Chemical Engineering Journal 185–186 (2012) 178–186

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Rapid removal of chromium from aqueous solution using novel prawn shell activated carbon

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ARTICLE INFO

Article history:
Received 23 June 2011
Received in revised form 13 January 2012
Accepted 14 January 2012

Keywords:
Activated carbon
Adsorption
Chromium
Prawn shell
Response surface methodology
Tannery effluent

ABSTRACT

The rapid removal of chromium ions from aqueous solutions using prawn shell activated carbon (PSAC) was established in the present study. Response surface methodology (RSM) was used to optimize the process variables for the maximum chromium removal. The optimization result shows that 0.04 g of PSAC was sufficient to remove 100.6 mg L^{-1} of chromium in 31.4 min time period. Adsorption of chromium obeyed both Freundlich and Langmuir adsorption isotherms and followed second-order kinetic reaction. This results suggest that the PSAC as a good candidate for the rapid removal of chromium from tannery effluent.

1. Introduction

The pollution of aquatic environment has been increased mainly due to the non-degradable hazardous compounds present in the effluents emanating from industries. Heavy metals are the most important constituents among toxic compounds in the effluents [1], which is used in industries for leather tanning, metal finishing, petroleum refining, wood preservation, corrosion inhibition in power plants, nuclear facilities and manufacturing of pigments, dyes, textiles, carpets, magnetic tapes, jet aircrafts and automobile parts [2,3].

Chromium exists in its stable oxidation state of hexavalent chromium (Cr VI) and trivalent chromium (Cr III), which are the main form of chromium found in many water bodies [1,4]. Chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) are considered a greater health hazard than the other valency states [4]. Permissible limit of chromium is 0.5 mg L^{-1}, but usually effluent discharged from the industries contained above the level [5,6]. Consumption of chromium contaminated drinking water may affect cell and humoral immunity through increasing the level of antibodies [7]. Considering, chromium's toxic and carcinogenic nature, the maximum levels permitted for trivalent chromium in wastewater is 5 mg L^{-1} and for hexavalent chromium is 0.05 mg L^{-1} [8,9]. In the present study, we focused mainly on tannery industries because there are about 2161 tanneries in India excluding cottage industries, which process around 500,000 tonnes of hides and skins annually which introduce 2000–5000 mg L^{-1} of chromium in the aqueous effluents [10–12].

Nearly 9,420,000 m^3 of wastewater was discharged from tannery industries annually [10]. Many tanneries are located in Vellore and Erode districts in Tamil Nadu, India and removal of discharged wastewater containing chromium is great challenge for the modern science. Chromium removal from aqueous system can be achieved with various methods such as chemical precipitation, ion exchange, membrane processes, electro dialysis and adsorption [13–16]. Among all other investigated methods, activated carbon adsorption is a highly promising method for the chromium removal. However, the cost of activated carbon preparation from coal and other natural sources are too expensive.

In search of new and alternative source as a precursor for the preparation of activated carbon from many biological materials with low or null cost have been studied. It includes agricultural wastes [17,18], natural wastes [19], stones and shells [20], bamboo [21], marine biomass *Posidonia oceanica* (L.)[22], marine macroalgal biomass *Sargassum longifolium* and *Hypnea valentiae* [23] etc. In the present study, we made an attempt to produce low cost activated carbon with rapid adsorption properties from easily available and highly abundant marine/river waste. One such material is fresh water prawn (*Penaeus esculentus*) shell.

Growing of prawn in cottage and industrial scale is one of the largest fast-growing trends commonly in India. After processing,

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doi:10.1016/j.cej.2012.01.071

Nomenclature

List of symbols

Z_i	uncoded value of ith independent variable
Z_i^*	uncoded value of ith independent variable at center point
ΔZ_i	step change value
X_i	coded value of ith independent variable
Y_j	observed response
$\hat{Y}_j$	predicted response
R^2	correlation coefficient
RSM	response surface methodology
SEM	scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
CCD	central composite design
PSAC	prawn shell activated carbon

prawn shells are discarded as a waste in large scale. Many research works has been done on chromium adsorption, however, to our knowledge there is no one has used prawn shell waste as activated carbon (PSAC). The main objectives of this paper were (i) to explore the chromium removal capacity of PSAC, (ii) to optimize the variables for maximum removal of synthetic chromium and (iii) to perform column study for the industrial scale establishment of chromium removal.

