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Fenton's reagent and coagulation-flocculation as pretreatments of combined wastewater for reuse

A. Durán Moreno*, E. González Lorenzo*, C. Durán De Bazúa*, J. Malpica De La Torre and R.M. Ramírez Zamora****

* Facultad de Química, UNAM, Conj. E, Laboratorio 301, Ciudad Universitaria, Coyoacán, 04510 México, D.F. (E-mail: *alfdur@servidor.unam.mx*)

** Instituto de Ingeniería, UNAM, Apdo. Postal 70-472 Coyoacán, 04510 México, D.F.

Abstract In Mexico City, drinking water is mainly produced from groundwater (70%). This practice has caused collateral problems such as Mexico City's soil sinking (5–30 cm/year). One of the most viable alternatives to palliate this problem is the treatment of wastewater for reuse in either irrigation or for groundwater artificial recharge. This paper presents the evaluation of two physicochemical pretreatment systems to treat the wastewater from the metropolitan area of the Mexican Valley that are conducted by two main sewage systems called Great Canal and Churubusco River. In this research two treatment processes were studied: 1) coagulation–flocculation and, 2) Fenton's reagent. For each one of these processes suggested, tests were performed with wastewater samples of the Great Canal and the Churubusco River mixed in a volume ratio of 1:1. In the case of the coagulation–flocculation process, additional experiments were performed to determine the optimal conditions by applying an experimental design technique. In this experimental design, six coagulant agents were considered (alum, ferric chloride, three coagulant reagents of polymeric kind with aluminium and a coagulant reagent of natural origin), and three flocculant agents (an anionic, a cationic, and a non ionic polymers). Concerning the application of the Fenton's reagent (Fe^{2+}:H_2O_2), the experimental variables were the weight ratio of the ferrous iron and the hydrogen peroxide and the concentrations of these reagents. The pH value was controlled to be near to 4. For the best experimental conditions, the effluent of the Fenton's method showed similar physicochemical characteristics to the wastewater treated by coagulation–flocculation. Nevertheless, Fenton's reagent showed two very important advantages compared to the coagulation–flocculation process: a disinfecting effect and a lower production of residual sludges.

Keywords Coagulation–flocculation; Fenton's reagent; reuse; wastewater

Introduction

Mexico City consumes 34.8 m^3/s of drinking water. Almost 70% of this total flow is obtained from the former Mexican basin, now Valley aquifer. This practice, due to soil characteristics, has caused collateral problems such as uneven soil sinking. Sánchez-Bribiesca *et al*. (1997) showed that a flow of 10 m^3/s is necessary for the artificial recharge of this aquifer. Since Mexico City produces 21.5 m^3/s of wastewaters, this recharging amount could be completely covered by treating and reusing these wastewaters. Physicochemical treatment systems, such as advanced primary treatment (APT), and biological treatment plants are installed in Mexico City to treat wastewaters for reuse. The APT efficiently removes most of the colloidal and suspended solids. Fenton's method can be considered as an APT variant due to the fact that it is composed of the coagulation–flocculation–sedimentation processes but also of a chemical oxidation stage. This latter process would allow the Fenton's method to be more efficient than the APT.

The first application of the Fenton's reagent was the removal of organic pollutants in municipal wastewater (Barb *et al*., 1951; Bishop *et al*., 1968). The principle of this method is the formation of hydroxyl radicals ($OH^•$) and other organic radicals ($ROH^•$) in order to improve the removal by oxidation of organic substances.

