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Investigation of Cr(VI) adsorption onto chemically treated *Helianthus annuus*: Optimization using Response Surface Methodology

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ABSTRACT

In the present study, chemically treated *Helianthus annuus* flowers (SHC) were used to optimize the removal efficiency for Cr(VI) by applying Response Surface Methodological approach. The surface structure of SHC was analyzed by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Analysis (EDX). Batch mode experiments were also carried out to assess the adsorption equilibrium in aqueous solution. The adsorption capacity (q_e) was found to be 7.2 mg/g. The effect of three parameters, that is pH of the solution (2.0–7.0), initial concentration (10–70 mg/L) and adsorbent dose (0.05–0.5 g/100 mL) was studied for the removal of Cr(VI) by SHC. Box–Behnken model was used as an experimental design. The optimum pH, adsorbent dose and initial Cr(VI) concentration were found to be 2.0, 5.0 g/L and 40 mg/L, respectively. Under these conditions, removal efficiency of Cr(VI) was found to be 90.8%.

1. Introduction

Many studies have been reported on heavy metals adsorption in batch or continuous mode using agricultural waste materials in yesteryears (Garg et al., 2007) due to its ease for removing heavy metal ions from wastewaters.

But in recent years, use of Response Surface Methodology (RSM) has been emphasized which is a combination of mathematical and statistical techniques used for developing, improving and optimizing the processes and to evaluate the relative significance of several process parameters in the presence of complex interactions (Garg et al., 2008). RSM has been used in various scientific fields such as biochemistry (Kumar and Satyanarayana, 2004; Fu et al., 2007), film properties of diamond like carbon (Wachter and Cordery, 1999) process parameter optimization. However, few studies have been carried out in the field of biosorption (Hasan et al., 2010; Ozer et al., 2008; Amini et al., 2008; Gönen et al., 2008; Goel et al., 2006). RSM has certain advantages over other processes like higher percentage yield, reduced process variability, closer confirmation of output response to nominal, target achievement and less treatment time with minimum cost (Box and Hunter, 1957).

Principal Response Surface Methodologies which are used in experimental design are central composite, Box–Behnken, and Doehelrt design (Souza et al., 2005). Box–Behnken which is a spherical revolving design requires an experiment number according to $N = k^2 + k + cp$ where k is the factor number and cp is the replicate number of central point (Souza et al., 2005). It has been applied for the optimization of several chemical and physical processes. However, its application in analytical chemistry is much smaller than the central composite and Doehlert matrix design (Souza et al., 2005).

This paper is mainly concerned with the investigation of combined effect of various process parameters like Cr(VI) concentration, pH of the solution and adsorbent dose on removal of Cr(VI) from aqueous medium by chemically treated *Helianthus annuus* (SHC) using Box–Behnken model experimental design in Response Surface Methodology (RSM) by Design Expert Version 6.0.10 (Stat Ease, USA).

2. Methods

2.1. Preparation of sunflower head waste carbon (SHC)

Deseeded sunflower heads were collected at the time of harvesting from agricultural fields of a village in Kurukshetra district, Haryana (India). The adsorbent was prepared by following the procedure given in paper (Jain et al., 2010). FT-IR analysis in solid phase was performed to get qualitative and preliminary information of the main functional groups that might be involved in metal uptake, using Fourier Transform Infrared Spectrum (FTIR-8400S, Shimadzu, Japan). Finely ground sample (5–10 mg) was mixed homogenously with dry potassium bromide in the ratio of 1:20 (w/w) and made pellets in disc by applying pressure and the spec-

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tra was recorded in the range of 4000–400 cm^{-1}. Scanning Electron Microscopy along with Energy Dispersive X-ray analysis (model Quanta 200 EFG, FEI, Netherlands) was used as a tool for adsorbent characterization. Surface area of the adsorbent was determined using surface area analyzer (Micro Meritics, Chemisorb-2720). The particle size was in the range of 1–300 μm (Jain et al., 2010).

Thousand milligram per litre of stock solution of hexavalent chromium was prepared in double distilled water using potassium dichromate (AR grade). Working solutions of different concentrations were prepared by successive dilution. The pH of the solution was adjusted after adding the adsorbent to required value by adding either 0.01 M HCl or 0.01 M NaOH using pH meter after calibration with pH 4.0, 7.0 and 9.2 buffers. The Cr(VI) concentration in the test solution was determined by Atomic Absorption Spectrophotometer (Shimadzu AA 6300, Japan).

