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Response surface modeling of Pb(II) removal from aqueous solution by *Pistacia vera* L.: Box–Behnken experimental design

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ABSTRACT

A three factor, three-level Box–Behnken experimental design combining with response surface modeling (RSM) and quadratic programming (QP) was employed for maximizing Pb(II) removal from aqueous solution by Antep pistachio (*Pistacia vera* L.) shells based on 17 different experimental data obtained in a lab-scale batch study. Three independent variables (initial pH of solution (pH_0) ranging from 2.0 to 5.5, initial concentration of Pb(II) ions (C_0) ranging from 5 to 50 ppm, and contact time (t_C) ranging from 5 to 120 min) were consecutively coded as x_1, x_2 and x_3 at three levels (−1, 0 and 1), and a second-order polynomial regression equation was then derived to predict responses. The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA) with 95% confidence limits ($\alpha = 0.05$). The standardized effects of the independent variables and their interactions on the dependent variable were also investigated by preparing a Pareto chart. The optimum values of the selected variables were obtained by solving the quadratic regression model, as well as by analysing the response surface contour plots. The optimum coded values of three test variables were computed as $x_1 = 0.125$, $x_2 = 0.707$, and $x_3 = 0.107$ by using a LOQO/AMPL optimization algorithm. The experimental conditions at this global point were determined to be $pH_0 = 3.97$, $C_0 = 43.4$ ppm, and $t_C = 68.7$ min, and the corresponding Pb(II) removal efficiency was found to be about 100%.

1. Introduction

With growing urbanization and rapid industrialization, the problem of the release of toxic heavy metals into the ecosystem has been of increasing concern in many parts of the world. Since heavy metals can significantly contaminate the receiving water bodies even in trace amounts, potential risks of heavy metal pollution cannot be ignored any longer. Therefore, the removal of heavy metals from water and wastewater has recently become the subject of considerable interest due to more strict legislations introduced in many countries to control water pollution [1].

Lead has been recognized one of the most hazardous heavy metals since mining, acid battery manufacturing, metal plating, printing, textile, photographic materials, ceramic and glass industries, explosive manufacturing, and also lead-containing piping material are the main sources of lead contamination [1,2]. The resultant higher concentrations of lead in the ecosystem have substantial impacts on the environment and human health. Lead poisoning causes various severe health problems in vital organs of humans, such as damage to the kidney, liver, blood composition, nervous system, reproductive system and retardation in mental function [3].

Because lead is non-biodegradable and tends to bioaccumulate in cells of the living organisms, stricter environmental requirements and urgent treatment solutions are needed for lead removal from water and wastewater [3,4]. Current methods for lead removal include precipitation as hydroxide, carbonate and sulfide precipitates [5], coagulation/flocculation [6], membrane process [7], electrochemical process [8], ion exchange [9], biosorption [10], and adsorption techniques [11]. Among these methods, precipitation of heavy metals as metal hydroxides or sulfides has been practiced as the prime method of treatment for heavy metals in industrial wastewater for many years. However, this process may lead to a special problem of sludge handling and costly disposal [3]. Although membrane filtration and electrochemical process are proven techniques, their high costs limit their use in practice. In addition, activated carbon is regarded as an effective adsorbent for removal of metal ions from water, however, due to its high cost and loss during regeneration, unconventional low-cost adsorbents such as fly ash, peat, lignite, bagasse pith, wood, saw dust etc. have attracted the attention of several investigators in recent years [3]. The shell of *Pistacia vera* L. used as an adsorbent in both our previous and the present studies is an agricultural by-product produced in very large

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quantities particularly in the southeastern part of Turkey. The main advantages of Pb(II) removal by using pistachio shells is that it is in abundance and easy availability. This makes it a strong choice in the investigation of an economic way of Pb(II) removal. From the economical point of view, pistachio shells can be used as an alternative media to activated carbon, as well as to gain an understanding of the adsorption process [3].

Even though the dynamic characteristics of the adsorption process is very complicated, a number of attempts in developing an experimental-based optimization methodology may help to provide a better understanding of the process in terms of the effects of independent variables and their interactions on the dependent variable. However, Liu et al. [12] have stated that carrying out experiments with every possible factorial combination of the test variables is impractical because of a large number of experiments required. Hence, response surface modeling (RSM) can be a useful approach for studying the effects of several factors influencing the responses by varying them simultaneously and performing a limited number of experiments [13]. Unlike conventional optimization, suchlike statistical optimization methods can take into account the interactions of variables in generating process responses [14]. Similarly, Guo et al. [15] have reported that the statistical methods are believed to be effective and powerful approach for screening key factors rapidly from a multivariable system for the optimization of a particular process.

