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Taguchi design and equilibrium modeling for fluoride adsorption on cerium loaded cellulose nanocomposite bead

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ABSTRACT

The cooperative influence of operational variables for fluoride adsorption on cerium loaded cellulose nanocomposite bead (CCNB) was assessed using Taguchi design tool. The percentage contribution of each operational variable was determined. The solution pH, with a maximum contribution of 80.78%, indicates its highest influence on the response, the adsorption percent of fluoride. The quality and validity of the experimental design were assessed from ANOVA and subsequently by the confirmation experiment. The equilibrium adsorption data showed that the Temkin isotherm is the most suited one compared to the Langmuir and Freundlich model. It is found that almost 90% adsorbed fluoride can be eluted with 0.01 (N) NaOH and the regenerated bead can successively be reused for at least three times.

1. Introduction

Fluoride in minute quantity, although, is an essential component for normal mineralization of bones and formation of dental enamel (Teutli-Sequeira, Solache-Ríos, & Balderas-Hernández, 2012), consumption of fluoride rich drinking water may cause fluorosis, a detrimental manifestation in human (WHO, 2008). Due to its high bioavailability fluoride may easily be absorbed by the gastrointestinal tract without intervention of interfering elements such as Ca^{+2}, Mg^{+2} and Al^{+3} (Viswanathan, Jaswanth, Gopalakrishnan, & Siva ilango, 2009). Fluoride reacts readily with the positively charged calcium and is known to affect predominantly the skeletal system, teeth, brain and spinal cord (Mohan, Ramanaiah, Rajkumar, & Sarma, 2007; Viswanathan & Meenakshi, 2008). Fluoride, even in a level of one part per million or less, is known to inhibit over 100 different enzyme systems, such as acetyl cholinesterase and ATPase which play important roles in brain and nerve function (Yiamouyiannis, 1983).

Conventional removal of fluoride following chemical precipitation (Chang & Liu, 2007), coagulation (Hu, Lo, & Kuan, 2005), lime treatment (Meenakshi & Maheshwari, 2006), ion exchange (Meenakshi & Viswanathan, 2007), membrane separation (Sehn, 2008) and electrolysis (Drouiche et al., 2008) have serious limitations in terms of high cost, techno feasibility, simplicity and generation of secondary pollutants. Jagtap, Yenkie, Labhsetwar, and Rayalu (2012) discussed the removal strategies together with the prevalence of fluoride in drinking water around the globe and the associated health menace. Adsorption is found to be a popular and cost effective simple approach considering its versatility for removal of a large variety of pollutants. Adsorptive removal from aqueous environment with the advantage of techno-feasibility and recycling of adsorbent using a range of adsorbents viz. activated carbon (Alagumuthu & Ranjan, 2010), alumina (Tang, Guan, Su, Gao, & Wang, 2009), sol–gel-derived activated alumina (Camacho, Torres, Saha, & Deng, 2010), calcite (Turner, Binning, & Stipp, 2005), fly ash (Sarkar, Manna, & Pramanik, 2008), bone char (Medellin-Castillo et al., 2007), laterite (Sarkar, Banerjee, Pramanik, & Sarkar, 2006) etc. are available. Improved fluoride adsorption was reported using different materials viz. resins, composites, oxides, gel, polymer, fibrous protein, carbon etc. modified with metals particularly aluminum (Luo & Inoue, 2004; Ramos, 1999), iron (Zhao, Li, Liu, & Chen, 2008), lanthanum (Fang, Ghimire, Kuriyama, Inoue, & Makino, 2003; Kamble et al., 2007; Rao & Karthikeyan, 2012; Wasay, Haron, & Tokunaga, 1996; Zhou, Yu, & Shan, 2004), cerium (Deng & Yu, 2012; Sivasankar, Murugesh, Rajkumar, & Darchen, 2013) and cerium-titanium (Xiuru, Kuanxiu, Jianping, Liuchang, & Zhaohui, 1998). Adsorbents derived from biomaterials such as chitin (Davila-Rodriguez, Escobar-Barrios,

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Shirai, & Rangel-Mendez, 2009; Jayapriya, Ramya, Rathinam, & Sudha, 2011) and chitosan (Swain et al., 2010; Viswanathan, Sundaram, & Meenakshi, 2009) are particularly important in terms of their easy availability and biodegradable character. Cellulose being the most abundant natural polysaccharide might be a suitable renewable substrate material for the synthesis of adsorbent through modification with metal such as iron, aluminum, titanium, lanthanum, cerium etc. for fluoride removal.

The present study deals with modeling of fluoride adsorption using cerium loaded cellulose nanocomposite bead (CCNB) characterized by Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and electron paramagnetic resonance (EPR) study. In an aim to improve the precision of operation simultaneous optimization of process variables was made using statistical design of experiment following Taguchi tool. Taguchi tool utilizes a standard orthogonal array comprising of each experimental variable with different levels. The signal-to-noise (S/N) ratio corresponding to each combination is computed and is analyzed, based on ANOVA, to determine the optimal settings (experimental variable with its level) as well as the validity of the design. The feasibility of adsorption was determined following isotherm analysis. The utility of the present adsorbent was judged from the regeneration study.

