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Factors Influencing the Ultrasonic Degradation of Emerging Compounds: ANN analysis

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The Ultrasound technology is proven to be effective for destroying organic pollutants in water. The degradation process has been recently exploited as an innovative option in the treatment of persistent emerging compounds. Although the consistent number of experimental studies in the field, practical information for process analysis and optimization is still needed in order to make ultrasound an effective wastewater treatment process.
This paper provides a predictive model for the ultrasonic degradation of organic pollutants. The model is able to consider different parameters in contemporaneity and it is realized through an Artificial Neural Network (ANN) analysis. Some fundamental variables have been individuated among the easily-measurable ones for describing the phenomenology of sonication and a multilayer ANN has been built up and trained for predicting the kinetic constant of several emerging compounds. One of the main peculiarity of the proposed model is the possibility of choosing the ANN input neurons among both operating variables and physical-chemical characteristics of the pollutants. In this way, it has been created a tool for virtually predicting, optimizing and controlling any kind of oxidative process by the means of ultrasound. By linking the model to the pollutant characteristics, the simulation results are *ad hoc* for the application of interest. The results of the ANN training and the simulations of some factor influences are presented in this paper.

1. Introduction

The control of emerging and persistent pollutants in the environment has become a major regulatory issue in recent years (Erto et al., 2010). In order to address it, scientific research is focusing on the technologies aiming at the separation (Di Natale et al., 2009) or destruction (Capocelli et al., 2012) of problematic compounds.
Sonochemical techniques utilize ultrasound to produce an oxidative environment via acoustic cavitation due to the formation and subsequent collapse of micro-bubbles. The implosions result in great energy concentration. Hot spots can reach temperatures as high as 5,200 K and pressures higher than 1,000 atm. This phenomenon provides the cleavage of water molecules (and contaminants) with the formation of reactive species such as hydroxyl radical (•OH) and the initiation of oxidation reactions. Therefore, the application of ultrasonic cavitation to remove pollutants from drinking water and wastewater has drawn increasing interest in last decades (Chowdhury and Viraraghavan, 2009).
Literature is rich of theoretical studies relating to the reactive cavitating bubbles. Usually the simulations, with different levels of approximation, are aimed at the prediction of cavitation intensity in terms of pressure, temperature and radical species concentration (Capocelli et al., 2012) but are unable to predict the removal efficiency of a definite compound (Capocelli et al., 2013a). Therefore, the direct comparison between cavitation and its observed chemical consequences is not fully achieved (Capocelli et al., 2014). Xiao et al. (2013) have discussed about the effect of physiochemical parameters on the kinetic constant in

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the presence of pulsating ultrasounds; this work represents a first effort in transcending the singularity of a determined experiment and evaluating the global effect of parameters. Some indications can be found in reference to the effect of molecular weight and size of molecules in the paper of Fu et al. (2007) while the effect of compound volatility is discussed in the work of Goel et al. (2004). To address the removal efficiency of new compounds on the basis of their physiochemical properties and ultrasound operating parameters is challenging but usually furnish inconsistent results; interaction with operating parameters generally ends up in nonlinearities and unpredictable behaviour. Despite the promising experimental results, there are few applications on full scale and there is still a lack of know-how for designing and optimizing the process (Capocelli et al., 2013a). Additionally, due to the stringent correlation among operating conditions, designers still find many difficulties in linking experimental results obtained in different devices (Capocelli et al., 2013b). To generalize the process and estimate the effect of more than one parameters is still an open field of research (Capocelli et al., 2014).

Artificial Neural Network (ANN) analysis is a valid option for modelling complex phenomena and individuating hidden correlations and influences, thanks to its flexibility and capability in treating nonlinear relationships. ANN consists of an input layer and an output layer interconnected by several nodes. They can rapidly process a large amount of information, have excellent generalization capability for noisy or incomplete data and do not require mathematical interpretations with hypothesis and constrains but reproduce cause-effect relationships through the training and learning the system behavior. Indeed ANN are currently employed in the field of chemical engineering process analysis and optimization (Kumar et al., 2010).