2. Materials and methods

2.1. Chemicals

$K_2Cr_2O_7$ (purchased from Merck Co., Darmastdt, Germany), diphenylcarbozide and all other chemicals are of analytical grade.

2.2. Estimation of chromium

The pink-colored complex, formed from 1,5-diphenylcarbazide and Cr(VI) in acidic solution, was spectrophotometrically analyzed at 540 nm (PerkinElmer Lambda 25, Germany). To estimate the total chromium concentration, Cr(III) was first converted to Cr(VI), at high temperature (130–140 °C), by the addition of excess potassium permanganate prior to the 1,5-diphenylcarbazide reaction. The Cr(III) concentration was then calculated from the difference between the total chromium and Cr(VI) concentrations.

The hexavalent chromium in samples was analyzed at 540 nm in UV–vis spectrophotometer (PerkinElmer Lambda 25, Germany) after complexation with 2,5-diphenylcarbazide. The chromium (III) content in spent chrome liquor was estimated according to Haupt [24].

Diphenylcarbazide (1%) reagent was prepared in acetone and a drop of glacial acetic acid was added to this solution and stored at 4 °C. The effluent contained chromium is in trivalent state [25].

2.3. PSAC preparation

Collected prawn shells (*P. esculentus*) were washed several times with water and allowed to dry in shade. About 25 g of dried shells was treated with 20 mL of concentrated H_2SO_4 to form slurry and dried at 100 °C in hot air oven. Then, the dried slurry was washed with double distilled water until constant pH was reached. Activation was done in a muffle furnace at 400 °C and care was taken to avoid the formation of ash during the activation process in muffle furnace. The activated carbon was cooled to room temperature and kept in air tight bottle for further studies [18].

2.4. Physico-chemical characterization of PSAC

Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) was used to observe the physico-chemical properties of PSAC and synthetic chromium adsorbed PSAC. Scanning electron microscope (SEM; JEOL JSM-6390) was used to identify the surface microscopic structural properties of the materials. The bonding configurations of the materials were characterized by means of Fourier-transform infrared spectroscopy (FTIR; PerkinElmer, Spectrum One model Spectrometer, England).

The X-ray diffraction (XRD; Rigaku X-ray diffractometer D-Max Rint 2200 Series, Japan) was performed for the characterization of crystallographic structure of the materials.

2.5. Response surface methodology (RSM)

Response surface methodology (RSM) is a statistical design used to problems analysis in which a response of interest is influenced by several variables and the objective is to optimize this response and it is also used to determine the regression model equations and operating conditions from an appropriate experimental data [26]. Central composite design (CCD), a standard RSM design was applied to study the variables for removal of chromium by PSAC. Optimization of effective parameters with minimum number of experiments was done by fitting a quadratic surface and it analyze interaction between the selected variables [27]. CCD consists of a 2^k factorial runs with $2k$ axial runs, x_0 number of center points and six replicates. The dependant variables of this study were adsorption time (X_1), adsorbent dosage (X_2) and adsorbate concentration (X_3). The following equation can be used to find the number of experimental runs:

$$N = 2^k + 2K + x_0 \quad (1)$$

where N is the number of experimental run required, k is the number of variables and x_0 is the number of central points. Thus for this design total number of experimental runs will be 20 ($k = 3$, $x_0 = 6$) [18].

Table 1 shows the experimental range and independent variables. A 2^3 fractional factorial CCD for three independent variables with 20 experiments was used in the present study (Table 2). Independent variables were coded according to the equation $X_i = (Z_i - Z_i^*)/\Delta Z_i$, where Z_i represent the uncoded value of ith independent variable, Z_i^* denotes uncoded value of ith independent variable at center point and ΔZ_i is a step change value [18]. The obtained results were analyzed using Design Expert software 7.1 (Stat Ease, Minneapolis, USA) for developing regression and graphical analysis. The dependant response of this study was adsorptive removal of chromium. Analysis of response surface contour plots and maximum principle calculus were helpful to determine optimal conditions for the maximum removal of chromium.

The reproducibility of the experimental data and error was calculated from center points. Low and high levels are represented as −2 and +2, respectively. Randomization of the experimental sequence was helped to minimize the effects of the uncontrolled factors. The three variables were adsorbent dosage (X_1), adsorption time (X_2) and adsorbate concentration (X_3). Each response was used to develop an empirical model which correlated the response to the chromium removal variables using a second degree polynomial equation as follows:

$$\hat{y} = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (2)$$

where $\hat{y}$ is the predicted response, b_0 the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic