International Journal of Chemistry and Material Science Vol. 2(2), pp. 074-079, November 2014
Available online at http://academeresearchjournals.org/journal/ijcms
ISSN 2327-5553 ©2014 Academe Research Journals

Full Length Research Paper

Treatment on industrial wastewater for removal of surfactants

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Accepted 10 October, 2014

Surfactants are among the most widely disseminated xenobiotics that contribute significantly to the pollution profile of sewage and wastewaters of all kinds. Among the currently employed chemical unit processes in the treatment of wastewaters, coagulation-flocculation has received considerable attention for yielding high pollutant removal efficiency. Jar-test experiments are employed in order to determine the optimum conditions for the removal of surfactants, COD and turbidity in terms of effective dosage, and pH control. Treatment with FeCl3 proved to be effective in a pH range between 7 and 9. The process is very effective in the reduction of surfactants and COD, the removals are 99 and 88% respectively, and increased BOD/COD index from 0.17 to 0.41. In addition to the precipitation coagulation process, adsorptive micellar flocculation mechanism seems to contribute to the removal of surfactants and organic matters from this rejection.

Key words: Iron chloride, industrial wastewaters, surfactants, coagulation flocculation.

INTRODUCTION

Surfactants are in widespread use throughout the world. The use of surfactant is gradually increased day by day; the world surfactant production was 1.7, 1.8 and 9.3 million tons in the years 1984, 1987 and 1995, respectively. A wide range of these products are actually synthesized and used in several domains such as textiles, fibers, food, paints, polymers, cosmetics, microelectronic, mining, oil recovery, pulp-paper industries, etc. Anionic surfactants are the major class of surfactants used in detergent formulations and represent about 59% of surfactants used in 1989 (Mathis, 1992). Surfactants are among the most widely disseminated xenobiotics that may enter waste streams and the aquatic environment (Sigoillot and Nguyen, 1992; Margesin and Schinner, 1998; Eichhorn et al., 2001, 2002). They are harmful to human beings, vegetation; and are responsible to cause foams in rivers and effluent treatment plants and to reduce the quality of water. Surfactants cause short term as well as long-term changes in ecosystem. Due to all these reasons, many environmental and public health regulatory authorities have fixed stringent limits for anionic detergent as standard 0.5 mg/L for drinking water and relaxable up to 1.0 mg/L for other purposes (Rao, 1995). Surfactants removal operations involve processes such as chemical and electrochemical oxidation (Lissens et al., 2003; Mozia et al., 2005), membrane technology (Sirieix-Plénet et al., 2003; Kowalska et al., 2004; Fernández et al., 2005), chemical precipitation (Shiau et al., 1994; Talens-Alesson et al., 2002), photocatalytic degradation (Rao and Dube, 1996; Ohtaki et al., 2000; Zhang et al., 2003), adsorption (Ogita et al., 2000; Lin et al., 2002; Adak et al., 2005) and various biological methods (Matthew and Malcolm, 2000; Dhouib et al., 2003; Chen et al., 2005). Each has its merits and limitation in application. Surfactants containing wastewaters treatment by biological processes such as activated sludge is problematic due to the low kinetics of degradation and to foam production (Dhouib et al., 2003). Among the currently employed chemical unit processes in wastewater treatment, coagulation-flocculation has received considerable attention for yielding high pollutant removal efficiency. This process can be directly applied to wastewaters without being affected by the toxicity in the wastewater and could constitute a simple, selective and economically acceptable alternative. The objectives of this study are the examination of coagulation precipitation process efficiency for the treatment of industrial wastewaters with high surfactants content, especially in terms of organic matter and surfactants removals. More specifically, the aim is the determination of the most appropriate iron chloride dose, the examination of pH effects on removal capacity and the identification of optimum experimental conditions for the efficient application of this process.

MATERIALS AND METHODS

Sampling procedures

Samples of effluent are collected from outfall of a microelectronic factory situated in an industrial park of the Casablanca city, Morocco. The generated effluent is discharged into the sea without any treatment. Sampling of the wastewater is carried out according to standard methods for the examination of wastewater.

