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Optimization of Fenton's reagents by means of surface response model

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Remediation of industrial wastewaters represents a stringent problem in modern society, which needs particular understanding and ad-hoc solutions. In this work, we performed extensive experimental research of chemical Fenton oxidation in order to understand the optimal operative conditions to be applied in real industrial wastewaters treatment.
We analyzed the effectiveness of COD removal from different wastewaters within a wide range on initial COD content.
Using a factorial experimental approach on the Fenton's reagents ([H_2O_2] and [Fe^{2+}]), we analyzed the results developing an analytical second-order model to asses the role of different variables on the COD removal.
We discuss the role of different terms of the model by statistical analysis and underline the importance of the inclusion of the initial [COD] in the model, to account for the variability of initial conditions.
An efficient surface response function is developed choosing three variables, namely: the initial [COD] of the sample, the [COD]/ [H_2O_2] and [H_2O_2]/ [Fe^{2+}].
We obtained an accurate description of the % COD removal in different initial conditions.
In particular, we observe that the proportions of Fenton's reagents needed to reach maximum COD removal is simple function of the initial COD.
These discoveries will help efficient treatment of wastewaters with different chemical conditions, allowing time and money saving.

1. Introduction

The effective treatment of industrial wastewaters represents nowadays an urgent and timely problem that the fundamental engineer research must consider (Metcalf and Eddy, 2002).
In particular, treatment plants must face problems related to the great diversity of composition and volume of the wastewaters that come from many different industries (textile, photographic, paper, pharmaceutical among the others). These heterogeneous

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wastewaters pose serious problems as potential hazards for both health and environment due to many recalcitrant organic compounds, toxic materials and heavy metals.
Advanced oxidation processes (AOPs) represent, at the moment, one of the treatment methods that combine both economical advantages and effectiveness in the contaminant reduction. In particular, AOPs using Fenton's reagents (Neyens and Baeyens, 2003) represent one of the best methods for clean and safe processes for the degradation of organics.
The oxidation using Fenton's reagents (Fenton's process) causes the dissociation of the oxidant and the formation of reactive hydroxyl radicals that destroy organic pollutants to harmless compounds (CO_2, water and inorganic salts) (Huang et al., 1993).

Fenton's reagents are H_2O_2 and ferrous ions.
They generates hydroxyl radicals following the reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \qquad (1)$$

The ferrous iron (Fe^{2+}) starts the reaction and catalyses the decomposition of H_2O_2 in hydroxyl radicals (Neyens and Baeyens, 2003).
The generation of the radicals involves many chain reactions and can be schematized as follow:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad \text{(chain initiation)} \qquad (2)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \quad \text{(chain termination)} \qquad (3)$$

However, the newly formed ferric ions (Fe^{3+}) many decompose hydrogen peroxide in water and oxygen (forming ferrous ions and radicals):

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^{+} \qquad (4)$$

$$Fe-OOH^{2+} \leftarrow HO_2^{\bullet} + Fe^{2+} \qquad (5)$$

The above reactions are referred as Fenton-like reaction.
The organics (RH) are oxidised by hydroxyl radicals proton abstraction ending with the production of organics radicals (R·). These last products are highly reactive and can be further oxidised:

$$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} \quad + \text{further oxidation}$$

The advantages of the Fenton's reagents are the high efficiency, simplicity, the lack of residues and capacity to treat many different compounds.
In addition, it was found that they allow the increasing of biological treatment stages and the degradation of volatile organic compounds (VOC) (Bianco et al, 2009a).

Many different applications of the Fenton's reaction can be found in the literature (Trujillo et al., 2006, Yoon et al., 1998, Wei et al., 1990)

In fact, varying the relative amount of the reagents [H_2O_2], [Fe^{2+}], the process can be tuned to be effective in different conditions.
The performance of the process is monitored measuring the COD removal.
Due to the great variability of the wastewaters in the treatment plants, the amount of reagents must be determined in order to achieve optimal reaction conditions to maximize the efficiency.
Studies along this line were conducted on different wastewaters. By means of a factorial analysis, the optimal conditions of the reaction (in terms of Fenton's reagents concentration) was determined (Benatti et al., 2006). However, many of these studies, varied the initial COD of the wastewaters by dilutions. This ensures that the chemical composition of the samples were constant, and only their concentration is varied within a limited range.
Although the procedure is exact in principle, it can be ineffective if adopted in real wastewaters plants. In fact, there the composition can be heterogeneous and the COD content of the wastewaters can be very different.
In order to investigate further the optimal conditions for the oxidation, in this work we conducted a series of factorial analysis of COD removal by Fenton's oxidation in "real" wastewaters obtained from a treatment plant of industrial's wastewaters.
The factorial analysis, varying the concentrations of the reagents, was used to construct a response model to find the optimal conditions in a wide range of initial COD.

