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Artificial neural network modeling of biotreatment of malachite green by *Spirodela polyrhiza*: Study of plant physiological responses and the dye biodegradation pathway

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ABSTRACT

Phytoremediation is an environmental friendly and sustainable means of pollutant remediation through the use of plants. The ability of duckweed (*Spirodela polyrhiza* L.) for decolorization of malachite green was evaluated. Effect of some operational parameters such as initial plant biomass, the reaction time, initial dye concentration, pH and temperature on dye removal efficiency was determined. The importance of each parameter was assessed by artificial neural network (ANN) modeling and the plant initial biomass and pH were found to be the most important factors. The findings indicated that ANN provided reasonable predictive performance ($R^2 = 0.98$). The metabolic fate of the dye was proposed by identification of 6 intermediate compounds produced during this process by GC–MS technique. Some physiological responses of the plant were studied at 10 and 20 mg/L of the dye. The activities of antioxidant enzymes were increased at high concentration of the contaminant but there was a significant decrease in photosynthetic pigments content at 20 mg/L of malachite green.

1. Introduction

Among different industries, textile industries, dyestuffs, paper and plastic use dyes for their products by consuming substantial volumes of water and discharging considerable amount of colored wastewater to the environment (Pilon-Smits, 2005; Robinson et al., 2001). These dye containing effluents are difficult to treat and exhibit toxic and carcinogenic effects toward biological systems (Ali, 2010; Forgacs et al., 2004).

Malachite green (MG), a triarylmethane dye, is most widely used for coloring purposes such as dyeing silk, leather, wool and paper in textile industries. In addition, it is extensively used in aquaculture industries as a biocide worldwide (Srivastava et al., 2004). However, there are many reports describing its hazardous effects on immune, respiratory and reproductive systems and its carcinogenic properties (Anbia and Ghaffari, 2011; Khataee et al., 2011). Due to its harmful effects, the treatment of effluent containing such dye is receiving increasing attention. Though the use of the dye has been banned in several countries, it is still being used in many part of the world due to its low cost and availability (Srivastava et al., 2004).

Several remediation techniques such as physical, chemical and biological have been subjected to effectively remove different dyes but these methods vary in efficiency, cost and environmental impacts (Rangabhashiyam et al., 2013). Compared with physicochemical processes, bio-friendly approaches have been the main focus for treatment of dye containing waste water as they require low costs, are eco friendly, and produce fewer toxic metabolites (McMullan

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et al., 2001; Rauf and Ashraf, 2012). Numerous researches on microorganisms belonging to different taxonomic groups like bacteria (Ölmezoğlu et al., 2012), fungi (Sanghi et al., 2011; Zamir et al., 2011), yeast (Dönmez, 2002), and algae (Khataee et al., 2010, 2011) confirmed their ability to eliminate and decolorize different class of dyes.

Moreover, higher plants can be used as a bioremediation tool for treating environmental problems (Torbati et al., 2015). In fact, phytoremediation is the technology that evolved the use of plants to clean-up pollutants from the environment. This method is not only an economical, energy efficient, innovative and cost effective alternative to the more conventional water treatment methods, but also it can be useful for treating a wide variety of contaminants (Susarla et al., 2002; Pilon-Smits, 2005).

During the last decade, many species of macrophytes are used for ecotoxicological and phytoremediation researches. One of the most commonly used aquatic plant families is leamnaceae (duckweed). the genus of this family (*Lemna*, *Spirodela*, *Wolffia* and *Wolffiella*) have many advantages in ecotoxicological area including a simple structure and morphology, small size, rapid growth rate, ease of cultivation and sensitivity to wide range of pollutants (Böcük et al., 2013; Zezulka et al., 2013).

One of the main purposes of the present investigation is to evaluate the potential of *S. polyrhza* for phytoremediation of malachite green (MG). study of changes in some physiological parameters including growth, photosynthetic pigments content and activity of some major antioxidative enzymes including peroxidase (POD), catalase (CAT) and superoxide dismutase (SOD) that can be involved in plant resistance to dye and/or its metabolism. The effects of experimental parameters such as initial dye concentration, pH, temperature and amount of plant on bioremediation efficiency were determined. Moreover, biodegradation process was identified from adsorption by reusability experiments and some possible by-products were recognized and characterized using GC–MS technique.