Chemical coagulation and analysis

Laboratory scale evaluation of chemical coagulation and flocculation is performed using a four-place jar test apparatus. The experimental process consisted of three subsequent stages: initial rapid mixing stage at 160 rpm took place for 5 min, followed by a slow mixing stage for 20 min at 30 rpm, and the final settling step lasted for another 1 h. Four equal volume polyethylene beakers are used to examine the four different dosages of coagulant or initial pH values in each run. Sample bottles are thoroughly shaken, for resuspension of possibly settling solids and the appropriate volume of sample is transferred to the corresponding jar test beakers. First, the optimum pH for the function of iron is determined. A known volume of prepared ferric chloride solution is added to a jar containing 1 L of wastewaters at different pH values adjusted with H_2SO4 and NaOH. To investigate the optimum coagulant dose, the pH value of the wastewater is maintained at an optimum pH as determined above; and varying doses of iron are then added. After 60 min settling, the supernatant is withdrawn for analyses. To assess the efficiency of iron on wastewater treatment, the following are determined: turbidity, chemical oxygen demand (COD) and surfactants.

- Turbidity: The turbidity is determined by turbidity meter (HI 93703 Microprocessor turbidity meter).
- Chemical oxygen demand: COD and other physicochemical parameters (BOD, NTK, Pt….) for wastewater characterization measurements are performed according to Standard Methods (AFNOR, 1999).
- Surfactants: Detergent compounds are determined using solvent extraction-spectrophotometric with Ethyl Violet method (Motomizu et al., 1982).

RESULTS AND DISCUSSION

Fluctuation ranges of the measured values for COD, BOD, NTK, surfactants, total phosphorus etc., are given in Table 1. The wastewater is characterized by substantial organic matter and high surfactants contents. The company uses a liquid anionic surfactant on the manufacturing process, it is a mixture of ammonium nonylphenol ether sulphate (60%), ethanol (15%), water (25%), dioxane (<0.1%) and ethylene oxide (<0.0015 %). In fact, the wastewaters did not meet the proposed Moroccan effluent standards. In order to meet these trade-related demands and to respect acceptable environmental standards, it is necessary to subject effluents to an appropriate treatment. BOD/COD ratios indicate that a biological treatment seems to be not suitable (Metcalf and Eddy Inc, 1985; Al- Momani et al., 2002), and then a physicochemical process is required.

Coagulation flocculation process is examined for the treatment of the effluent. Numerous jar tests are carried out in order to establish a practical understanding of the coagulation performance for this application. Initially, the tests are carried out to determine the optimum pH for the function of iron. A fixed dose of iron is added to the effluent wastewater and the pH of the mixture is then adjusted with sodium hydroxide and sulphuric acid. The effects of pH on turbidity and COD removal from jar tests for coagulation of wastewater using ferric chloride are shown in Figures 1 and 2. It can be seen that turbidity and COD removals are most effective at a pH range between 7 and 9. The rate of turbidity and COD removal decreased if the pH was lower than 7 or higher than 9. Experiments were carried out to determine the optimum dose of iron. The coagulation flocculation of wastewater is investigated using iron doses of 600–1100 mg/Lat coagulation pH = 8. Coagulated wastewater samples are tested for residual COD and surfactants. The removal rate is shown to increase with the $FeCl_3$ dosage (Figures 3 and 4).

Figures 4 and 5 indicate that a minimum dosage of FeCl3 of 900 mg/L is required on the reduction of COD and surfactants load from the wastewater by coagulation to an acceptable level. At this optimum dosage, the COD removal reached 88% and it is reduced to approximately 400 mg/L, and then the treated wastewaters respect the Moroccan acceptable environmental standard in terms of COD (500 mg/L). The process is also effective in the reduction of surfactants which reached 99%. However, residual surfactants in treated wastewaters (Table 2) are slightly above the one recommended by Moroccan legislation (3 mg/L). Then, a further treatment is necessary to allow the surfactants guide level. The effect of iron on pollutants reduction shows that there is a comparable evolution between COD and surfactants removals. Figure 5 shows positive correlation between COD and surfactants removals, R^2 = 0.99. It indicates that there exists similar mechanism for the removal of

Table 1. Microelectronic plant wastewater characteristics.

