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Artificial neural networks developed for prediction of dye decolorization efficiency with UV/$K_2S_2O_8$ process

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ABSTRACT

The present work has focused on modeling the decolorization of C.I. Direct Red 16 (DR16) using UV/$K_2S_2O_8$ process. The experiments were conducted in an air bubbled batch photo-reactor with three liters capacity, and equipped with a UV-C light source of only 6 W, placed horizontally in its center. An artificial neural network (ANN) model was developed to model and predict the behavior of the process. Five important operational parameters and decolorization efficiency were introduced as the inputs and outputs of the network. Six three-layered ANNs with different component functions and also one four-layered ANN were constructed. A developed three-layered ANN provides the best results, using BFGS quasi-Newton backpropagation learning algorithm (trainbfg), "tansig" and "purelin" as transfer functions in hidden and output layers. Also, application of 9 neurons in the hidden layer and 400 iterations for the network calibration caused to satisfy network training while overfitting was prevented. For the four-layered ANN the 5-4 mode of the 9 neurons repartition is the best among all the possibilities. The K-fold cross-validation method, employed for the performance evaluation, showed high correlation coefficient (0.9968) and low mean square error (2.56×10^{-4}) for testing data. Sensitivity analysis indicated order of operational parameters relative importance on the reaction as: time > $[DR16]_0$ > $[S_2O_8]_0$ > pH ≈ temperature.

1. Introduction

More recently, the application of advanced oxidation processes, AOPs, based on sulfate radicals in the field of wastewater treatment has been the subject of interest because sulfate radical anion, $SO_4^{\bullet -}$ (E° = 2.5–3.1 V vs. NHE), possesses higher oxidation potential than hydroxyl radical. Several studies have been carried out with sulfate radicals for the degradation of a variety of chemical contaminants [1–5]. Peroxydisulfate anion, $S_2O_8^{-2}$, by itself, is a strong oxidant and can be used as source of sulfate radicals but it slowly reacts with many organics [6]. It can be chemically via transition metals [7], photo-chemically or thermally [8] activated to generate the stronger oxidant sulfate radicals with a kinetically fast reacting tendency. A summary of the peroxydisulfate chemistry can be presented by the following reactions [9,10]:

$$S_2O_8^{2-} \xrightarrow{h\nu/heat} 2SO_4^{\bullet -} \quad (1)$$

$$SO_4^{\bullet -} + H_2O \rightarrow H^+ + SO_4^{2-} + {}^{\bullet}OH, \quad \text{atallpHvalues} \quad (2)$$

$$SO_4^{\bullet -} + {}^{-}OH \rightarrow SO_4^{2-} + {}^{\bullet}OH, \quad \text{mostlyatalkalinepHvalues} \quad (3)$$

$$SO_4^{\bullet -} \text{or} {}^{\bullet}OH + \text{pollutant} \rightarrow \text{degradationofpollutant} \quad (4)$$

As can be seen in the above reactions the degradation process proceeds with production of the sulfate and hydroxyl radicals. Sulfate ion will be generated as the end-product, which is practically inert and not considered to be a pollutant. The peroxydisulfate is ordinarily available as a salt associated with ammonium, sodium, or potassium. It has been reported that potassium peroxydisulfate $K_2S_2O_8$ (KPS) gives better results in photo-oxidative removal of some organic materials than $(NH_4)_2S_2O_8$ under natural pH [9]. In view of this, and the general unsuitability of adding ammonia to waters, KPS can be the best choice for using in the UV/$S_2O_8^{2-}$ process. Alternatively, potassium peroxydisulfate is much cheaper than other oxidants like hydrogen peroxide.

It has been documented that a considerable amount of the total world azo dyes production is lost during the dyeing processes and provides major wastewater pollution in wastewaters [11]. It is while, most azo dye compounds are resistant to bacterial activity and direct biological treatments are not effective. Consequently azo dye effluents are becoming an important source of environmental pollution [12].

Wastewater treatment by applying AOPs is, in general, quite complex. Since the processes depend on several factors, the mod-

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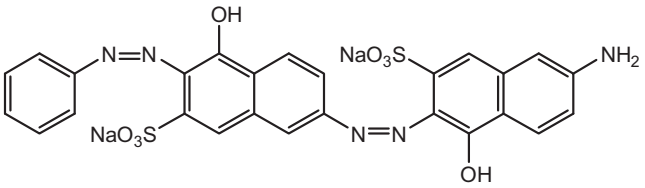

Fig. 1. Structure of the dye molecule.

eling of these processes involves many problems, i.e., a multivariate system is involved. It is evident that these problems cannot be solved by simple linear multivariate correlation [13]. Artificial neural networks (ANNs) are computer based systems that are designed to simulate the learning process of neurons in the human brain. ANNs have been attracting great interest during the last decades as predictive models and pattern recognition. Also, they possess the ability to "learn" from a set of experimental data (e.g., processing conditions and corresponding responses) without actual knowledge of the physical and chemical laws that govern the system. This is one of the main benefits of ANNs when compared with most empirical and statistical methods. Therefore, application of ANNs in the data treatment is especially important where systems present nonlinearities and complex behavior. Feed-forward ANNs are the most often used to map input–output relationships [14]. Recently, ANNs have been increasingly applied in the area of environmental engineering as well as modeling of AOPs in water and wastewater treatments [15,16].

