Measurement 59 (2015) 314–328

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Estimation of the effect of catalyst physical characteristics on Fenton-like oxidation efficiency using adaptive neuro-fuzzy computing technique

Shima Rahim Pouran [a], A.R. Abdul Aziz [a,*], Wan Mohd Ashri Wan Daud [a], Shahaboddin Shamshirband [b,c,*]

[a] Chemical Engineering Department, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Computer System and Technology, Faculty of Computer Science and Information Technology, University of Malaya, 50603 Kuala Lumpur, Malaysia
[c] Department of Computer Science, Chalous Branch, Islamic Azad University (IAU), 46615-397 Chalous, Iran

ARTICLE INFO

Article history:
Received 10 August 2014
Received in revised form 11 September 2014
Accepted 19 September 2014
Available online 28 September 2014

Keywords:
Adaptive neuro-fuzzy system (ANFIS)
Adsorption capacity
Central composite design
Heterogeneous Fenton treatment

ABSTRACT

Catalyst size, which determines surface area, is one of the major factors in catalytic performance. In this study, response surface methodology (RSM) and an adaptive neuro-fuzzy inference system (ANFIS) were applied to quantify the effects of physical characteristics of magnetite on Fenton-like oxidation efficiency of methylene blue. For this purpose, two magnetite samples (M and N) were used and characterized by XRD, BET surface area, particle size analyzer and FE-SEM. Central composite design (CCD) was applied to design the experiments, develop regression models, optimize and evaluate the individual and interactive effects of five independent variables: H_2O_2 and catalyst concentrations, pH, reaction time (numeric factors) and the type of catalyst (categorical factor). For each categorical factor, three quadratic models were developed regarding target responses: decolorization (Y_{MB}), COD (Y_{COD}) and TOC (Y_{TOC}) removal efficiencies (%). The quadratic models were estimated by CCD and ANFIS methodologies. ANFIS was implemented using Matlab/Simulink and the performances were investigated. ANFIS models performed better for catalyst N compared to catalyst M, for color, COD and TOC separately. On contrary, it performed better for catalyst M compared to catalyst N, for combinations of color, COD and TOC. The obtained RMSE and R^2 for the ANFIS networks show the effectiveness of catalyst N compared to catalyst M in Fenton oxidation process.

1. Introduction

Fenton oxidation process is an effective advanced treatment technology for degradation of a wide range of organic contaminants [6,26]. In this process, the reaction between H_2O_2 and Fe^{2+} ions in an acidic solution produces highly oxidative species, mainly hydroxyl radicals, based on Eq. (1) [17]:

$$Fe^{2+}_{aq} + H_2O_2 \rightarrow Fe^{3+}_{aq} + OH^- + OH^{\cdot} \quad (1)$$

$$\equiv Fe^{2+}_{surf} + H_2O_2 \rightarrow \equiv Fe^{3+}_{surf} + OH^- + OH^{\cdot} \quad (2)$$

This oxidation system is highly efficient in terms of organic contaminant removal with relatively less operational cost and under ambient conditions of temperature and pressure [13]. However, in homogeneous Fenton

* Corresponding authors. Tel.: +60 03 79675300 (office) (A.R. Abdul Aziz). Address: Department of Computer System and Technology, Faculty of Computer Science and Information Technology, University of Malaya, 50603 Kuala Lumpur, Malaysia. Tel.: +60 146266763 (S. Shamshirband).
E-mail addresses: azizraman@um.edu.my (A.R. Abdul Aziz), shamshirband@um.edu.my (S. Shamshirband).