In this paper, a three layer ANN is created and trained with several experimental data of emerging pollutants sonication. The network is used to predict the effect of the main process variables: both operating parameters and physical-chemical features of pollutant. This novel approach allows to increase the predictive potentiality for designing experimental campaign as well as to optimize and control the process. The success in obtaining a reliable and robust network strongly depends on the choice of the involved process variables as well as the available set of data and the domain used for training purposes. An agreement between experimental and calculated data underline the existence of a phenomenological relation between input and output model parameters; this relation, which is hardly recognizable though deterministic prediction, is individuated mathematically through the ANN black-box approach.

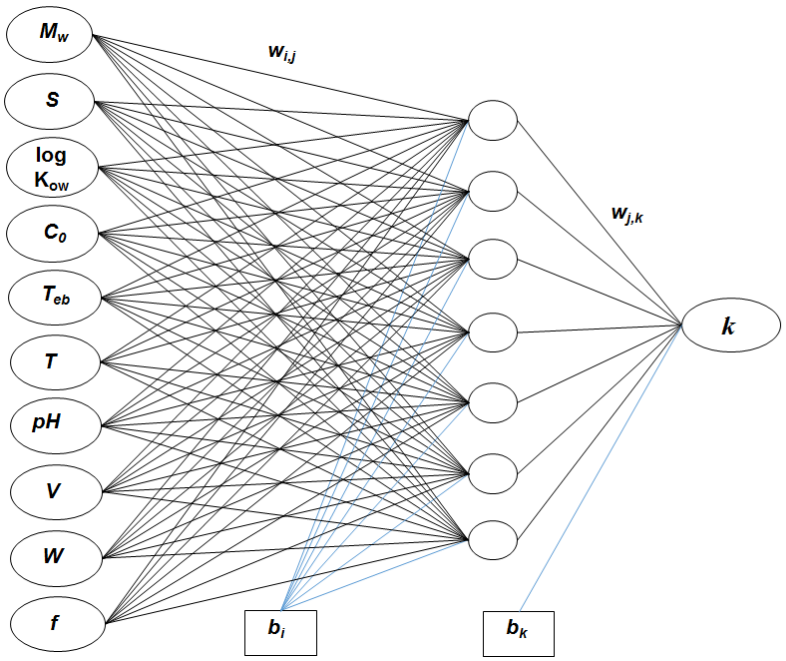

Figure 1: Structure of ANN multilayer feed-forward

2. ANN modelling and training

In the present study a feed-forward network with three layers was constructed to model and simulate the ultrasonic degradation of emerging pollutants. The target variable to predict is the pseudo first order kinetic constant reported in literature in different experimental studies. The Feed-forward ANN is sketched in Figure 1 and allows the information signals to flow only from input to output and adjusts the transfer function that is associated with the inputs and outputs. The sigmoidal function is chosen as representative of the arches. The training phase consists of assigning the values of the net weights $w_{i,j}$ and the bias b_i in the connections between the *i* input neurons and the *j* hidden ones and similarly the weights $w_{j,k}$ and bias b_k (hidden-output). The ANN was trained using the back-propagation algorithm, the mean square error (MSE) between predicted and experimental values of the output variable is the error function to minimize (Kumar et al., 2010).