The oxidation efficiency of the UV/KPS process for a given wastewater or parent substrate concentration depends on several variables. Previously, ANN has been used for modeling of four key factors (reaction time, initial concentration of KPS and Basic Blue 3 and light intensity) in the UV/KPS decolorization process [10]. They used a three layered feed-forward network using scaled conjugate gradient (trainscg) algorithm and sigmoid transfer function (tansig). The network was only modified based on neuron numbers in the hidden layer and finally the structure of 4:8:1 was proposed.

The present work is dealing with modeling the effect of five important operational parameters (initial pH of the reaction medium, temperature, reaction time, initial peroxydisulfate dosage and initial concentration of pollutant loading) on obtained decolorization efficiency (DE) of C.I. Direct Red 16 (DR16) in dye aqueous solution via UV/KPS process. To find the model with the best prediction ability, development of six different components three-layered feed-forward back-propagation networks are done. Also, application of a four-layered ANN with different repartitioning neuron numbers in the two hidden layers is investigated. The numbers of hidden layer neurons and calibration iteration are found using simple and commonly used practiced trial and error method in all the applications herein; it is while, some other methods such as empirical or statistical methods [17], hybrid methods such as fuzzy inference [18], constructive and/or pruning algorithms [19], evolutionary strategies through application of genetic operators [20] have been used. Finally, K-fold cross validation method is applied for assessing the reliability of the desired ANN and using the results, sensitivity analysis is done for indicating the relative importance of each operational parameter on the ANN responses.

2. Experimental

2.1. Materials

All materials were used as received without further purification. The azo dye, Direct Red 16, $C_{26}H_{17}N_5Na_2O_8S_2$ (C.I. 27680, MW 637.26) was purchased from Alvan Sabet company (Iran), 99% pure. Fig. 1 displays the structure of this dye. $K_2S_2O_8$, H_2SO_4 and NaOH were all purchased from Merk Company. Distilled water was used throughout this study.

Table 1
The ranges of input and output parameters.

Variable	Range of the parameter value
Input layer	
pH	2–9.35
$[KPS]_0$ (mg/L)	250–1500
$[DR16]_0$ (mg/L)	10–50
T (°C)	15–40
Time (min)	0–30
Output layer	
Decolorization efficiency (DE)	0–1

2.2. Reactor structure

Experiments were performed in a stainless steel rectangular cubic photo-reactor with 3.3 L capacity. A UV-C lamp (6 W, Philips, radiation wavelength less than 280 nm with a peak at 253.7 nm), placed horizontally in a quartz tube at the center of the reactor, was used. Also, a micro-air compressor bubbled air through a distributor from the reactor bottom into the solution for well mixing of reactor contain. The reactor was equipped with a stainless steel water-flow coil for regulating the temperature by means of an external circulating flow of a thermostat bath (OPTIMA-740, Japan) with an accuracy of ±0.1 °C.

2.3. Procedure and analysis

In order to perform each run, 3 L of the solution containing initial concentration of 30 mg/L of the dye (about 5×10^{-5} M) which is within the range of typical concentration in textile waste-waters was prepared and transferred into the reactor [21]. The pH was adjusted to the desired value by means of a pH meter (Denver, UB-10) using dilute H_2SO_4 or NaOH solutions. After adjusting the temperature (which maintained constant during all experiments), appropriate amount of KPS reagent was added into the reactor. Samples (4 mL) were taken at regular times. The dye concentration was analyzed using a spectrophotometer (Perkin Elmer, 55 OSE) by measuring the absorbance at the maximum wavelength, λ_{max} = 526 nm, in the visible region, and using the appropriate calibration curves. Therefore, DE of the process can be calculated as:

$$DE = \frac{[DR16]_0 - [DR16]_t}{[DR16]_0} \quad (5)$$

where $[DR16]_0$ and $[DR16]_t$ are the initial and the appropriate concentration of the substrate at any time, t, respectively.

Chemical oxygen demand (COD) was measured in order to investigate the mineralization of the substrate, using a closed reflux digester reactor (HACH, DRB 200) and the corresponding spectrophotometer (HACH, DR 2800).

Experimental data sets at different operational conditions were used to train and test the ANN model. Different operational parameters ranges are given in Table 1.

2.4. ANN strategy

For every ANN, the first layer constitutes the input layer (independent variables) and last one forms the output layer (dependent variables). One or more neuron layers called hidden layers can be located between them. In this work, input variables are initial concentration of the dye, initial pH, KPS initial dosage, temperature and time of the reaction. DE values are experimental and introduced to the networks as output variable (network response). The topology of an artificial neural network is determined by number of