Parameter	Fluctuation range	Average	Moroccan guide level
pH	7.00 - 7.60	7.3±0.25	6.5 - 8.5
Conductivity (ms/cm)	0.60 - 0.75	0.66±0.06	2.7
Turbidity (NTU)	15.91 - 34.50	24.35±7.75	-
Sulphate (mg/L)	45.6 - 58.2	52.2±5.89	-
Pt (mg/L)	1.27 - 1.42	1.335±0.06	10
NTK (mg/L)	65.38 - 72.58	69.24±3.19	30
COD (mg/L)	5253.62 - 6333.44	5846.76±508	500
BOD_5 (mg/L)	951.21 - 1051.45	998.16±41.28	100
Surfactants (mg/L)	915.32 - 956.51	935.45±17.31	3
BOD_5/COD	0.16 - 0.18	0.16±0.008	-

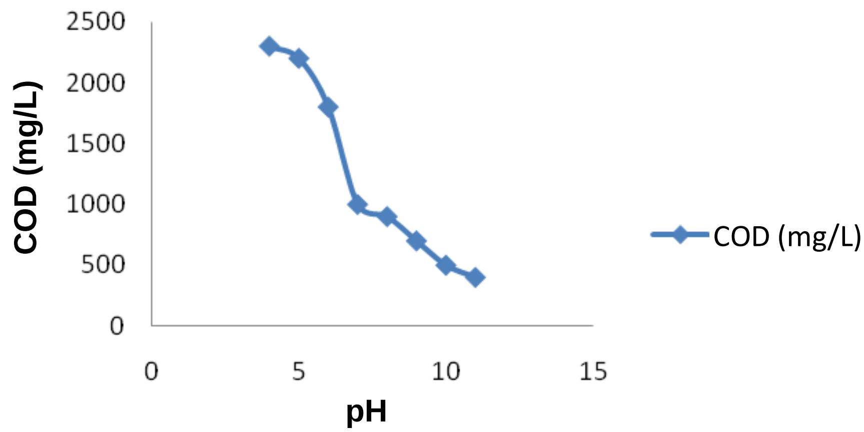

Figure 1. Effect of coagulation pH on $FeCl_3$ efficiency.

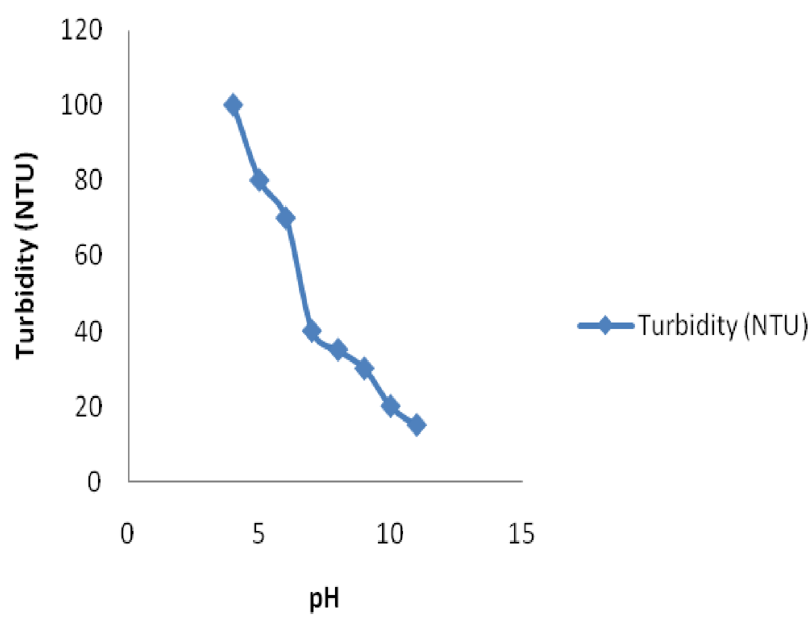

Figure 2. Effect of coagulation pH.

