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Enhanced removal of Cr(VI) by cerium oxide polyaniline composite: Optimization and modeling approach using response surface methodology and artificial neural networks

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In the present research, cerium oxide polyaniline (CeO_2/PANI) composite has been prepared to investigate the removal efficiency of Cr(VI) from water. The experimental design, parametric appraisal and prediction of the adsorption process are performed using response surface methodology (RSM-CCD) and artificial neural network (ANN) method, respectively. Adsorption studies with respect to various process variables such as dose, time, pH, temperature and initial concentration is carried. The characterization of CeO_2/PANI composite has been done by various physicochemical techniques followed by mechanistic explanation of Cr(VI) adsorption. A second order predictive quadratic equation relating to removal percentage and important process variables was developed and adequacy (ANOVA) of the model was checked. Nelder–Mead simplex algorithm was used for numerical optimization. The result indicates that 93.9% removal can be achieved under reaction conditions: dose = 0.82 g/L, pH 6, time = 60 min, temperature = 40 °C and initial concentration = 49 mg/L. The kinetic studies revealed that the adsorption process followed pseudo-second-order kinetics. The adsorption data were best fitted to Langmuir model. The adsorption capacity for Cr(VI) ions was 357 mg/g at pH 6. Prediction of removal percentage by ANN model has been found to be best than RSM model with high correlation value (R^2) of 0.994.

Introduction

Chromium is listed among the most reactive and toxic element in the environment due to its mobility and oxidative properties that exists in the form of Cr(III) and Cr(VI) [1]. Cr(VI) is five hundred times more toxic than Cr(III) and is found present in the form of oxyanions ($Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-}) in aqueous environment formed due to high electrostatic repulsion force between chromium ions and negatively charged soil particles [2]. The prime sources of chromium pollution to environment are mining of chrome ore, wood preservation and from industries such as electroplating, leather, iron and paint [1–5]. The very renowned health problems from chromium poisoning are allergic skin diseases [1,3], kidney malfunction [6] and liver problem [7]. Considering the toxicity of chromium in water, the world health organization [8] recommends the highest permissible limit of chromium in drinking water should not exceed 0.05 mg/L.

Literature reports standard processes such as adsorption, chemical reduction, ion exchange, electro-dialysis, evaporative-recovery, membrane-filtration, precipitation, phytoremediation and reverse osmosis [2,6–10] for chromium removal from water. Among these, adsorption and ion exchange are most promising techniques, as they are very simple, reliable and cost effective process [6]. The most important issue for an environmental process is the parametric appraisal of the method and subsequently improvement through modeling and optimization without incurring extra cost. However, the removal of Cr(VI) by this method depends on a number of variables. The non-linear behavior and profound impact of these parameters for removal process make researchers to profoundly use modeling approaches.

Modeling of such process by response surface methodology (RSM) and artificial neural network (ANN) can make it easy to understand the influence of different variables affecting the removal of Cr(VI) from water. In recent years, RSM and ANN are widely used to solve the environmental issues [11]. RSM not only develops a non-linear predictive equation, but also helps to analyze influence of each parameter on removal efficiency. On the other hand, neural networks can map non-linear relationship between inputs and outputs using the data structure. In this study,

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two different predictive models namely RSM and ANN are compared to gain insight into the prediction capability of each model. However, both the models have their own advantages and disadvantages. RSM can show the influence of each parameter and interaction between parameters on response, but ANN can improve and simulate any process performance in any form of non-linearity without any regular experimental design. ANN also overcomes quadratic non-linear correlation hypothesis of RSM. Although a considerable amount of research is carried utilizing RSM and ANN separately in removal process, few studies documented are arsenic removal by solid waste vegetable with Fenton reagents [11], bio sorption of lead using black cumin [12], Cr (VI) removal by solid biodiesel waste residue [13] and lead removal by industrial sludge leachate on red mud [14]. In these studies, ANN and RSM techniques are compared for their predictive and generalization capabilities, optimization and sensitivity abilities. However, removal of Cr(VI) using CeO_2/PANI composite has not been reported in literature but laboratory preparation of CeO_2/PANI has already been documented by Kumar [15]. Hence, the main motivation behind the study is to investigate the removal possibility of Cr(VI) from water using synthesized CeO_2/PANI with removal efficiency prediction by using RSM and ANN techniques. Finally, the adsorption isotherm, adsorption kinetics and thermodynamics of the adsorption process for Cr(VI) removal by CeO_2/PANI composite are also documented. The main advantage of the material CeO_2/PANI is that the material has higher surface area and high adsorption capacity as compared to the material reported in literature and is insoluble in water. The material is selective in removing the target ions from water.