Table 1: Experimental parameters of organic pollutant degradation by means of ultrasound

Parameter	M_w	**S**	$Log\ K_{ow}$	C_0	T_{eb}	**T**
description	*molecular weight*	*solubility in water*	*oct-wat partition coefficient*	*Initial concentration*	*boiling temperature*	*operating temperature*
unit	g/mol	mg/L	-	mM	K	K
min	*94*	$1.52\ 10^{-2}$	*1.46*	$4\ 10^{-3}$	*334*	*286*
max	*319*	$9.41\ 10^{4}$	*5.85*	$2.5\ 10^{2}$	*742*	*333*
Parameter	**pH**	**V**	**W**	**f**	**k**	
description	*pH*	*solution volume*	*power density*	*frequency*	*kinetic constant*	
unit	-	L	W/L	kHz	min^{-1}	
min	*2.00*	*0.03*	*20*	*20*	$3\ 10^{-6}$	
max	*12.7*	*7*	*3750*	*1000*	$9.8\ 10^{-1}$	

The experimental data corresponds to the sonication of several emerging compounds. These data are chosen from the cited literature and can be grouped in: phenolic and chlorinated from the work of Enterazi et al. (2003), Hamdaoui and Naffrechoux (2008) and Bagal et al. (2013) and aromatic, studied by De Vischer et al. (1996) and Dewulf et al. (2001). A particular attention is given to the degradation of endocrine disruptors (Andaluri et al., 2012) previously investigated also by the Authors of this paper (Capocelli et al., 2012). A recent work of review grouping a large number of experiments with the related main operating conditions is realized by Chowdhury and Viraraghavan, (2009). The collected 154 experiments constitute the ANN training patterns. The parameters have been chose according to their importance as well as availability in original research papers. The operating values of pH, initial concentration of pollutant, temperature, power density and frequency of Ultrasound have been found in the cited. The pollutants have been characterized through the values of molecular weight, solubility, octanol-water partition and boiling point. All the samples have been normalized in the 0-1 range. The simulations indicated that the introduction of 7 hidden neurons minimizes the MSE ($9.127 \cdot 10^{-4}$). The system of variables together with description and the variability range implemented in this research are reported in Table 1.

3. Results and discussion

The data sets were divided into training, validation and test subsets (respectively containing 70 %, 15 % and 15 % of the data). Figure 2 illustrates, in a parity diagram, the simulation of the ANN in comparison

with the whole set of experimental data; a good agreement is found after the ANN validation. The model, once tested, can be used for predicting Ultrasound behavior in any kind of configuration. In order to discuss the effect of the main process parameters, two example of simulation are presented.

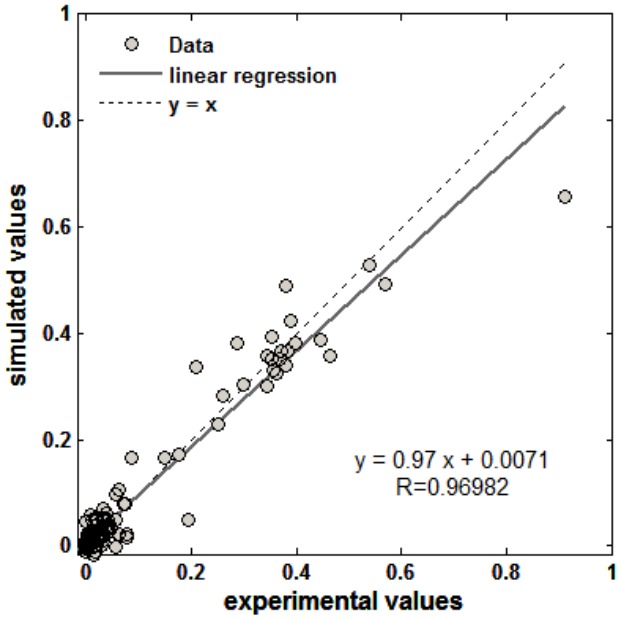

Figure 2: Parity diagram of the ANN: simulated versus experimental data (normalized)

