici. *Phytopathol. Mediterr.* 34: 7–14 (1995).

[18] G. Schinella, H. Tournier, J. Prieto, P. Mordujovich, J. Rios. Antioxidant activity of anti-inflammatory plant extracts. *Life Sciences.* 70: 1023–1033 (2002).

[19] A. Alkofahi, A. Atta, Pharmacological screening of the anti-ulcerogenic effects of some Jordanian medicinal plants in rats. *J. Ethnopharmacol.* 67: 341–345 (1999).

[20] H. Wamidh, H. T. Musa, A. Zarga and A. M. Mahasneh., Antiproliferative, Antimicrobial and Apoptosis Inducing Effects of Compounds Isolated from Inula viscosa, *Molecules.* 17: 3291-3303 (2012).

[21] P. Quezel, S. Santa, 1963. Nouvelle flore de L'Algérie et des régions désertiques méridionales. *Editions du Centre National de la recherche scientifique.* Tome II (1963).

[22] K. Slinkard, V. L. Singleton, Total phenol analysis: automation and comparison with manual methods. *Am. J. Enol. Vitic.* 28: 49-55 (1977).

[23] H-B. Li, C-C. Wong, K-W. Cheng, F. Chen, Antioxidant properties *in vitro* and total phenolic contents in methanol extracts from medicinal plants. *Food Sci. Technol.* 41, 385-390 (2008).

[24] T. Hatano, H. Kagawa, T. Yasuhara, T. Okuda, Two new flavonoids and other constituents in licore root: their relative astringency and radical scavenging affects, *Chem. Pharm. Bull.* 36: 1090-1097 (1988).

[25] W. Brand-Williams, M.E. Cuvelier, C. Berset, Use of free radical method to evaluate antioxidant activity. *Lebensm.-Wiss. Technol.* 28: 25-30 (1995).

[26] A. Arvouet-Grand, B. Vennat, A. Pourrat, P. Legret, Standardisation d'un extrait de propolis et identification des principaux constituants. *J. Pharma. Belg.* 49: 462-468 (1994).

[27] T. A. Pereira, Effects of flavonoids on thermal autooxidation of Palm oil: structure- activity relationship. *J. Am. Oil Chem. Soc.* 67: 255-258 (1990).

[28] A. Matkowski, Plant *in vitro* culture for the production of antioxidants - A review. *Biotechnol. Adv.* 26: 548-560 (2008).

[29] K. Shimoi, S. Masuda, B. Shen, B. Furugori, N. Kinae, Radioprotective effect of antioxidant plant flavonoids in mice. *Mutat. Res.* 350: 153-161 (1996).

(2016) ; www.mocedes.org/ajcer