The following oxidizing species are generated as a result of the reaction between ferrous iron and hydrogen peroxide (Sawyer, 1997):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH- + OH^{\bullet} \qquad k_1 = 41\ mol^{-1}\ l\ s^{-1} \tag{1}$$

$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \tag{2}$$

$$R^{\bullet} + H_2O_2 \rightarrow OH^{\bullet} + ROH^{\bullet} \tag{3}$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH- \qquad k_2 = 3 \times 10^{8}\ mol^{-1}\ l\ s^{-1} \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\bullet -} + H^{+} \qquad k_3 = 2 \times 10^{-2}\ mol^{-1}\ l\ s^{-1} \tag{5}$$

Some kinetic studies applying the Fenton Method to different toxic substances (phenols, atrazine, dioxine, etc.) have concluded that the optimum pH to accomplish the reaction is between 3 and 5 (Arslan and Balciglou, 1999). These studies also show that the ferrous sulphate and hydrogen peroxide doses are a function of the initial concentration of the compounds that have to be eliminated. The determination of the dose and the optimum reaction time must be experimentally found through kinetic oxidation tests in batch reactors.

Ramírez-Zamora *et al*. (2001) have studied the characteristics of coagulation–flocculation sludges (aluminium sulfate) and Fenton's reagent sludges produced from the treatment of a municipal wastewater. The authors found that the Fenton sludges presented preferable characteristics such as the specific resistance to filtration (SRF), metals and pathogen content (fecal and total coliforms, helminth eggs, and *Salmonella* sp.). The SRF of the Fenton sludges (1.55×10^{13} m/kg) was 24% less than the alum sludge value (1.92×10^{13} m/kg). The concentrations of fecal coliforms (0 MPN/g TS), *Salmonella* sp. (0 MPN/g TS), Helminth ova (22 HH/g TS) and metals correspond to the limits for biosolids Class B for land application according to the Mexican legislation. The Fenton's reagent efficiently removes most of the pathogens, considered by this legislation, by means of the combined action of the different stages that constitute this process. These results exhibit the Fenton's reagent as a feasible treatment option for generating sludges with characteristics of biosolids class B for land application.

Methodology

For each one of the physicochemical wastewaters pretreatment proposed, laboratory tests were performed with wastewater samples from two of the main sewage lines in Mexico City, the Great Canal and the former Churubusco River, in a ratio of 1:1. The coagulation–flocculation and Fenton's reagent experiments were accomplished through the jar-test technique.

The coagulant and flocculant agents employed are listed in Table 1. The coagulant agent Tanfloc was provided by the Brazilian company Tanac. The flocculant zwitterionic agent 2PNOD2R was developed at the Metropolitan Autonomous University of Mexico (UAM). All the other coagulant and flocculant agents were provided by Kemwater Mexico.

In order to optimize the number of experiments of coagulation–flocculation to be performed, an experimental design technique, of a factorial type with two levels 2^k, was employed (k represents the number of experimental variables). Three experimental variables were chosen: pH value, coagulant agent dose and flocculant agent dose. Therefore, according to the mathematical expression 2^k, the number of experiments performed, for each couple of coagulant and flocculant agents, was 8. Four global physicochemical parameters (color, turbidity, total suspended solids, TSS, and total chemical oxygen demand, COD) were quantified in the influent and effluent of each experiment. Table 2 shows the values of the experimental conditions for coagulation–flocculation tests.

In the case of the Fenton's reagent experiments, the experimental variables chosen were: the ratio and concentration of the two chemical species that constitute the Fenton's reagent, ferrous iron (Fe^{2+}) and hydrogen peroxide (H_2O_2). This part of the experimental work was divided into two stages: selection of the best doses and mass ratio of Fe^{2+}/H_2O_2. The pH values were adjusted with hydrochloric acid near to 4 according to the literature recommendation (Walling, 1975).

In each experiment, samples of the raw and treated wastewater were analyzed to evaluate removal of COD, color, turbidity and total suspended solids (TSS). For the experiments which showed the best removal of these physicochemical parameters, microbiological contents (total and fecal coliforms and *Salmonella* sp.) were also performed. The analytical methods applied were those recommended by the *Standard Methods for the Examination of Water and Wastewater* (APHA *et al.*, 1998). All the experiments and chemical analyses were performed in duplicate.