The first one regards the degradation of an endocrine disruptor compounds (EDC), the Bisphenol A. The simulation is realized by fixing all the process variables but the Ultrasound frequency (*f*) and power density (*d*); the results are shown in Figure 3 as contour plots. It is possible to observe that the best degradation rates (higher kinetic constant values, *k*) are reached at higher frequencies and power levels, as indicated in literature (Andaluri et al., 2012). The phenomena are mainly addressed to the bubble dynamics: generally at higher power and frequency, the bubble collapse is more violent resulting in higher local pressure, temperature and radical production (Capocelli et al., 2012). Moreover, at a fixed value of power density, the increase of frequency may cause the lowering of *k* therefore suggesting the existence of an optimal operating frequency. Also this aspect is in accordance with the literature (Capocelli et al., 2012).
A more practical information is given in Figure 4, where the results are expressed in terms of energy consumed per order E_{EO} (kWh/m^3), a very useful parameter in comparing treatment technologies from an economical-feasibility point of view (Andaluri et al., 2012). The contour plots are calculated by ANN simulation for the whole set of experimental data used in the training stage. The results are extended for different levels of frequency and reported versus the *log* K_{ow} of the compounds. The highest energy consumption for pollutant degradation is required globally at lower frequency, thus confirming the previously discussed phenomena. Furthermore, a critical value of the *log* K_{ow} at a fixed frequency, can be individuated in Figure 4; this should be addressed to the different mechanism of degradation occurring near or inside the cavitating bubbles (Xiao et al., 2013). The more lipophilic substrate reacts mainly in the interface or gas region, while the hydrophilic compound degradation occurs in the bulk solution through oxidative species capable to migrate out of the collapsing bubbles. Clearly, a single physicochemical property is unlikely to define the sonication; nevertheless the behavior shown in Figure 4 can be explained by the combination of the cited degradation mechanisms in dependence of the frequency.
As suggested in the work of Xiao et al. (2013), other physiochemical properties should be investigated. Moreover, other fundamental operating parameters (rarely reported in literature for experimental parameters) should be included in the ANN modelling for taking into account the reactor shape and the ultrasound intensity [W/m^2].

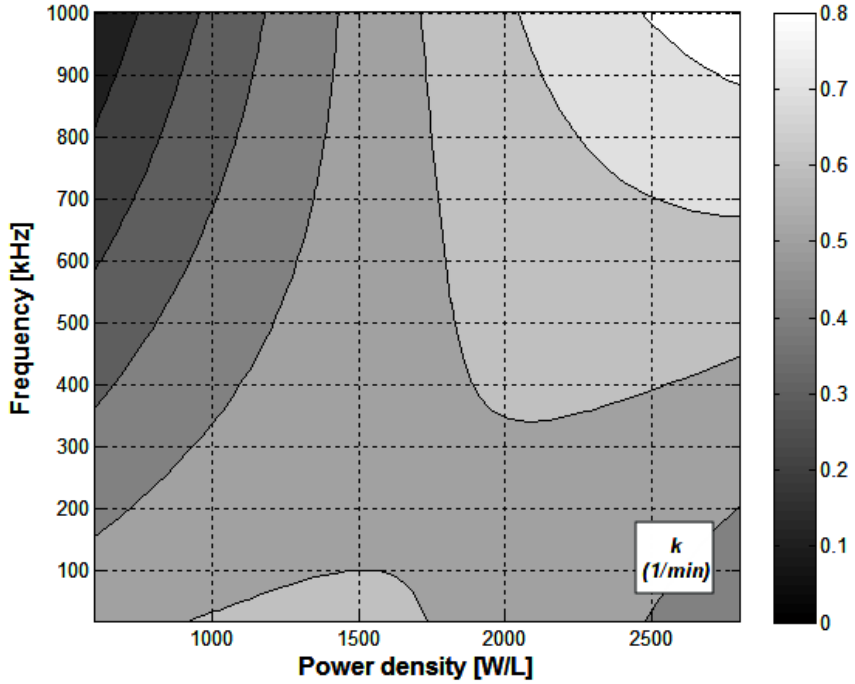

Figure 3: ANN Simulations of Bisphenol A degradation kinetic constant k (min^{-1}) for different values of Ultrasound frequency f [kHz] and power density d [W/L]. C_0=1mM, V=0.250 L, T=293 K, pH=3