2. Materials and methods

The wastewaters were obtained from the GSA-Veteres industrial's wastewater treatment plant in Civitacastellana, Italy. We choose the wastewater samples with the aim to include different typologies of wastes in order to cover the maximum range of variability of the treated wastewaters in the plant.
To this end, we sampled the wastewaters in a period ranging from April to May 2008.
This period ensured that the obtained samples are well representative of the different operational conditions of the plant and thus allow an extensive statistical analysis.

The experiments were conducted in batch reactor containing 100 ml of sample, continuously mixed at 200 rpm with magnetic stirred bar. Oxidation was carried out with the following steps: pH was adjusted with sulphuric acid (H_2SO_4) 2 M and sodium hydroxide (NaOH) 1 M around to value 3, and the temperature was raised to 30-35 °C with a heating plate. At this time $FeSO_4 \cdot 7H_2O$ was dissolved and then slowly mixed with H_2O_2. After the reaction is completed (1 h) the samples were taken from the beaker and centrifuged for 10 min. at 10.000 rpm. Before the measurements of COD, the samples were properly diluted.

COD was measured with Dr. Lange's kit, cuvette-test LCK 114.

3. Results and discussion

In order to optimize the Fenton's process we applied a surface response methodology (Benatti et al., 2006). COD removal defined as:

$$\eta(\%) = 100 \times \frac{(COD_i - COD_f)}{COD_i}$$

(COD_i and COD_f are the values of COD before and after the Fenton's process reaction, respectively) was considered as the variable to optimize.
The independent variables are: [COD]/[H_2O_2], [H_2O_2]/[Fe^{2+}] and [COD_i].
Although the Fenton's reagents are only H_2O_2 and Fe^{2+}, the inclusion of CODi as an independent variable resulted to be essential to describe the process taking into account the variability of the initial COD (see below).

An histogram of the initial COD for all the sample considered in this work is reported in Fig. 1

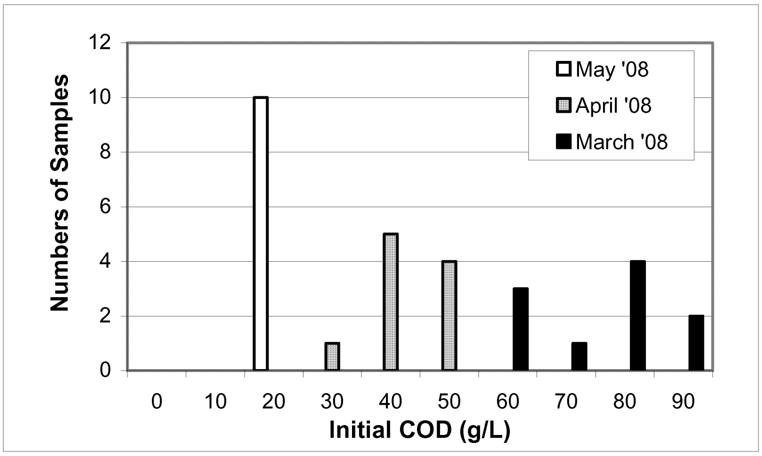

Fig.1: Histogram of the initial COD of the samples considered. Different colours refer to different periods.

We note how the three kinds of wastes present a wide distribution of initial COD with high values (60 < CODi< 100), intermediates (30 < CODi < 60) and low (CODi < 20).

The experimental factorial analysis was performed with 30 tests, with the following limiting values for the independent variables: 0.23 < [CODi]/[H_2O_2] < 3.40, 10 < [H_2O_2]/[Fe_{2+}] < 20 and 11.62 < [CODi] (g/L) < 85.30.
A complete report of all the details for each test will be reported in a dedicated work (Bianco et al., 2009b).

In order to understand the role of each variable in the determination of the COD % removal, we constructed a second order response function, considering the COD % removal as a response function (*y*), while [CODi]/[H_2O_2] (*x1*), [H_2O_2]/[Fe_{2+}] (*x2*) and [CODi] (*x3*) are considered as independent variables.

The choice, as discussed before, is dictated by the wide variation of the initial COD's.
A 2 factor model (using *x1* and *x2*), although effective to describe a single wastewater typology (with similar initial conditions), does not allow a complete regression over the 3 different typology we analyzed.

Thus we used the following quadratic model:

$$y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{j=1}^{k} b_j x_j^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} b_{ij} x_i x_j$$

With $k=3$ and coefficients to be determined from the regression on the experimental data. The three independent variables (*x1*, *x2* and *x3*) are normalized by means of the following relation:

$x_i = \frac{(X - \overline{x})}{\sigma}$ where X represents the non codified value, $\overline{x}$ is the median ($\overline{x} = \frac{X_{\max} + X_{\min}}{2}$) and $\sigma = \frac{X_{\max} - X_{\min}}{2}$.

In this way the coded variables are within -1 (minimum value) and +1 (maximum value).
The regression results in a $R^2 = 0.85$, indicating an excellent agreement between the model-predicted and the experimental values.
Inspection of the significance for each parameters of the model, reveal that the $[H_2O_2]/[Fe^{2+}]$ ratio represents the parameter with less significance (P-value > 0.05). This results is in perfect agreement with other similar studies (Vlyssides, A. et al, 2008).
Omitting the parameters related to *x3*, the significance of the remaining parameters were increased leaving the total R^2 unchanged.
This evidence testifies that the calculated response function is a good predictor of the real experimental results. n Fig. 2, we plot the COD % removal predicted and observed.
The qualitative and quantitative agreement is satisfactory, especially in view of the great chemical variability of the samples.
It can be useful to investigate the response function as a function of two indipentent parameter *(x2, x3*) at fixed *x1* (the initial COD).
We note that the surface presents a maximum for the COD % removal for the range of parameters investigated, with a absolute maximum of about 80%.
In particular, this maximum of removal is dependent (as observed before) on the initial COD of the samples. For example, for high initial COD values (*x1 > 0.7*) the maximum of the surface is for high values of both *x2* and *x3*, while for very low initial COD values we need a lower $[H_2O_2]$ respect to the [CODi] and lower values of $[H_2O_2]/[Fe^{2+}]$.

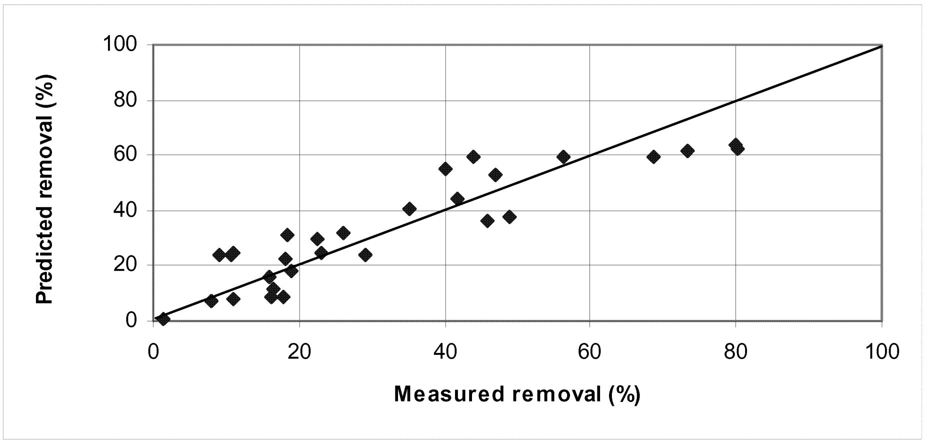

Fig. 2: Regression plot of measured data against predicted values from the second-order model for the Fenton process.

4. Conclusions

The experimental factorial analysis on wastewaters samples taken from a treatment plant, were used to construct a model response function to be applied in real conditions. The second-order model was modified to include the initial COD as an independent variable in order to account for the wide range of initial COD in the treatment plant.
The regression shows an excellent quantitative agreement between the predicted and measured values of COD for different experimental conditions.

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