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Optimized preparation of *Phragmites australis* activated carbon using the Box-Behnken method and desirability function to remove hydroquinone

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ABSTRACT

In this study, preparation of *Phragmites australis* activated carbon (PAAC) was optimized and applied for the removal of hydroquinone from aqueous solution. The Box-Behnken surface design (3^3) was used to statistically visualize the interactions among microwave power (A), microwave radiation time (B) and the ingredient ratio (C) (H_3PO_4: *P. australis* powder, in g). The desirability function was utilized to simultaneously optimize the multi-response indicators. A regression analysis showed that the experimental data of BBD optimization experimental results fit well to a quadratic model. PAAC was characterized according to its morphology, structure and composition. Dynamic adsorption data showed that the best fit was obtained by a pseudo-second-order model and the Freundlich isotherm model. The maximum adsorption capacity for hydroquinone adsorption onto PAAC was 156.25 mg/g at 30 °C and the adsorption mechanism may be attributed to multi-layer surface and chemisorption via donor-acceptor and coupling interaction of the electron. The present study showed that PAAC has the potential for use as a biosorbent for the adsorption treatment of water pollutants.

1. Introduction

Water pollution caused by organic contaminants has drawn widespread attention, especially pollution caused by phenolic compounds and their derivatives. Phenolic compounds are important organic intermediates for industrial and agricultural products (Korbahti and Tanyolac, 2003). However, a large number of phenolic compounds and their derivatives have not been controlled and thus have been released into water systems (Tang et al., 2015). Phenolic compounds and their derivatives are characterized by toxic effects caused by their refractory nature, ubiquitous presence and carcinogenic properties toward living organisms and ecosystems (Buyukgungor, 2013; Qiu et al., 2014). Therefore, certain phenolic compounds have been listed as priority pollutants in a number of countries as well as by the United States Environmental Protection Agency (Qiu et al., 2014).

For hydroquinone, a phenolic derivative in which two para- positions of the benzene ring are occupied by hydroxyl groups, has been applied in various industries, including textiles, steel, petroleum refining, rubber epoxy resins and adhesives, plastics, and is highly toxic to the eyes, skin, and respiratory tract (Suresh et al., 2012; Li et al., 2018). Currently, the adsorption, enzymatic catalysis and electrochemical oxidation are the main methods for the removal of hydroquinone (Yildiz et al., 2005; Wang et al., 2015; Suresh et al., 2011a, 2011b; Li et al., 2018, 2013). Among these technologies, using adsorption method to remove hydroquinone has developed a popular technology due to its high efficiency, operation simplicity and economic efficiency. In the selection of various adsorbents, to remove hydroquinone from aqueous solutions, activated carbon is widely used for its high efficiency and reusability. Therefore, the materials and prepared method of activated carbon become extremely urgent.

To reduce the production costs and improve the adsorption capacity of activated carbon, researchers have gradually changed the raw materials used to prepare activated carbon from coal-based to raw waste materials, including coal slag (Tang et al., 2015), sewage sludge (Puchana-Rosero et al., 2016), agro-industrial waste (Maldhure and Ekhe, 2011; Sun et al., 2012a; Zhong et al., 2012; Mukherjee et al., 2007; Gokce and Aktas, 2014; Duran et al., 2011; Sathishkumar et al., 2012), tire waste (Acevedo et al., 2015), and cotton seed cake (Malathi et al., 2015). In addition, the advantages associated with microwave irradiation preparation of activated carbon, including the rapid temperature rise, uniform temperature distribution, and reduced processing time and energy consumption, have led to a wide range of applications for this method (Njoku et al., 2014; Foo and Hameed, 2009). *Phragmites australis* is an annual aquatic emergent plant widely employed for environmental landscaping and water decontamination. However, optimizing the preparation process of microwave-induced activated carbon

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from *P. australis* has not been reported.

To obtain a form of activated carbon that is desirable and effective, the processing parameters of the material must be identified and optimized. The response surface methodology (RSM), which is used for developing, optimizing, and improving products for industrial processes, is useful for solving multi-factor problems that affect processing indicators, such as the yield and adsorption capacity (Danmaliki et al., 2016; Kumar et al., 2017). The RSM is established via the design of experiments (DOEs) to reduce the number of experimental runs and the establishment of a regression model and operating conditions (Danmaliki et al., 2016; Mondal and Roy, 2015). The RSM is a set of mathematical and statistical techniques that include three-level factorial designs, such as Central Composite Design (CCD), Doehlert Matrix and Box-Behnken Design (BBD) (Danmaliki et al., 2016). Moreover, when more than one response indicator is observed and these indicators multiply during the procedure of optimization, a desirability function must be applied for the analysis and transformation of a unitive optimal region to achieve optimization (Candioti et al., 2014).