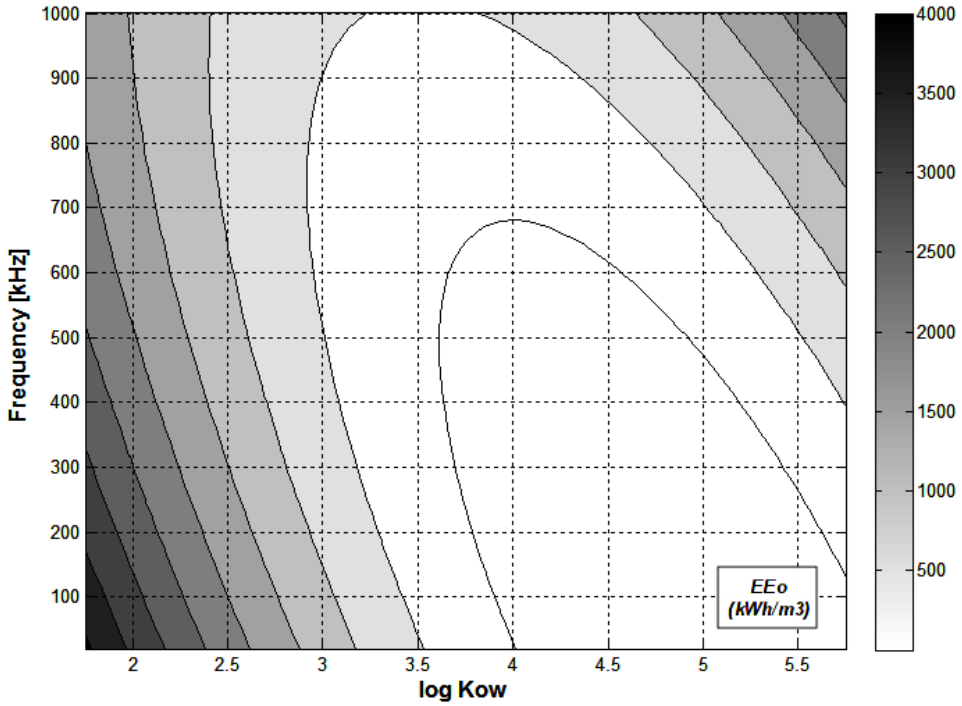

Figure 4: ANN simulations of energy-per-order E_EO (kWh/m^3) for all the considered compounds (different values of log Kow and Mw) at different frequency levels: f = 20-1000 kHz, C_0=1 mM, T=293 K, pH=4, d=600 W/L, V=0.25 L

4. Conclusions

In this work, an artificial neural network has been created and implemented for evaluating the Ultrasound oxidation process parameters. A three layer feed forward ANN has been created and tested with experimental data of emerging compound sonication. The variables have been chosen from both operating parameters and physiochemical characteristics of the contaminants. ANN model was found to simulate clearly the collected experimental data. The effect of some parameters has been addressed in according to the scientific literature. The first order kinetic constant has been found in the range highlighted by experimental results (the case of Bisphenol A is reported) and an energy consumption of 10^3 kWh/m^3 as order of magnitude has calculated for several compounds. The model allows to estimate the feasibility of ultrasonic treatment for any emerging pollutants. Moreover, the dependence of the critical frequency to the log K_{ow} is highlighted by the ANN simulation.

This effort of abstraction allowed to realize a valid tool for predicting the feasibility of the treatment and for designing new experimental campaigns. Further advances should include the implementation of additional properties (such as Henry constant and Molar volume) and parameters (such as aspect factor and power intensity) in order to improve the characterization of pollutant degradation mechanisms. The model development will end up in the individuation of parameter correlation and relative importance and in the evaluation of the economic feasibility of the process.

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