2. Experimental

2.1. Materials

All the chemicals and solvents used are of analytical grade (Merck, India). The cellulose power used was procured from Loba Chemie, Mumbai, India.

2.2. Preparation of CCNB

Cerium loaded cellulose nanocomposite bead was synthesized by wet chemical process via sol–gel formation technique (Hench & West, 1990). 1.0 g of cellulose powder (precursor) was first soaked in 20 mL of 19% (w/w) aqueous sodium hydroxide (NaOH) which on aging for 3 days at room temperature yields a colloidal suspensions, the sol. 1.0 mL of carbon disulfide was subsequently added to the mixture and shaken (150 spm) for 8 h for esterification. 10 ml of 6% (w/w) NaOH solution was added to the sol of esterified cellulose and stirred for 3 h (Wang, Hao, Shi, & Sun, 2007) and allowed for syneresis at room temperature for 72 h. The viscose solution, the gel formed by condensation of the sol, was purged drop by drop into de-aerated methanol through a needle. Faintly red colored beads initially formed were filtered and immediately washed several times with double distilled water. The cellulose beads appeared as snow white, were stored under de-ionized water. It is probable that the sol–gel transition controls the shape and size of the formed cellulose nanocomposite bead.

The cellulose beads were next poured into a solution of 0.10 M cerium ammonium nitrate at pH 1.6 and shaken at a speed of 100 spm at room temperature for 2 h. A faint orange yellow colored cerium loaded cellulose nanocomposite bead, (CCNB) was formed, washed with distilled water and stored under de-ionized water.

2.3. Characterization of CCNB

CCNB was characterized by field emission scanning electron microscope (FESEM) with a JEOL, JSM 6700F microscope to study its surface morphology and energy dispersive spectroscopy (EDS) with FEI QUANTA FEG 250 for element detection. Electron paramagnetic resonance (EPR) spectrum, to identify the binding pattern of cerium in the bead, was recorded with a Varian X-band EPR spectrometer (Model E-109). The Fourier transformed infrared (FTIR) spectral study was carried out using Perkin Elmer L120-000A.

2.4. Batch adsorption and regeneration studies

Batch adsorption experiment was performed for fluoride adsorption on CCNB in a 100 mL Teflon stoppered conical flask. 25 mL of fluoride solution at a concentration of 2.0–10 mg L^{-1} was shaken with 1.0 g of CCNB for 1 h at a constant shaking rate of 120 spm in a temperature-controlled shaker until the equilibrium is attained. The initial solution pH was adjusted using either 0.1 M HCl or 0.1 M NaOH. The experiment was performed at different temperatures ranging from 293 to 323 K. Fluoride concentration in solution was determined potentiometrically using fluoride ion sensitive electrode (9609BNWP) in an Orion ion meter (VSTAR52). Adsorption efficiency, expressed as percent adsorption, was calculated using the following equation:

$$\text{percent adsorption}\,(\%) = \frac{(C_0 - C_e) \cdot 100}{C_0} \quad (1)$$

where C_0 and C_e are the initial and equilibrium fluoride concentration (mg L^{-1}) respectively in solution.

The elution of fluoride and regeneration of CCNB were made using definite concentration of NaOH in batch mode.

2.5. Statistical design of experiment using Taguchi tool

The design of adsorption experiment through Taguchi tool was made with the following objectives:

(i) to select the appropriate orthogonal array (OA) using each operational variable with all selected levels,
(ii) to categorize the variables and analyze the design quality from statistical analysis of variance (ANOVA),
(iii) to predict the response (percent adsorption) at the optimum level of the operational variables,
(iv) to run a confirmation experiment for validation of the predicted response.

2.5.1. Selection of orthogonal array (OA) and statistical analysis

An orthogonal array is made using five operational variables [pH, concentration (mg L^{-1}), adsorbent dose (g L^{-1}), contact time (min) and temperature (°C)] each with four levels and combinations in equal number of occurrence (Table 1) to yield a balanced design.

Taguchi approach based on the analysis of loss function was applied to yield the signal-to-noise (S/N) ratio and is used as the guiding parameter to judge the quality of experiment together with the validity of the result (response) (Atil & Unver, 2000). The S/N ratio, in fact, reflects the variability or level of precision of each response for each single experiment (trial) in the total set (replication). Any factor affecting the precision, mostly random and inherent for the operation, is termed as the noise. The response corresponding to the change of each operational variable is known as the signal which is used to correlate the response with the value of the operational variable.

Usually, three categories of S/N ratio analysis viz. 'larger is better' (LIB), 'nominal is best' (NIB) and 'smaller is better' (SIB) are available (Box, 1988; Ross, 1995). As the present study demands maximum adsorption, S/N ratio analysis following Eq. (2) for the LIB category is applied.

$$\frac{S}{N} = -10 \log \frac{1}{n} \left(\sum \frac{1}{y^2} \right) \quad (2)$$

where n is the number of observations, and y is the observed response (adsorption percent).