2.2. Batch studies

The batch studies were performed to study the removal of Cr(VI) from aqueous solution. A predetermined amount of adsorbent was added to 100 mL solution of known concentration in 150 mL Erlenmeyer flasks at temperature 25 ± 1 °C and equilibrated at 180 rpm on thermostatic orbital shaker (Scigenics Biotech ORBITEK) for 180 min. At predetermined time interval, the adsorbent was separated by centrifugation at 4000 rpm for 10 min. The residual Cr(VI) concentration in the supernatant was determined as stated in Section 2.1. The percent chromium removal (*R*%) was calculated for each run by following expression:

$$Y(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

where C_i and C_e were the initial and final concentration of chromium in the solution in mg/L. The metal uptake loading capacity (mg/g) of SHC for each concentration of Cr(VI) ions at equilibrium was determined as follows:

$$q_e(\text{mg/g}) = \left[\frac{C_i - C_e}{M}\right] \times V \tag{2}$$

where C_i and C_e are defined above, V is the volume of the solution in mL and M is the mass of the dry adsorbent (g).

2.3. Optimization of biosorption process using Response Surface Methodology

Many statistical experimental designs have been recognized as useful techniques to optimize the process variables. Response Surface Methodology (RSM) is used when a few significant factors are involved in optimization. A modified central composite experimental design and Box–Behnken design is an independent, rotatable or nearly rotatable quadratic design (contains no embedded factorial or fractional factorial design) in which the treatment combinations are at the midpoints of the edges of the process space and at the centre. RSM contains three steps: (1) design and experiments; (2) response surface modeling through regression; (3) optimization. To determine the optimum operational conditions of the process or a region that satisfies the operating specifications is the main objective of RSM (Myers and Montgomery, 2001). RSM is an efficient, cost effective method to model and optimize bioprocess as it enables researcher to identify interactions between studied variables present with few possible experiments.

The optimization of Cr(VI) uptake was carried out by three chosen independent process variables. The ranges and levels of variables investigated in the research are given in Table 1. In experimental design model, metal ion concentration (10–70 mg/L), pH (2.0–7.0) and adsorbent dose (0.05–0.5 g/100 mL) were taken as independent input variables (Table 1) and percent removal of Cr(VI) was taken as response of the system. The experimental design matrix derived from the Box–Behnken model is shown in Table 2. The amount of metal uptake was taken as the response of the design experiments. Seventeen experiments in total are required to calculate 10 coefficients of second-order polynomial equation which were fitted in experimental data (Toles et al., 1997).

A second-order polynomial model where interaction terms have been fitted to the experimental data obtained from the Box–Behnken model experiment can be stated in the form of following equation:

$$Y = b_o + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \tag{3}$$

where Y is the percentage of Cr(VI) adsorbed, b_o is the offset term, b_i is the first-order main effect, b_{ii} is the second-order main effect and b_{ij} is the interaction effect. The goodness of fit of the model was calculated using coefficient of determination (R^2) and the analysis of variance.

Table 1
Experimental range and level of independent variables.

Factors range and levels (coded)	−1	0	+1
Adsorbent dose (g/100 mL)	0.05	0.28	0.50
pH	2.0	4.5	7.0
Cr(VI) conc. (mg/L)	10	40	70

Table 2
Box–Behnken design matrix for three variables together with the observed response.

Experimental run	Coded values of the variable			
	Adsorbent dose (*A*)	Cr(VI) conc. (*B*)	pH (*C*)	Adsorption (%) (*Y*)
1.	−1.00	1.00	0.00	47.30
2.	1.00	−1.00	0.00	49.02
3.	−1.00	1.00	0.00	27.00
4.	1.00	1.00	0.00	37.06
5.	−1.00	0.00	−1.00	67.19
6.	1.00	0.00	−1.00	90.81
7.	−1.00	0.00	1.00	29.91
8.	1.00	0.00	1.00	19.80
9.	0.00	−1.00	−1.00	75.13
10.	0.00	1.00	−1.00	48.00
11.	0.00	−1.00	1.00	10.30
12.	0.00	1.00	1.00	5.200
13.	0.00	0.00	0.00	12.22
14.	0.00	0.00	0.00	12.50
15.	0.00	0.00	0.00	12.10
16.	0.00	0.00	0.00	12.30
17.	0.00	0.00	0.00	12.1

3. Results and discussion

3.1. FT-IR, SEM and EDX analysis of adsorbent

The main functional groups involved in the binding of Cr(VI) are —OH, C—H, C=C, C—O, $—OCH_3$ (Jain et al., 2010). The SEM microscopic photos of native SHC at 1500× magnification showed irregular cavities in fibrous network which are considered helpful for the accessibility of Cr(VI) to the biosorbent surface. EDX measurement of SHC (native and exhausted) was also undertaken for qualitative analysis of the elemental constitution of the adsorbent. Chromium loaded SHC showed distinct peaks of chromium indicating the corresponding ion present onto the adsorbent surface. The appearance of gold in the spectra is due to the fact that the samples were coated with gold prior to analysis. EDX analysis therefore