Since, many parameters may be responsible for the adsorption of Pb(II) ions from aqueous solution, it is important to select a suitable experimentation technique which will evaluate the effects of important parameters along with possible interactions, with minimum number of experiments, as suggested by Bhunia and Ghangrekar [16]. For this purpose, statistical design of experiments have been widely reported for the process characterization, optimization and modeling in recent years [15,17–22]. Although the experimental design technique has been widely studied by many researchers as an established and promising method for optimization and formulation of various types of processes, however, there are no systematic papers in the literature specifically devoted to a study of the response surface modeling of Pb(II) removal from aqueous solution by *P. vera* L. using an experimental design technique. Therefore, clarification of the place of Pb(II) adsorption by *P. vera* L. in the scheme of experimental design methodology can be considered as a particular field of investigation to develop a continuous control strategy, as well as to achieve an optimum Pb(II) removal.

Based on the above-mentioned facts, the specific objectives of this study were: (1) to apply a three factor, three-level Box–Behnken experimental design combining with RSM and quadratic programming (QP) for maximizing Pb(II) removal from aqueous solution by *P. vera* L.; (2) to examine the effects of three independent variables (initial pH of solution, initial concentration of Pb(II) ions, and contact time) and their interactions on the Pb(II) removal efficiency; and (3) to verify the validity of the proposed model by several additional batch experiments conducted in the experimental area of the Box–Behnken design.

2. Materials and methods

2.1. Adsorbent preparation

Antep pistachio (*P. vera* L.) shells used in the batch experiments were obtained from lands near to Zohrecik Village of Gaziantep city in the southeastern part of Turkey. Because Pb(II) concentration in the air may affect the Pb(II) amount in the adsorbent, Pb(II) analysis was first in raw pistachio shells prior to determining of Pb(II) ions concentration of aqueous solutions. Our previous results indicated that there was no detectable lead levels present in raw pistachio shells to have an effect on the experimental data [3]. This was attributed to the fact that the lands near to Zohrecik Village, where the pistachio shells were collected, are quite away from urban freeways, as well as from industrial areas [3]. Elemental analysis was performed with an elemental analyzer (EA 1108, Fisons Instruments). The elemental composition of used pistachio shells (in wt.%) was moisture – 4.22, ash – 0.2, carbon – 47.83, hydrogen – 5.32, nitrogen – 0.34, total sulfur – 0.19, oxygen – 41.9. True density and surface area of pistachio shells were determined as 770 kg/m^3 and 0.41 m^2/g, respectively [3]. Prior to batch adsorption tests, the shells were washed with distilled water to remove soluble and coloured components, and then dried in an oven (Nuve FN 500) at 80 °C for 24 h. The dried pistachio shells were sieved through a 1 mm sieve (Endecotts Ltd.) and stored in polythene bags for further shake flask studies.

2.2. Shake flask studies

A stock solution of 1000 ppm of Pb(II) was first prepared by dissolving analytical grade $Pb(NO_3)_2{\cdot}6H_2O$ (Merck Chemical Corp.) in distilled water. Then, synthetic wastewater samples were prepared to give Pb(II) concentrations ranging between 5 and 50 ppm by diluting appropriate amounts of $Pb(NO_3)_2{\cdot}6H_2O$ stock solution with distilled water for batch adsorption experiments. From the physical point of view, experimental ranges of the initial pH of the solution and contact time were chosen between 2.0–5.5, and 5–120 min, respectively. The selected ranges of the present independent variables were considered based on our previous findings [3]. Series of lab-scale shake flask studies were carried out to determine the effects of initial pH (pH_0), initial concentration of Pb(II) ions (C_0) and contact time (t_C) on the Pb(II) removal efficiency. A known amount of the dried adsorbent (1 g) was added into 250 mL glass flasks with 200 mL solution giving a liquid (solution)–solid (adsorbent) ratio of 200. The flasks were then placed in an orbital shaker (Gallenkamp Orbital Incubator Shaker) and agitated up to a total contact time of 120 min at a fixed agitation speed of 250 rpm at an ambient temperature of 30 °C. Samples were taken at predetermined time intervals, and then separated by centrifugation prior to any analysis done.

2.3. Box–Behnken experimental design and optimization by RSM

The optimum conditions for maximizing the adsorption of Pb(II) by *P. vera* L. were determined by means of a three factor, three-level Box–Behnken experimental design combining with response surface modeling and quadratic programming. RSM consists of a group of empirical techniques devoted to the evaluation of relationships existing between a cluster of controlled experimental factors and measured responses according to one or more selected criteria [23,24]. In the first step of RSM, a suitable approximation is introduced to find true relationship between the dependent variable (response) and the set of independent variables (factors). If knowledge concerning the shape of true response surface is insufficient, the preliminary model (generally a first-order model) is upgraded by adding high-order terms to it [23]. In the next step, the behaviour of the system is explained by the following quadratic equation [13,23,24]:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i x_i + \sum_{i=1}^{k}\beta_{ii} x_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k}\beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where Y is the process response or output (dependent variable), k is the number of the patterns, i and j are the index numbers for pattern, β_0 is the free or offset term called intercept term, $x_1, x_2, \ldots, x_k$ are the coded independent variables, β_i is the first-order (linear)