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Abatement of chromium by adsorption on nanocrystalline zirconia using response surface methodology

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ABSTRACT

Application of nanocrystalline zirconia was investigated for the removal of chromium from aqueous solutions. The nanozirconia was synthesized by 'precipitation method'. The parameters namely initial concentration (5–65 ppm), pH (0.5 to 10.5), adsorbent dose (2 to 10 g/l) and temperature (298 K to 318 K) were optimized employing central composite design of response surface methodology. The removal of Cr was most affected by pH, followed by an initial concentration and adsorbent dose. Maximum removal (%) was achieved at an initial concentration of 20 ppm, pH = 3, adsorbent dose = 4 g/l and 313 K. The experimental data were best fitted in Langmuir's isotherm equation and the removal followed pseudo second order kinetics. The mechanism of removal was explained by boundary layer diffusion via intraparticle diffusion and was further confirmed by Boyd plot. Thermodynamic parameters revealed that the removal process was spontaneous, endothermic and physiosorptive in nature. Adsorbent was regenerated with hydroxides (0.1 N NaOH, KOH and NH_4OH) for further reuse.

1. Introduction

All living beings including humans require water to survive except in certain ecosystems like hydrothermal vents. Water employed in various sectors is concisely categorized into three categories i.e. industry, agriculture and domestic. The ever increasing population has resulted in an immense stress on water quantity and quality. The pressure on water resources is further added by increasing population, industrialization and modern agricultural practices. Heavy metal pollution is one of problems retro-grading the aqueous ecosystems. Chromium is one of the metals with applications in various industries such as, electroplating, textile, stainless steel, leather, and paint industries. Higher intake of chromium in human body results in weakening of immune system, DNA strand breaks, alteration in cellular signaling pathway, ulcers, allergic dermatitis and ultimate death in many cases [1–3].

Because of well documented adverse health effects of chromium and its widespread applications, it is mandatory to remove it from industrial effluents prior to discharge. Chemical precipitation, coagulation and flocculation, electro-coagulation, ion exchange, membrane separation, nano-filtration, solvent extraction, reverse osmosis [4–10], and adsorption [11–14] are some of the techniques widely reported for the treatment of chromium laden aqueous solutions and waters. Each of these techniques has merits but they suffer from certain drawbacks like high operational cost, along with regeneration and need of trained personnel. But adsorption has advantages over other technique due to ease in operation, regeneration, high efficiency, low energy input and removal of pollutants even at trace concentrations. Various adsorbents like activated carbon, carbon nanotubes, lignin, chitosan, clay, fly ash, bacteria, fungi, and nanostructured oxides such as iron oxide and aluminum oxide [12–23] have been reported for the removal of Cr from aqueous solutions. Present study addresses removal of chromium by adsorption on nanocrystalline zirconia. Zirconia has excellent chemical inertness and is known to be biocompatible with system [24]. Removal efficiency of the synthesized adsorbent, nanozirconia for removal of Cr was examined and reported. Response surface methodology was used for optimization of experimental parameters and thermodynamic studies for the removal of Cr were also carried out and reported.

2. Experimental

2.1. Materials and analytical instruments

Potassium dichromate ($K_2Cr_2O_7$) and ammonium hydroxide (NH_4OH) were procured from Merck, Mumbai, India. Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) was obtained from Himedia, India. Tubular Furnace (IKON, India), Analytical balance (VIBRA), pH meter (IKON, India), X-ray diffractometer (MINIFLEX II, Desktop XRD, RIGAKU), DTA/TGA (Labsys™ TG–DTA 16, SETARAM Instrumentation), Scanning electron microscope (Quanta 200 f. FEI), Transmission electron microscope (TECNAI G2, FEI), water bath shaker (Narang scientific), and atomic adsorption spectrophotometer (Szhimadzu AA 7000) were used in the present studies.

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2.2. Design of experiments or response surface methodology

Experiments were designed via response surface methodology (RSM). RSM is a collection of statistical and mathematical tools used to optimize the response governed by several independent variables. It has been useful for modeling and analysis of problems in which a response of interest is influenced by several variables and its objective is to optimize this response [25]. Classically, response is optimized by varying one parameter one at a time and keeping other parameters constant. Classical method is time consuming and does not provide the correct picture of quantitative interactions between various parameters. To overcome these drawbacks, RSM is employed to know interaction among various parameters. By taking into account various independent parameters, optimization is achieved through RSM.

RSM contains two designs: Box–Behnken design (BBD) and Central composite design (CCD). In BBD, cubic points are taken into consideration, whereas in CCD, axial points, in addition to cubic points are taken into consideration. It means that BBD has only 3 degrees of freedom ($-1, 0, +1$), whereas CCD system has five degrees of freedom ($-\alpha, -1, 0, +1, +\alpha$). In present studies, the four parameters studied were concentration of solution (X1), pH of the solution (X2), dose of adsorbent (X3) and temperature of solution for reaction conditions (X4) at five levels ($-\alpha, -1, 0, 1, +\alpha$) with a significance level of 0.05. Here, each parameter is coded by $-\alpha$, -1, 0, 1, and $+\alpha$. -1, 0 and $+1$ are the minimum, central and maximum coded cubic values respectively. Likewise $+\alpha$ and $-\alpha$ represent minimum and maximum coded axial values used in the model, respectively. The value of α depends upon the number of process independent variables taken in the design [26].

The value of α for orthogonal design is calculated as follows:

$$\alpha = 2(\text{number of independent variables}/4).$$

Here number of variables was 4. So,

$$\alpha = 4/4 = 2. \quad (1)$$

The relationship between coded and uncoded variables was obtained from the following equation [25]:

$$\text{CODED VALUE} = X_i – X_n/\Delta X. \quad (2)$$

Here X_i is the value of uncoded value of the ith factor, X_n is the midway average value of low high, and ΔX is the step change.

The total number of experiments obtained by operating CCD of RSM in a MINITAB 16 software was 31. In the experiments, there were 16 factorial points, 8 axial points and 7 replicates [26].

$$N = 2k + 2k + n_o = 24 + 2 \times 4 + 7 = 31 \quad (3)$$

where N is the total number of experiments, k is the number of factors and n_o is the number of central runs.

On the basis of the results, a second order polynomial is applied to explain the relationship between response and processed variables [26] as follows:

$$Y = \beta_0 + \Sigma\beta_i x_i^{\,2} + \Sigma\beta_{ii} x_i^{\,2} + \Sigma\Sigma\beta_{ij} x_i x_j + \epsilon_r. \quad (4)$$

Y denotes the predicted response, and i and j take values from 1 to the number of independent process variables. $\beta_{0,}$ β_i, β_{ii}, and β_{ij} are the offset terms, linear effect, square effect and interaction effect predicted by the method of least squares, ϵ_r denotes the error of prediction and x_i and x_j are coded independent process variables [26,27].

2.3. Synthesis of the adsorbent

Nanocrystalline zirconia was synthesized by precipitation method [28,29]. Solution of $ZrOCl_2 \cdot 8H_2O$ (0.075 M) was prepared in distilled water and was precipitated with 25% ammonia while stirring till its pH reached 10 to 10.5. It resulted in formation of zirconium hydroxide. After complete precipitation, it was filtered and subsequently washed with distilled water to remove chloride from the filtrate which was ascertained by titrating the filtrate with $AgNO_3$. After complete removal of chloride, precipitate was dried in an oven at 353 K to 363 K for 24 h. The dried zirconium hydroxide was calcined at 773 K at a heating rate of 10 °C/min resulting in the formation of nanocrystalline zirconia as follows [28]:

$$ZrOCl_2 \cdot 8H_2O + 2NH_4OH \rightarrow Zr(OH)_4 + NH_4Cl \quad (5)$$

$$Zr(OH)_4 \rightarrow ZrO_2 + H_2O. \quad (6)$$

2.4. Batch experiments

Stock solution of Cr(VI) (1000 ppm) was prepared by dissolving $K_2Cr_2O_7$ in distilled water. Experimental conditions with four variables at five degrees of freedom, as suggested by the model were used to perform the experiments. For adsorption experiments, a known amount of adsorbent, nanozirconia, was added to 50 ml of Cr solution in 100 ml reagent bottles. The contents were agitated at 90 rpm in a water bath shaker up to equilibrium time, 45 min. pH of the solutions was maintained by adding 0.1 N NaOH/HCl to the solutions. Isotherm data were obtained by carrying out experiments at different initial concentrations (20 to 70 ppm, pH = 3, dose = 4 g/l, temperature = 293 K to 343 K). Thermodynamic parameters were similarly determined by performing experiments at different temperature (293 K to 343 K).

After equilibrium, the adsorbent was separated from the solutions by filtration followed by subsequent centrifugation at 6000 rpm for 10 min. Residual concentration of Cr in the aliquot was determined by an atomic absorption spectrophotometer (Shimadzu AA7000). All experiments were conducted as triplets and the values presented here are average of the three replicates.

The amount of chromium adsorbed per unit mass of the adsorbent ($mg\ g^{-1}$) was determined by the following expression [23]:

$$q_e = (C_i – C_e/W) * V \quad (7)$$

where q_e is the amount adsorbed on per unit mass of the adsorbent ($mg\ g^{-1}$) at equilibrium, C_i and C_e (both in mg/l) are the initial and the equilibrium concentrations of Cr respectively, and W is the weight of adsorbent (g). Percentage removal of Cu(II) was calculated by applying the following expression [23]:

$$\%\text{Removal of metallic ions} = (C_i – C_e/C_i) * 100. \quad (8)$$

2.5. Regeneration batch experiments

For regeneration, the used adsorbent was placed in 1 l chromium solution of initial concentration of 50 ppm, pH = 2 and adsorbent dose of 5 g/l. Afterwards, the solution was stirred at 350 rpm on magnetic stirrer for 2 h. Chromium loaded adsorbent was isolated by filtration and subsequently dried in an oven at 323 K. The used adsorbent was regenerated by taking regenerating agent in a beaker along with used adsorbent viz. chromium loaded nanocrystalline zirconia. It was stirred at 350 rpm on magnetic stirrer for 2 h. Afterwards, adsorbents were filtered and dried in an oven.

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