Results and discussion

Coagulation–flocculation

According to the experimental design presented in Table 2, jar test experiments were performed at two different values of pH (6 and 9). Eight experiments were performed for each one of the couple of coagulant and flocculant agents, at minimal and maximal concentrations of each one of them. Since six coagulants and three flocculants agents were tested, the whole number of coagulation–flocculation experiments performed was 288 (considering that all experiments were performed in duplicate).

Figures 1 to 4 show, respectively, the best removal performance of COD, color, turbidity, and TSS with each couple of coagulant and flocculant agents (pH = 6; coagulant

Table 1 Coagulant and flocculant agents employed in these experiments

Coagulant agents	Flocculant agents
C1: PAX XL-60 (*polychlroride sulfate, total aluminium 7.5%*)	**F1**: Prosifloc (*anionic*)
C2: PAX16 (*polychlroride sulfate, total aluminium 8.2%*)	**F2**: Technifloc (*cationic*)
C3: Ferrix (*ferric chloride, total iron 20%*)	**F3**: 2PNOD2R (*non ionic*)
C4: Aluminium sulfate	
C5: Technifloc-plus (*polychlroride sulfate, total aluminium 12.7%*)	
C6:Tanfloc (*natural organic coagulant*)	

Table 2 Experimental conditions for the coagulation–flocculation tests performed

Experiment	pH Value	Doses of coagulant agent* (mg/L)	Doses of flocculant agent (mg/L)
1	9	100	1.0
2	9	100	0.1
3	9	20	1.0
4	9	20	0.1
5	6	100	1.0
6	6	100	0.1
7	6	20	1.0
8	6	20	0.1

* In the case of the coagulants agents based on aluminium, the dose added was specified considering a same dose of aluminium. For Ferrix, the dose of ferric iron was equivalent to these of aluminium. For Tanfloc the dose in mg/L corresponds to the raw product

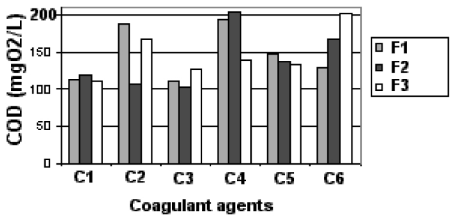

Figure 1 Removal of COD by C-F

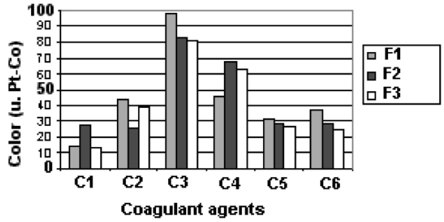

Figure 2 Removal of color by C-F

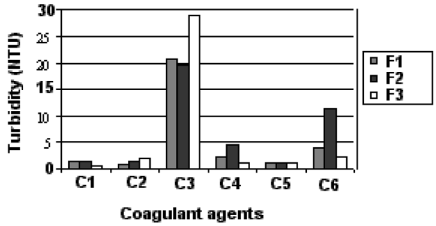

Figure 3 Removal of turbidity by C-F

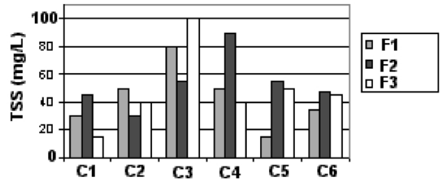

Figure 4 Removal of TSS by C-F

dose 20 mg/L; flocculant dose = 0.1 mg/L). It must be noted that, for each couple, the best removal values were obtained at different experimental conditions. For the four parameters studied, coagulant PAX XL60 offered the best results. In general, the flocculant zwitterionic (ZW) agent produced the lowest residual values of the four physicochemical parameters studied.

All results obtained with PAX XL60 combined with the three flocculants agents show that the best removals were obtained with the couple PAX XL60 – ZW in experiment 5. The best experimental conditions applied to the raw wastewater were: PAX XL60 at 20 mg Al/L, ZW at 0.1 mg/L and pH 6. At these conditions, the residual values of COD, color, turbidity and TSS were 169 mg O_2/L, 47 units Pt-Co, 3.9 NTU and 20 mg TSS/L, respectively.

