Chemical Engineering Journal 172 (2011) 207–218

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Process optimization for Cr(VI) adsorption onto activated carbons by experimental design

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ARTICLE INFO

Article history:
Received 24 February 2011
Received in revised form 22 May 2011
Accepted 24 May 2011

Keywords:
Chromium removal
Activated carbon
Box–Behnken Response Surface Methodology
Experimental design
Process optimization

ABSTRACT

A study on the adsorption of Cr(VI) onto raw and modified activated carbons was conducted and the process parameters were optimized using Response Surface Methodology (RSM). Apricot stones have been converted to microporous activated carbon with considerably high surface area (1462 $m^2 g^{-1}$) by phosphoric acid activation. Produced carbons have been characterized by using different physicochemical methods. In order to determine the effects of process parameters namely temperature (20–60 °C), initial solution pH (2–6) and initial Cr(VI) concentration (30–60 $mg L^{-1}$) on Cr(VI) uptake from aqueous solution, a three-level, three-factor, Box–Behnken design has been employed. The second order mathematical model was developed by regression analysis of the experimental data obtained from 17 batch runs. The optimum pH, temperature and initial concentration were found to be 2.0, 60 °C, and 60 $mg L^{-1}$, respectively. Cr(VI) adsorption capacity was 262 $mg g^{-1}$ at the optimum combination of process parameters. The enthalpy change of Cr(VI) adsorption was found to be 54.05 $kJ mol^{-1}$. Dynamic adsorption data were applied to pseudo-first-order and pseudo-second-order rate equations. Pseudo-second-order kinetic model well expressed Cr(VI) adsorption onto activated carbon. The results of both thermodynamic and kinetic study indicated the chemical interaction between Cr(VI) species and surface functional groups on carbon surface.

1. Introduction

Activated carbons, with well-developed pore structure, are widely used as an effective adsorbent for the recovery and removal of heavy metals and organics from aqueous solutions. They can be produced from a variety of lignocellulosic precursors, which are generally considered waste and used as fuel. The comprehensive utilization of waste products is very important for the economy, and also simultaneously brings a solution to the solid waste problem. Apricot stone is an inexpensive material that is available in large quantities, thus, provides a promising application for the production of cheap and efficient activated carbons. The world's largest apricot producer is Turkey with 18% of world apricot production. Apricot is produced in almost all areas of Turkey except Black Sea region. Although apricot is principally consumed as dried fruit, production of it also contributes to the manufacture of fruit juice and liqueur.

Water pollution by chromium is due to both natural sources and various industrial processes such as metal plating, leather tanning, textile industries, battery and pigment production [1]. Hexavalent chromium is toxic, carcinogenic, mutagenic in the nature and more toxic than the trivalent form [2]. The maximum permission level of hexavalent chromium in potable waters is 0.05 $mg L^{-1}$ [3]. Hexavalent chromium usually exists in aqueous solution as oxyanions such as hydrogen chromate ($HCrO_4^-$), chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) [4]. The most common methods of Cr(VI) removal from aqueous solutions are chemical precipitation, ion exchange, membrane processes, electrodialysis and adsorption [5]. Activated carbon is the most widely used adsorbent to remove impurities from aqueous media depending on its specific surface area, pore structure and surface functionality. The surface modification with suitable chemicals and impregnation techniques not only increases the adsorption capacity but also adds selectivity to the carbon. Chemical activation consists of impregnation of raw material with a strong dehydrating agent and then heating the mixture to the temperatures of 400–800 °C. Phosphoric acid is commonly used as dehydrating chemical and requires relatively low carbonization temperature (usually around 400–500 °C). The carbonization temperature is also important parameter that governs the development of porous structures and surface functional groups of activated carbon.

The aim of this study is to investigate the effects of process parameters such as initial concentration, pH of the solution and temperature on the adsorptive removal of Cr(VI) from aqueous

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doi:10.1016/j.cej.2011.05.091

solution by using apricot stone based activated carbons. For that reason, Box–Behnken experimental design model was used to evaluate the effects of individual process parameters and their interactions. The experimental data was analyzed using a second order polynomial model, validated by statistical analysis, and process optimization was achieved. Moreover, Cr(VI) adsorption was also evaluated with the aspect of kinetics and thermodynamics.

The classical approach of changing one variable at a time and studying the effect of the variable on the response is a complicated technique especially in a multi-factor system. Design of experiments (DoE) is a general approach that can be used effectively for optimizing such systems. The primary goal of DoE is to determine the maximum information regarding the response variables affected by input parameters by using as few observations as possible. Response surface method (RSM) is one of the approaches to evaluate the effective factors and select optimum conditions in limited number of experiment, and it gives an approximate description of an experimental region around a center of interest with validity of interpolation.

2. Materials and methods

2.1. Materials

All the chemicals/reagents used in this work were of analytical reagent grade.

2.2. Preparation of activated carbons

The apricot stones were obtained from a fruit juice factory in Bursa, Turkey. Apricot stones were crushed and sieved to the particle size of 2–4 mm. The prepared apricot stones were placed into a quartz tube reactor (with a length of 250 mm and an inner diameter of 60 mm). Prior to carbonization, nitrogen (500 $cm^3 min^{-1}$) was circulated through the entire system for 1 h to purge air from the system. Carbonization was accomplished under N_2 flow in two successive stages. In the first step, apricot stones were heated to 300 °C with the rate of 3 °C min^{-1}. In the second stage, the temperature was raised to 400 °C with the rate of 1 °C min^{-1} and kept at this temperature for 2 h. This carbonized sample was abbreviated as AC.

For chemical activation, approximately 20 g of dried apricot stones were impregnated with 50% (wt.) H_3PO_4 for 24 h. Impregnation ratio was 1.5:1 (g H_3PO_4: g apricot stone). Acid impregnated apricot stones were carbonized by using the same procedure as described for AC sample. This activated carbon was abbreviated as IAC.

After cooling to the ambient temperature in nitrogen atmosphere, both carbons (AC and IAC) were put in separate columns to be treated with 2 L 0.1 M NaOH to remove excess of acid. Then they were washed with distilled water until neutral pH. Treatment of carbon samples with 2 L 0.1 M HCl to remove inorganic impurities was followed by rinsing again with distilled water until the pH of the washing solution reached to 5.5–6.0. After that, the produced carbons were dried overnight in an oven at 110 °C, and then they were stored in desiccators for further studies.

2.3. Characterization of activated carbons

N_2 adsorption measurements were performed using a Quantachrome Quadrasorb surface analyzer. The specific surface area and pore volume of samples were obtained from nitrogen adsorption data at 77 K. Prior to analysis, carbon samples were out gassed at 473 K for 24 h. The density functional theory (DFT) model was used to determine total pore volume and micropore volume. The surface area was calculated using Brunauer, Emmett, and Teller (BET) equation. All calculations were performed by the software provided with Quantachrome instrument.

The surface morphology of activated carbons was characterized by scanning electron microscopy (Philips XL30 SFEG), and elemental composition of these samples was determined by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). The samples were mounted on stubs using double faced adhesive tape and sputter coated in argon atmosphere with a thin gold layer in an auto sputter coater.

The relative concentrations of surface functional groups in the produced carbons were determined by Boehm-titration with sodium hydrogen carbonate, sodium carbonate, and sodium hydroxide [6,7]. The concentrations of acidic sites were determined under the assumptions that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3 reacts with both carboxylic and lactonic groups; and $NaHCO_3$ is consumed by carboxylic groups only. Approximately 200 mg of dried carbon samples (size range 75–100 μm) were weighed in 50 mL glass conical dry flasks prior to the addition of 20 mL of 0.1 N NaOH, Na_2CO_3, $NaHCO_3$ solutions. The mixtures were shaken for 72 h at room temperature. The equilibrated solutions were filtered to remove adsorbent particles. Aliquots of 5 mL were titrated with a 0.1 N volumetric standard solution of HCl using methyl red as indicator. All experiments were performed in duplicate. The results of Boehm-titration were supported by Fourier Transform Infrared Spectrum (FTIR). Analysis was performed with a Perkin Elmer Spectrum One model spectrometer using carbon samples dispersed in KBr-pellets.

2.4. Experimental design

A 3-factor 3-level factorial Box–Behnken (BB) experimental design technique was employed to investigate the effects of selected variables. BB designs are response surface methods (RSM), specially made to require only 3 levels, coded as −1, 0, and +1. BB designs are formed by combining two-level factorial designs with incomplete block designs that the geometry of this design suggests a sphere within the process space such that the surface of the sphere protrudes through each face with the surface of the sphere tangential to the midpoint of each edge of the space [9,10]. This procedure creates designs with desirable statistical properties but, most importantly, with only a fraction of the experiments required for a three-level factorial (3^{k-p}) designs. Since there are only three levels, the quadratic model is appropriate. The observations were fitted to a second order polynomial model as given below:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} {x_i}^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} x_i x_j \tag{1}$$

where Y is the predicted response associated with each factor level combination, b_0 is the intercept term, b_i is linear effect (denoted by 'L'), b_{ii} is the quadratic effect (denoted by 'Q'), and b_{ij} is the 2-way linear by linear interaction effect. Additionally, x_i and x_j represent the coded values of independent variables and k is the number of the independent variables. The important variables chosen for the BB design are initial pH, temperature and initial Cr(VI) concentration, designated as x_1, x_2 and x_3, respectively. The dependent variables (Y_i) are Cr(VI) adsorption capacity of raw (AC) and modified (IAC) activated carbons (mg g^{-1}). The range of experimental design matrix is shown in Table 1.

2.5. Statistical analysis

The regression analysis, statistical significance and response surfaces were obtained to find the most suitable combination of independent variables resulting in maximum Cr(VI) adsorption