Herein, the main objectives are to optimize and prepare the microwave-induced preparation of *Phragmites australis* activated carbon (PAAC) using the RSM and the desirability function methods, to evaluate the hydroquinone removal capacities of PAAC, and to ascertain the possible removal mechanisms of hydroquinone by a series experiment. The new adsorbent of PAAC was based on optimizing the preparation conditions for microwave radiation power, radiation time, and impregnation ratio during the microwave preparation process. After that, the obtained adsorbent was properly characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, nitrogen adsorption and X-ray photoelectron spectroscopy (XPS). Furthermore, batch adsorption experiments included different parameters influencing adsorption capacity of pH, temperature, ionic strength, reuse and equilibrium experiments, kinetics, were investigated to evaluate the PAAC adsorption capacity, mechanisms and practicability of hydroquinone from aqueous solution.

2. Materials and methods

2.1. Reagents

All organic and inorganic reagents used in this work were analytical grade.

2.2. Preparation of activated carbon

The stems of *P. australis* was used as a raw material for the preparation of activated carbon. The preparation process of PAAC mainly includes the raw material selection, chemical activation, microwave-induced carbonization, and post-processing.

P. australis was harvested from the shore of the Fenhe River in Shanxi, China. After removing the flowers, leaves and roots, the stems of *P. australis* for preparing the activated carbon was cleaned with distilled water to remove dust and inclusion. Samples were dried at 110 °C in an oven (GZX-9070 MBE, Shanghai Boxun Medical Biological Instrument Ltd. Corp., China) for 6 h to ensure complete evaporation of water. Then, the dried stems of *P. australis* was crushed and sieved into powder with a particle size of 178–250 μm using a pulverizer (LF-600 A, Lufeng, China) and mesh sieve.

For chemical activation, the obtained stems of *P. australis* powder was mixed with 50% (wt.) H_3PO_4 and impregnated for 24 h at room temperature. To optimize the formation of PAAC, the impregnation ratio (H_3PO_4: *P. australis* powder, in g) was considered when optimizing the preparation conditions.

After the activation process, the stems of *P. australis* powder samples were carbonized by microwave irradiation to obtain activated carbon. To begin this process, the microwave oven (MKX-M1, Microwave Institute of Physics and Chemistry, China) was filled with an inert nitrogen atmosphere (500 cm^3 min^{-1}) throughout the reaction. The samples were placed in a quartz crucible and then the microwave oven with the aid of a SiC plate for reaction at a selected microwave power and carbonization time. The resulting carbonized sample was abbreviated as PAAC.

The first post-processing step was treatment with 0.1 M NaOH to remove excess acid from the PAAC. Then, the PAAC was washed with distilled water until reaching a stable pH. Inorganic impurities were eliminated by washing with 0.1 M HCl followed with distilled water to reach a pH of 7.0. In the second stage, the PAAC was dried for 12 h in an oven at 110 °C and ground to an appropriate size (< 75 μm) for further study.

2.3. Response surface methodology: Box-Behnken experimental design

In the current study, the RSM was used to optimize the preparation parameters of PAAC. In this method, a quantitative polynomial equation (including linear equations and quadratic polynomial equations) can be used to accurately describe the quantitative mathematical relationship between the response variables (Y_1, Y_2, ..., Y_n) and the corresponding process variables (X_1, X_2, ..., X_n). The relationship is as follows:

$$Y = f \quad (X_1, \quad X_2, \cdots X_n) \pm \varepsilon \tag{1}$$

where f is a linear or quadratic polynomial equation, and ε is the error generated by the f function.

The BBD method is a standard RSM design approach, and it was selected to optimize the experimental operating parameters because this approach allows each factor to be considered individually while reducing the number of experiments required to develop quadratic fitting models. The number of experiments required (N) for the BBD method is determined by the equation below, which depends on the number of independent variables (k) and the number of replicates performed at the central point (C_p) (Varala et al., 2016).

$$N = 2k(k-1) + C_p \tag{2}$$

When evaluating the relationship between the response variables (Y) and the process variables (X), the interaction between any two process variables can be described. If three independent process variables (X1, X2, and X3) are involved, then their relationships can be expressed by the following quadratic second-order polynomial:

$$Y = \beta 0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_{11} + \beta_{22} X_{22} + \beta_{33} X_{33} \tag{3}$$

where Y is the response variable; β0 is the regression coefficient at the center point; β_1, β_2, and β_3 are the linear coefficients; β_{12}, β_{13}, and β_{23} are the interaction product coefficients; and β_{11}, β_{22}, and β_{33} are the quadratic coefficients (Varala et al., 2016). A polynomial regression analysis can be used to obtain the coefficients of the quadratic polynomial model, and the fit of the model can be tested by the coefficient of determination (R^2) and an analysis of variance (ANOVA) (Varala et al., 2016).

This BBD was created using Design-Expert 8.0.6.1. The microwave power (A), microwave radiation time (B) and impregnation ratio (C) (H_3PO_4: *P. australis* powder, in g) were regarded as process variables, and three indexes were selected as response variables to evaluate the adsorption properties of PAAC: iodine adsorption (Y1), methylene blue adsorption (Y2) and activated carbon yield (Y3). The 3-level, 3-factor design of the variables and their response values as well as the 17 experimental conditions for BBD are listed in Table S1 and Table 1, respectively.

2.4. Desirability function

In 1980, the desirability function was established by Derringer and