Experimental

Synthesis of CeO_2/PANI composite

In a 250 mL round bottom flask, a dispersion of CeO_2 was prepared with 100 mL (1 M) of HCl and to that, 3.5 mL of aniline was added drop wise under ultrasonic medium. The ultrasonic medium is used to reduce the agglomeration of cerium oxide particles. The above dispersion was kept in 50 °C for 1 h with constant stirring. Then 4.5 g of APS was (dissolved in 50 mL deionized water) dropped into the solution in constant stirring for 20 min. The resulting mixture was allowed to react for 8 h at room temperature. A dark green color precipitate was obtained which was separated by centrifugation and filtration. The precipitated material was washed with HCl and double distilled water to remove the unreacted aniline monomer and by-products. Afterward the material is dried at 70 °C in oven until green powder material was obtained. A series of composites are prepared by variation of different molar concentration of aniline and cerium oxide. The surface area, ion exchange capacity and particle size of all the materials are analyzed and the best performing material was used for further batch adsorption experiments. The present synthesis method follows the procedure and technique as reported by Kumar [15].

A series of composites are prepared by the addition of different molar concentration of cerium oxide. The best performing material based on high surface area, ion exchange capacity and low particle size is selected for further batch adsorption experiments.

Materials and instrumentation

The studies are conducted using various analytical instruments such as pH meter (Elico, India, Ltd.), Scanning Electron Microscope (SEM JEOL-JSM-6480LV, Japan) coupled with Energy Dispersive X-ray Spectroscopy (EDS), FTIR spectroscopy (spectrum RX I, PerkinElmer corp., USA), Particle size analyzer (Malvern Nano ZS 90, UK), X-ray diffractometer (Phillips model XRD, PW 1830, Almelo, Netherlands), TGA-DTA (DTG-60, Shimadzu Corporation, Japan), BET (Brunauer, Emmet and Teller) surface area (Quantachrome Autosorb I, Boynton Beach, FL) and atomic absorption spectrophotometer (AAS) (Elico SL-176, India), respectively.

Batch adsorption experiments

Batch adsorption study was carried to investigate Cr(VI) adsorption on the composite material as a function of dose, time, pH, temperature and initial concentration. The adsorption experiment was carried according to conditions of central composite design of response surface methodology. Each experiment was performed in a 250 mL conical flask by adding the required amount of adsorbent in 100 mL of 10 mg/L synthetic Cr(VI) solution. The solution was agitated at a definite speed for predetermined time at different temperatures. All the adsorption experiments, other than temperature variation, were carried at room temperature. Horizontal shaker was used for agitating the solution. After predetermined time interval, the solid material was separated by filtration using separating funnel. The chromium concentration in aliquot was measured by AAS. Each analysis was conducted in triplicate and the average data points are taken for further calculation.

The removal percentage and adsorption capacity (Q_e) was calculated using the following equations:

$$\text{Removal}\,\% = \left(\frac{(C_0 - C_e)}{C_0}\right) \times 100 \tag{1}$$

$$Q_e = \left(\frac{(C_0 - C_e)}{m}\right) \times V \tag{1a}$$

where C_0 and C_e (mg/L) are initial and equilibrium concentrations of Cr(VI), V is the volume of solution (L) and m is the mass of the adsorbent in gram. The zero point charge density (σ) of sorbent was determined by a potentiometric titration method. The following equation (Eq. (3)) is used to determine the surface charge density [16].

$$\sigma_0 = \left[\left(\frac{C_A - C_B(OH^-) - (H^+)}{m}\right)F\right] \tag{2}$$

where C_A and C_B are the molar concentrations of acid and base needed to reach a point on the titration curve, $[H^+]$ and $[OH^-]$ is the concentrations of H^+ and OH^-, F is the Faraday constant (96,490 C/Mol), m is the concentration of the sorbent in g/L.

Response surface methodology (RSM)

Response surface methodology has been widely used to optimize a response (output variable) by carefully designing the experiments, which is influenced by several independent variables [17]. The CCD (central composite design) based on the principle of fitting the quadratic equation by multiple regressions with the required minimum number of experiments is applied in the present study. A quadratic equation has been developed for expressing the correlation between response and the selected variables by using the second order multivariate model, which is represented as:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ij} X_i^2 + \sum_{i,j=1,\, i \neq j}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{3}$$

where, Y is the corresponding response of input variables, X_i, X_i^2, X_i and X_j are the square and interaction terms of factors, respectively. β_0, β_i, β_{ii} and β_{ij} are the unknown regression coefficients and ε is statistical error.