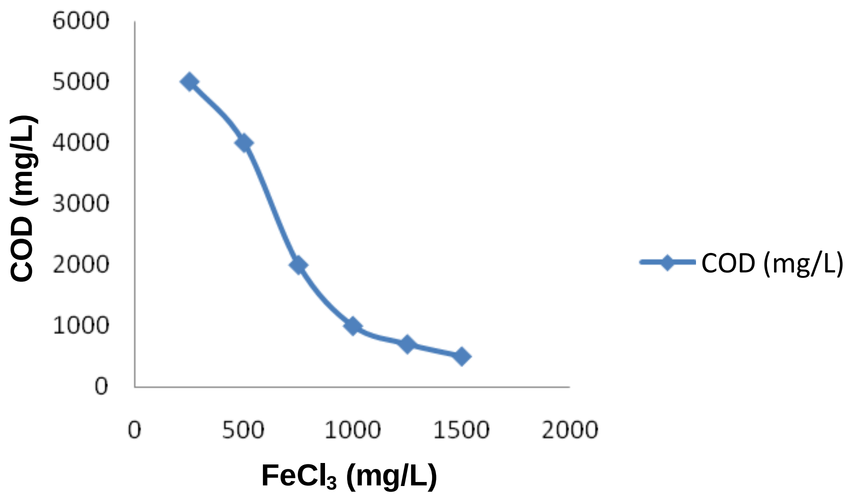

Figure 3. Effect of $FeCl_3$ on COD reduction.

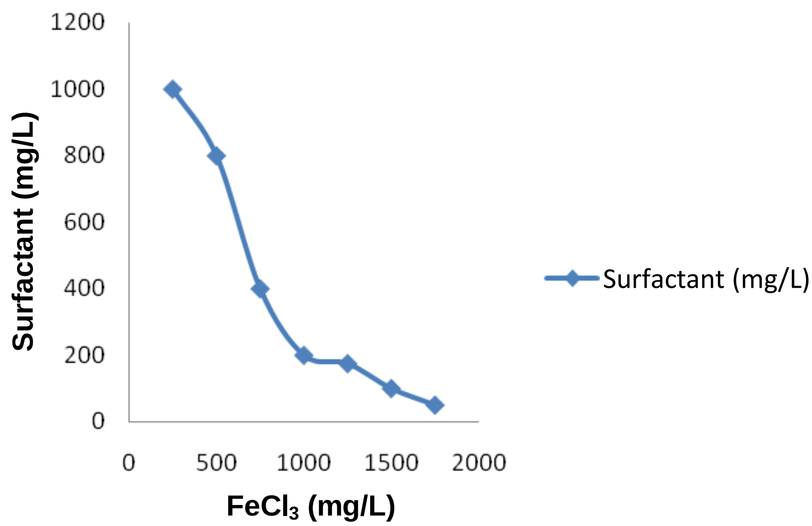

Figure 4. Effect of $FeCl_3$ on surfactant removals.

surfactants and organic matters. Thus the conditions for precipitation coagulation of the surfactant correspond with the conditions for precipitation coagulation of the other substances. Talens-Alesson et al. (2002) report that Fe^{3+} can be used as an alternative to Al^{3+} in adsorptive micellar flocculation (AMF). They concluded that the pH range of Fe^{3+} solutions resulting from flocculation of anionic surfactant sodium dodecyl sulphate solutions with Fe^{3+} is 1.8-2.5. On the basis of the results obtained on surfactants and COD removals and on the pH of coagulated wastewaters at pH = 2.4 (Table 2), it seems that, in addition to precipitation coagulation process, AMF mechanism contributes to the removal of surfactants and organic matters from this rejection. The cations Fe^{3+} binds itself to a micelle, causing two simultaneous effects: it suppresses repulsion between micelles flocculating them and effectively removing micellar surfactant from solution in the form of an aggregate, and it binds organic compounds to the flocs (Porras and Talens, 1999, 2000; Talens-Alesson, 2001). It can be concluded that, in addition to precipitation coagulation process, adsorptive micellar flocculation mechanism seems to contribute to the removal of surfactants and organic matters from this rejection. Many authors use the ratio of BOD/COD as biodegradability index (Chamarro et al., 2001; Scott and Ollis, 1995). Table 2 shows that BOD5/COD ratio for initial and treated wastewaters changed from 0.16 to 0.41. It can be seen that the process leads to noticeable improvement in the biodegradability index for the microelectronic plant wastewaters. This improvement in biodegradability is due to reduction in the proportion of COD not amenable to

