**Synthesis and characterization of novel activated carbon from Medlar seed for chromium removal: Experimental analysis and modeling with artificial neural network and support vector regression**

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**ABSTRACT**

In this study, for the first time the activated carbon has been produced from medlar seed (Mespilus germanica) via chemical activation with KOH. The carbonization process was carried out at different temperatures of 450, 550, 650 and 750°C. The Nitrogen adsorption-desorption, Fourier transform infrared spectroscopy (FTIR) and Field Emission Scanning Electron Microscope (FESEM) analyses were carried out on the adsorbents. The effect of operating parameters, such as pH, initial concentration of Cr(VI), adsorbent dosage and contact time were investigated. The experimental data showed better agreement with the Langmuir model and the maximum adsorption capacity was evaluated to be 200 mg/g. Kinetic studies indicated that the adsorption process follows the pseudo second-order model and the chemical reaction is the rate-limiting step. Thermodynamic parameters showed that the adsorption process could be considered a spontaneous (ΔG < 0), endothermic (ΔH > 0) process which leads to an increase in entropy (ΔS > 0). The application of support vector machine combined with genetic algorithm (SVM-GA) and artificial neural network (ANN) was investigated to predict the percentage of chromium removal from aqueous solution using synthesized activated carbon. The comparison of correlation coefficient (R\(^2\)) related to ANN and the SVR-GA models with experimental data proved that both models were able to predict the percentage of chromium removal, by synthetic activated carbon while the SVR-GA model prediction was more accurate.

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1. Introduction

Accessing clean water has become one of the major challenges today due to the industrial development and the growth of cities. Increasing disposal of wastewaters containing heavy metals by various industries such as mine extractions, metal plating, textile, metallurgy has raised a global concern in recent years [1]. Among heavy metals, Cr(VI) is considered to be one of the most dangerous metals, due to its strong oxidizing nature and the ability to pass through the cell walls which might lead to cancer or mutagenesis [2].

The methods have been applied widely to treat wastewaters containing Cr(VI), include ion exchange, membrane technology, reverse osmosis, dialysis/electrodialysis, and biosorption [3–5]. Nevertheless, few drawbacks could be considered for them, such as incomplete metal removal, low selectivity, high-energy consumption and toxic sludge or other secondary wastes produced during the treatment which require proper disposal.

Another renovated approach to removing heavy metals is adsorption process which is an effective way with advantages such as high efficiency, simplicity of design and application, being inexpensive, low sensitivity to toxic substances and avoiding the production of toxic sludge. Among different adsorbents, activated carbon has some characteristics such as highly developed porosity,
superb adsorption capacity and high degree of surface reactivity which make it unique [6,7]. Activated carbon could be prepared through two different processes: chemical activation and physical activation. The physical activation process is carried out in two steps which the first step is carbonization of a carbonaceous material. Afterwards, in the second step which high a temperature is required, activation of char in presence of activating agents such as CO₂ or steam takes place. In comparison, Chemical activation process is a single-step method in which carbonization and activation proceeds simultaneously. Chemical activation offers some advantages over physical activation which can be summarized as follows as: (1) chemical activation can take place at lower temperatures so it needs less energy, (2) impregnation of precursor materials with the chemical agents inhibits tar formation which results in better transformation of material to carbon, in other words carbon efficiency in chemical method is significantly higher than the physical one. Chemical activation is fairly important because the surface modification done using the impregnating technique with proper environmentally-friendly chemical materials not only will increase the adsorption capacity but will also add selectivity to carbon characteristics [8]. Lots of materials (i.e. H₂SO₄, H₃PO₄, FeCl₃, ZnCl₂) have been used as chemical agents, and although ZnCl₂ is widely used nowadays, it is not suitable for pharmaceutical and food industries due to the environmental issues it causes [9,10]. KOH has been known to be one of the most effective chemical agents in activated carbons production, nevertheless the only problem is the high temperature required in the process [11].

According to the multitude variety of agricultural wastes in different regions, novel and inexpensive adsorbents have been manufactured in order to be used in the industries. Various materials like olive bagasse, potato peel, soybean straw, nut shells and lots of other agricultural wastes have been applied to produce activated carbon [12–15]. Another solid waste with great potential for synthesis of activated carbon is medlar seed. The medlar (Mesplius germanica) is a pear/appleshaped fruit with brown or sometimes reddish tinged color which is varying in size (diameter: 1.5–3 cm, weight: 10–80 g). The medlar trees grow wild in different regions of Middle East especially in the north of Iran and Turkey. Nevertheless, it has recently been cultivated in large-scale because of its unique properties. The processed medlar in the form of jam, marmalade and jellies has been commercially regarded by food industries. Medicinal and healing properties of medlar are well-known. It has been used as treatment for diuretic, kidney and bladder stones. Therefore, these various consumptions and five large seeds (diameter: 1–1.25 cm) lead to produce tones of medlar core as the solid wastes every year [16].

In the recent years, in addition to finding a novel, effective and economic source of activated carbon with high adsorption capacity, prediction of the output water quality and determination of experimental optimal conditions for the removal of heavy metals from a water treatment plant has become noteworthy, due to the non-linear behavior and interaction of variables during the adsorption process, so modeling the experimental data with mathematical methods is a useful solution to overcome the problems that may occur in the industrial application. In the same recent years, artificial neural network (ANN) has been widely used for modeling of experimental data in environmental problems. An investigation of artificial neural network for modeling of Cu²⁺ adsorption from industrial leachate by pumice has been conducted by a three layer feed forward backpropagation network with 4, 8 and 4 neurons in first, second and third layers [17]. In another study the response surface methodology (RSM) and artificial neural network modeling were used to predict Cu²⁺ removal from aqueous solutions by light expended clay aggregate (LECA) [18].

Despite the fact that ANN model is a useful method for modeling of the experimental data, it has some disadvantages, such as possible problem in providing of high convergence speed, avoiding local minima, and over-fitting phenomenon, thus it lacks the generalization capability. Therefore, Support Vector Machines (SVM) based on machine learning method can be a good substitution for the ANN according to its efficacious capability in prediction and classification. Application of the SVM to solve the regression problems is called SVR which has been very successful in building nonlinear data driven models, also problems characterized by small samples, nonlinearity, high dimension space and local minima. It tries to find an optimal hyper-plane function in a high dimensional space [19,20].

To the best of our knowledge, no study has been carried out on the synthesis of activated carbon from medlar seeds, therefore in this research the novel and high performance mesoporous-activated carbon from medlar seeds was prepared through chemical activation using KOH for Cr(VI) removal from aqueous solutions. The optimal values of the parameters affecting the adsorption process of chromium by synthetic activated carbon were obtained in different experiments and experimental data was modeled using SVR-GA and ANN models. To avoid any possible errors and to obtain the best results of the adsorption process modeling, parameters influencing the method of SVR were optimized by genetic algorithm (GA). Finally, to evaluate the ability of the adsorbent to be used in industrial processes, kinetic, thermodynamic and equilibrium studies were also carried out.

2. Material and methods

2.1. Material

The Medlar seeds were supplied from a local small factory which produces jelly and jam. All the chemicals used were of analytical reagent (AR) grade and obtained from Merck (Darmstadt, Germany). The standard stock solution with a chromium concentration of 1000 ppm was obtained by dissolving 2.8286 g K₂Cr₂O₇ in 1000 mL of deionized water. The initial pH was adjusted using solutions of 0.1 M NaOH and 0.1 M HCL.

2.2. Preparation of activated carbon

The Medlar seeds were washed extensively with deionized water in order to remove the sugar and other impurities which were stuck to the surface. Then the seeds were dried overnight at 110 °C. Afterwards, they were crushed using a micro hammer miller and were sieved in a 40/60 mesh. The crushed seeds were agitated in KOH solution with the impregnation rate of 1:3 (mass of seed/mass of KOH) at 25 °C for 8 h. After impregnation, the samples were dried overnight at 110 °C. For carbonization of the samples a quartz reactor (5 cm i.d., 100 cm length) was utilized. The reactor was placed in a tubular furnace and heated at a constant rate of 10 °C/min and then held at different carbonization temperatures (450–750 °C) for 1 h under 300 mL/min N₂ flow. The samples were remained under N₂ flow until they reached the room temperature and then they were taken out of the reactor. The resulted activated carbon were washed with 0.5 mol/L hydrochloric acid, hot and cold deionized water, respectively, until the filtrate reached a neutral pH. Finally they were dried overnight at 110 °C in hot air oven and was kept in a desiccator. The activated carbon samples produced at 450, 550, 650 and 750 °C were named AC-4, AC-5, AC-6 and AC-7, respectively.

2.3. Characterization of samples

Measuring the amount of adsorbed nitrogen is a standard method for determining the surface area and porosity of activated carbon. The analysis was performed on the samples using
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