http://dx.doi.org/10.1016/j.measurement.2014.09.060
0263-2241/

system, the regeneration of iron ions is impracticable and the reaction is pH-dependent. This is because iron ions are precipitated as iron hydroxide sludge at pH values over 4.0 [10] and its elimination from the reaction medium affects Fenton degradation efficacy adversely. Accordingly, in many instances, soluble iron has been replaced with iron minerals to overcome inconveniences of homogeneous Fenton system [6,26]. These catalysts are environmentally benign compounds and iron is immobilized within their structure that activates Fenton reaction over broad range of pH and without sludge formation. Amongst iron minerals, magnetite, $Fe^{II}O–Fe_2^{III}O_3$, has gained considerable interest in heterogeneous Fenton-like system due to its structural Fe^{II} cations that are important for initiating Fenton reaction. The Fe^{II} cations are occupied in octahedral sites in which the catalytic activity of magnetite is chiefly attributed to octahedral cations exposed on the surface of catalyst (Eq. (2)) [19]. In addition, magnetite can be easily separated from the reaction medium by external magnetic field. Several studies have been explored for dye removal [12] and degradation of aromatic compounds in polluted soil [27] and water [6] using magnetite in Fenton reactions. The efficiency of magnetite catalyzed Fenton process for contaminants removal was reported to be less compared to soluble iron ions [28] because just a small fraction of iron atoms are on the surface of catalyst. In addition, the reaction efficiency for contaminant removal is dependent on operational conditions and physico-chemical properties of magnetite [18]. Therefore, several studies were put in practice to improve its activity through chemical modifications [31,32]. For instance, substitution of iron with other transition metal was reported that improves degradation effectiveness of magnetite via the production of thermodynamically favorable redox pairs and the growth in surface area/absorption capacity of the catalyst [18]. Therefore, it is important to evaluate the degree of the effects of physical properties such as surface area earlier to chemical modifications.

In typical multifactor experiments, one-factor-at-a-time approach is used by varying one factor while keeping other factors constant. This approach is expensive, slow and leads to a large number of experiments. In addition, it is less precise process as it does not evaluate the interaction effects amongst the experimental variables [5]. To solve these shortcomings, response surface methodology (RSM) has been used to design and optimize the experiments, considering the multi-dimensional interactions of the involved factors. The majority of the recent studies have applied RSM to optimize the main operational conditions of Fenton reaction for different hetero-catalysis processes ignoring the effects of catalyst physical characteristics on degradation efficiency [22,24,29], while the activity of catalyst is directly correlated to its surface area [14].

Adaptive neuro-fuzzy inference system (ANFIS) is a specific type of artificial neural networks with very good learning and prediction capabilities, which make it an efficient tool to deal with encountered uncertainties in any system [9]. Even though a number of models have been proposed for modeling pollutants, there are associated disadvantages for these models such as being very demanding in terms of calculation time. ANFIS can be used as an alternative as it offers the advantages of independency to knowledge of internal system parameters, providing compact solution for multi-variable problems and fast calculation [15]. To the best of our knowledge, no study has been done to integrate physical properties of catalyst in RSM for magnetite catalyzed Fenton-like reaction and support the obtained results statistically using ANFIS. Accordingly, in the present work, two magnetite samples (M and N) of different physical characteristics were used and integrated in the design model to quantify their synergistic effects on treatment efficiency along with other main parameters. Herein, the effects of five main process parameters: H_2O_2 concentration, catalyst load, initial pH, reaction time (numerical variables) and the magnetite samples (categorical variable) on the color, COD and TOC removal efficiencies of methylene blue solution was investigated using central composite design (CCD). In addition, experiments were conducted to extract training data for the ANFIS network. ANFIS was used to determine degree of the effects of the physical properties of catalysts on their activity in Fenton, using the data obtained from the DOE designed experiments. Subsequently, different statistical models were developed for both catalysts regarding the target responses and their significance were verified for defined optimum conditions. Methylene blue (MB) was chosen as model pollutant due to its recalcitrant nature, wide application in textile industry, powerful adsorption onto the surface of hetero-catalysts and it was usually chosen as a model contaminant in the similar studies [2,12,31]. In addition, a series of leaching tests were carried out to evaluate the stability of the applied catalysts. The main reason for conducting these experiments was to ensure that the degradation efficiencies of Fenton reaction with the both catalysts have proceeded through heterogeneous route and the instability of the samples or the leaching of iron into the solution, have not had a considerable role in the oxidation process. The present study is especially important when the activity of a catalyst is compared with its chemically modified one and to distinguish the degree of the influence of changes in physical properties on its performance in degradation reaction.

2. Materials and methods

2.1. Chemicals

All the chemicals were of reagent grade and were used as received without further purification. Methylene blue (MB), Hydrogen peroxide (H_2O_2, 30% w/w), Potassium iodide (*KI*), Sodium hydroxide (*NaOH*) and Sulfuric acid (H_2SO_4) were purchased from Merck. Two commercial magnetite samples (Fe_3O_4), Catalase (10,000–40,000 units/mg protein), Sodium sulfite (Na_2O_3S) and Sodium phosphate ($H_2NaO_4P{\cdot}H_2O$) were purchased from Sigma Aldrich. Some properties of the investigated dye, methylene blue, are presented in Table 1.

2.2. Catalyst characterization

The magnetite samples were analyzed with powder X-ray diffraction (XRD) to determine the crystalline phase