Fenton's reagent

A first set of experiments was performed in order to select the best ratio of the Fenton's chemical reactive species (Table 3). Chemical oxygen demand (COD) removal was considered as the key selection parameter.

Figure 5 shows the COD removal in treated wastewater produced under the experimental conditions listed in Table 3. The COD value for the raw wastewater was 370 mg/L. In

Table 3 Experimental conditions for the tests performed to select the best Fenton's chemical reactive species ratio

Experiment	Ratio Fe^{2+}:H_2O_2	Doses (Fe^{2+}:H_2O_2) mg/L	pH
1	0:1	0:50	3.99
2	0.5:1	25:50	3.2
3	1:1	50:50	3.17
4	1.75:1	75:50	3.11
5	2:1	100:50	3.23
6	3:1	150:50	3.21
7	4:1	200:50	3.15
8	5:1	250:50	3.16
9	6:1	300:50	3.16
10	7:1	350:50	2.95
11	8:1	400:50	2.93
12	9:1	450:50	2.9

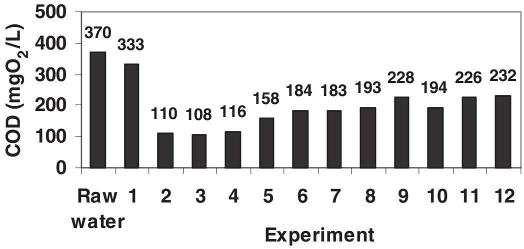

Figure 5 COD in wastewater treated by the Fenton's method at different weight reagents ratio

this graph, it appears that the best COD removal was accomplished with molar ratios ranging from 0.5:1 to 1.75:1 (experiments 2 to 4). These results agree with the stoichiometric relationship shown in Eqs (1) to (4). A molar ratio 1:1 was selected, and at this condition, the residual COD in treated wastewaters was 108 mg O_2/L, which represents a COD removal of 71%.

Afterwards, additional experiments were performed to establish an optimal concentration for ferrous iron and hydrogen peroxide (Table 4).

Figure 6 shows the results obtained at different Fenton's reagent doses, ranging from 10 to 50 mg/L, with a molar ratio 1:1. These results show that the higher is the Fenton's reagent concentration the higher is the COD removal. However, COD removal differences at Fenton's reagent concentrations of 20 mg/L and 50 mg/L were no higher than 14%. Additional experiments, performed at Fenton's reagent doses comprised between 20 and 30 mg/L, indicated that 24 mg/L is the best dose (residual COD concentration of 166 mg O_2/L, and a COD removal of 57%).

Coagulation–flocculation process versus Fenton's reagent

Characteristics of raw and treated wastewaters by the coagulation–flocculation (C-F) process and by Fenton's reagent (F-R), produced at the best experimental conditions, are

Table 4 Experimental conditions for the tests performed to select the Fenton's chemical reactive species concentration

Experiment	Doses (Fe^{2+}:H_2O_2) mg/L	pH
1	10:10	3.79
2	15:15	3.60
3	20:20	3.50
4	25:25	3.49
5	30:30	3.41
6	35:35	3.39
7	40:40	3.39
8	45:45	3.37
9	50:50	3.35

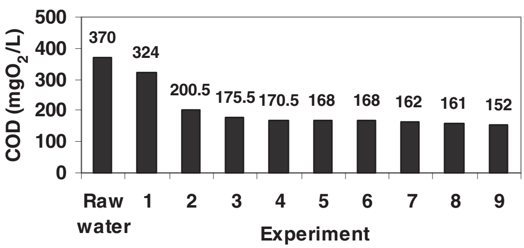

Figure 6 COD in wastewater treated by the Fenton's method at different reagents doses

Table 5 Characteristics of raw and treated wastewater by coagulation–flocculation and by the Fenton's method