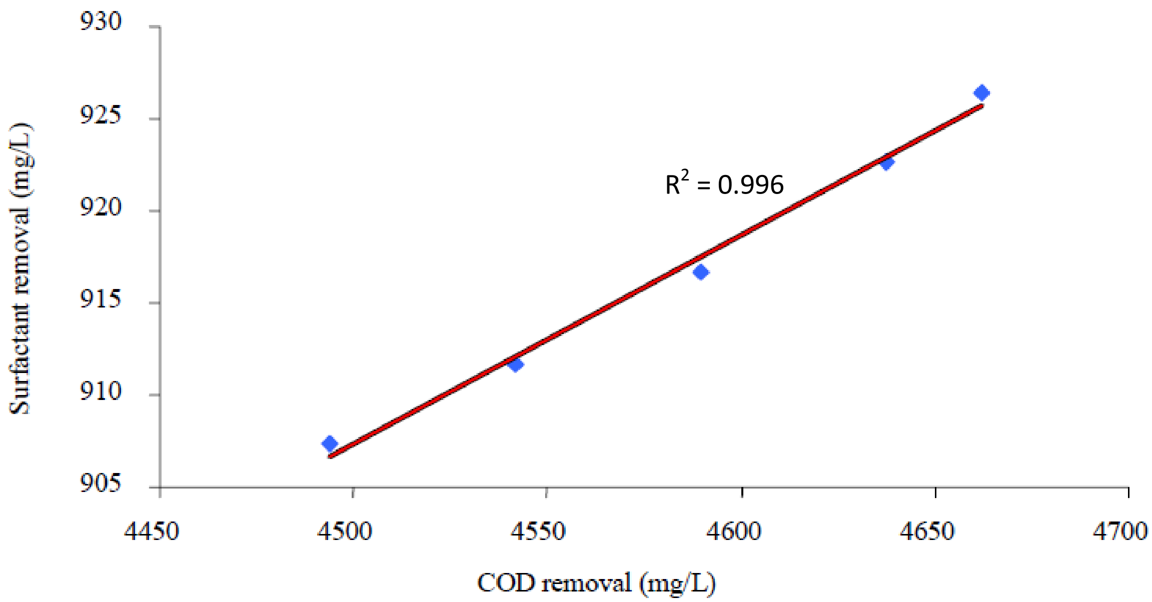

Figure 5. Correlation between COD and surfactants removals.

Table 2. Characteristics of raw and treated wastewaters.

Parameter	Raw wastewaters	Coagulated wastewaters
pH	7.3±0.25	2.4±0.25
BOD5/COD	0.16±0.008	0.408±0.01
Surfactants (mg/L)	935.45±17.31	4.6±1.25

biological mineralization. Wastewater can be considered readily biodegradable if it has a BOD5/COD ratio between 0.4 and 0.8 (Metcalf and Eddy, 1985; Al-Momani et al., 2002). This limit is reached for the microelectronic plant wastewaters, which indicates that a biological treatment can be applied as a further treatment to enhance the pollutants removal and to more reduction of surfactants contents to allow the guide level.

Conclusion

Surfactants are among the most widely disseminated xenobiotics that contribute significantly to the pollution profile of sewage and wastewaters of all kinds. Among the currently employed chemical unit processes in the treatment of wastewaters, coagulation-flocculation has received considerable attention for yielding high pollutant removal efficiency. Jar-test experiments are employed in order to determine the optimum conditions for the removal of surfactants, COD and turbidity in terms of effective dosage, and pH control. Treatment with $FeCl_3$ proved to be effective in a pH range between 7 and 9. The process is very effective in the reduction of surfactants and COD, the removals are 99 and 88% respectively, and increased BOD/COD index from 0.17 to 0.41. In addition to the precipitation coagulation process, adsorptive flocculation mechanism seems to contribute to the removal of surfactants and organic matters from this rejection.

ACKNOWLEDGEMENTS

The author gratefully acknowledges his family and friends for their guidance and help in the completion of this paper.

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