Bioprocesses are nonlinear, time varying and unstructured systems, which are not easy to model (Khataee and Kasiri, 2011). The main usage of artificial neural networks (ANNs) is that they offer the potential of the generic approach to the modeling of nonlinear systems (Shetty et al., 2008).

Thus, another feature of the present study was to confirm whether artificial neural networks could be used to predict biological decolorization efficiency of S. plyrhiza, and if so, to suggest an appropriate topology (i.e., input variables, number of ANN neurons, training algorithms, etc.) for a successful ANN.

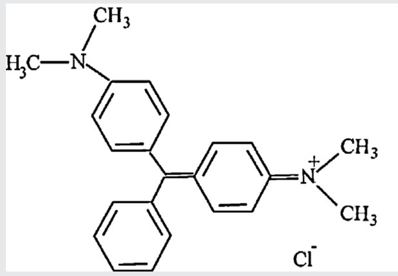
2. Materials and methods

2.1. Dye analysis and dye removal experiments

Chemical structure and characteristics of the dye, Malachite Green, was shown in Table 1. The dye was purchased from Mahfam Company (Iran) and its absorbance was determined by a spectrophotometer (UV/vis spectrophotometer WPA Light Biowave II, England) at maximum absorbance wave length, λ_{max} = 619 nm.

Decolorization experiments were carried out in 250 mL Erlenmeyer flask containing the synthetic dye solution. The flask was placed in 25 °C and a 16/8 h light/dark photoperiod.

Table 1 – Structure and characteristics of MG.

Chemical structure	
Chemical class	Cationic
Molecular formula	$C_{23}H_{25}ClN_2$
Color index number	42000
M_w (g/mol)	364.911
λ_{max} (nm)	619

The dye removal efficiency (%) was investigated during 8 days and expressed as the percentage ratio of decolorized dye concentration to that of the initial condition.

The decolorization experiments were carried out with different initial dye concentrations (5, 10, 20, and 40 mg/L), pH values (5, 6, 7, 8, and 9), temperatures (5, 15, and 25 °C) and initial biomass of plant (0.5, 1, 2, and 4 g) to assess the optimal efficiency of dye removal. The temperature was kept constant in the incubator (Sanyo, Ogawa Seiki Co., Japan) during the experiments. The initial pH of the dye solution was adjusted using diluted KOH and H_2SO_4 solutions and was measured by pH meter (654 pH meter Metrohm, Switzerland). All experiments were performed in triplicate, and the results expressed as mean values.

2.2. Plant material and growth condition

Plants were collected from Anzali Lagoon, north of Iran and after transferred to the laboratory, they were cleaned and washed using distilled water. Then, the plants were adapted for three weeks in a large aquarium containing growth medium (Dosnon-Olette et al., 2010) under laboratory condition (temperature of 25 °C and photoperiod of 16 h/8 h (light/dark)).

2.3. ANN software

Due to the complexity of the biological processes, a few studies have been performed involving the modeling of biological decolorization of water pollutants. Because of the nonlinear and time varying nature of bioprocesses, the modeling of such processes is problematic. Therefore the application of the artificial neural networks for prediction the performance of biological systems has received considerable interest during last few years (Khataee and Kasiri, 2011). In general, neural network model architecture consists of three main layers: an input layer (independent variables), an output layer (dependent variable) and one or more intermediate hidden layers. In the present study, all ANN calculations were performed using Matlab 7 mathematical software (MathWorks, Inc., USA) with an ANN toolbox. A three-layered feed forward back-propagation neural network with a tangent sigmoid transfer function (*tansig*) at hidden layer and linear transfer function (*purelin*) at output layer were applied for modeling of biological treatment of MG solution by *S. polyrhiza*. Input variables were decolorization time (day), initial pH, temperature (°C), initial dye concentration (mg/L) and initial amount of plant