Parameter	Raw waste-waters (C-F)	Coagulation – Flocculation effluent	Removal (%)	Raw waste-waters (F-R)	Fenton's method effluent	Removal (%)
COD (mg O_2/L)	468.5	169	64	389.5	166	57
Color (Pt-Co)	566	47	96	189.6	46.5	75
Turbidity (NTU)	179	3.9	99.2	130.2	5.2	96
TSS (mg/L)	155	20	87.1	155	21.5	89
pH units	7.7	6.37	–	4	3.6	–
Produced sludge (g TS/L)*	–	0.19	–	–	0.17	–

* TS: Total solids

Table 6 Microorganisms removal by coagulation–flocculation process and Fenton's reagent

Microorganisms	Raw wastewaters	Coagulation – flocculation effluent	Fenton's reagent effluent
Total coliforms (MPN/100 mL)	1.2×10^8	3×10^4	< 2
Fecal coliforms (MPN/100 mL)	5×10^6	1×10^3	< 2
Salmonella sp. (MPN/100 mL)	7×10^3	< 2	< 2

MPN = more probable number

listed in Table 5. It should be noted that raw wastewater characteristics in both cases were slightly different, due to the fact that raw wastewater sampling for coagulation–flocculation was performed two weeks before the Fenton's reagent experiments. From Table 5, it could be appreciated that both physicochemical pretreatments produce similar treated wastewater characteristics. The Fenton's reagent shows a lower sludge production compared to coagulation–flocculation. This result is important because in physicochemical treatments handling and disposal of produced sludges represent a very important fraction of the operational costs.

Table 6 shows the results of the microorganisms removal by the two wastewater pretreatments studied. Raw wastewaters presented a high content of microorganisms including some pathogens like *Salmonella* sp. (concentration was 7×10^3 MPN/100 mL). Contrarily to the coagulation–flocculation process, Fenton's method was able to completely eliminate the microorganisms in the treated wastewaters. The microorganisms removal observed with the coagulation–flocculation process was attributed to a microorganisms transfer from the wastewater to the chemical flocs produced, whereas microorganisms removal with the Fenton's method was attributed to a microorganisms lethal oxidation by the action of the hydroxyl radicals produced during Fenton's reaction (Ramírez-Zamora *et al.*, 2001).

Conclusions

In the case of combined wastewaters (municipal and industrial wastewater), like the ones produced in Mexico City, physicochemical treatments should be preferred to the most economical biological process due to the unexpected variations in composition and to the eventual presence of toxic compounds. Coagulation–flocculation is a classical water and wastewater physicochemical treatment that is very effective in the removal of particulated materials. Nevertheless, this process has a poor effect on toxic compounds and pathogens that remain in solution. Fenton's method is a physicochemical treatment composed of a combination of coagulation–flocculation and oxidation processes. In this work, application of Fenton's reagent produced a treated wastewater with characteristics similar to those obtained by commercial coagulant and flocculant agents. In both cases, COD removal was higher than 50%, and color, turbidity, and total solids suspended removal rates were above 85%. Fenton's reagent showed two important advantages compared to the coagulation–flocculation process: a disinfecting action, since the fecal coliforms and *Salmonella* sp. contents were completely eliminated in the treated wastewater, and the sludge production was 10% lower than the one found for coagulation–flocculation (0.17 and 0.19 TS g/L, respectively). Based on these results, Fenton's reagent appears as an interesting physicochemical pretreatment option for combined wastewater treatment, and its higher costs, if compared to those of commercial coagulant and flocculant agents, could be compensated by a lower consumption of disinfecting agents and by the lower costs of sludge handling and disposal. On the other hand, further research is being carried out in the laboratory in order to improve the economical feasibility of Fenton's reagent for wastewater treatment. Electrogeneration of Fenton's reagents (Fe^{2+} and H_2O_2) appears as a promising option for the classical Fenton's reaction. Recent results have shown that electrogeneration allows a significant reduction in wastewater treatment costs, to the extent that this process can be twice as economical as APT (Durán Moreno *et al*., 2002).

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