Environmental Nanotechnology, Monitoring & Management 6 (2016) 99–107

Contents lists available at ScienceDirect

Environmental Nanotechnology, Monitoring & Management

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

Kinetic and equilibrium modelling of adsorption of cadmium on nano crystalline zirconia using response surface methodology

Deepak Gusain [a], Prabhat Kumar Singh [b], Yogesh C. Sharma [a,*]

[a] Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, Varanasi 221 005, India
[b] Department of Civil Engineering, Indian Institute of Technology (BHU) Varanasi, Varanasi 221 005, India

ARTICLE INFO

Article history:
Received 30 April 2016
Received in revised form 8 July 2016
Accepted 11 July 2016

Keywords:
BBD-RSM
Isotherm
Kinetics
Nano iron oxide/hydroxide
Thermodynamics

ABSTRACT

Nano zirconia has been employed for adsorption of cadmium from aqueous solution. Adsorption parameters were optimized using Box-Behnken design. Adsorption parameters Initial concentration, adsorbent dose and temperature were optimized. Optimized conditions were found out at initial concentration = 1 ppm, adsorbent dose = 4 g/l and pH = 7. The best-fit equations of linear and non-linear forms of kinetics and isotherm models were compared among themselves. Results exhibit that chi-square reduction method in Microcal origin curve fitting tool is better than Error analysis method of solver add in for determination of isotherm parameters. However, linear model explains the system best fit on the basis of R^2_{adj} in isotherm analysis. Experimental q_e values were slightly closer to theoretical q_e values in linear pseudo-second order model as compared to pseudo-first order non linear model. The system follows Langmuir isotherm model and pseudo-second order model. Thermodynamic parameter by partition and Langmuir constant method suggests that the system is spontaneous in nature.

1. Introduction

Human body requires a few heavy metals like copper and zinc for normal metabolic activity of the body. But at higher concentration these heavy metal are of grave concern to the human health (Zhang et al., 2013). But, few heavy metals like cadmium mercury and lead are toxic even at low concentration (Zhang et al., 2013). Itai-itai disease occurred in Japan in 1950s due to the cadmium which led to studies related to its ill effects on bone and kidney (Zhang et al., 2014). Cadmium is used in number of industries like metal plating, manufacturing of Ni-Cd batteries and pigments application of phosphatic fertilizers, by product of mining and smelting of lead and zinc (De Lurdes Dinis and Fiúza, 2011; Boparai et al., 2013b). The aqueous solutions from aforementioned industry contains elevated metal concentration harmful to the aquatic environment and human health (Regmi et al., 2012).Cadmium finds its way from aquatic environment into the human body. Cadmium causes liver dysfunction, hypertension and act as endocrine disruptor, teratogen, carcinogen, mutagen (Gloria et al., 2011; Ali et al., 2013).

To resolve the issues associated with cadmium a number of techniques applied, a few of them are precipitation (Rojas, 2014),electro coagulation (Vasudevan et al., 2011), ion exchange (Elkady et al., 2011a), reverse osmosis, nano filtration (Kheriji et al., 2015) and adsorption (Boparai et al., 2013a; Luo et al., 2013; Venkatesan et al., 2014; Yaacoubi et al., 2014). In the current study adsorption is used for abatement of cadmium from aqueous solution using nano crystalline zirconia. Adsorption removes contaminant even at very low concentration. Maximum contaminant level goal (MCLG) for cadmium is 0.005 mg/l (Sheftel, 2000). Hence adsorption is used for current study. A number of adsorbents used for remediation of cadmium from water like magnetite/maghemite (Chowdhury and Yanful, 2013), mesoporous silica, activated carbon (Machida et al., 2012),Cerium oxide, Titanium oxide (Contreras et al., 2012). Present study use nano crystalline zirconia for removal of cadmium. Zirconia is chemical inert and biocompatible (Manicone et al., 2007; Gusain et al., 2014a). The fluorescence enhancement was used to distinguish phases of nanomaterials(Meng and Ugaz, 2015). But here, XRD is used to identify phases of synthesized nanocrystalline zirconia. Linear and non linear regression is frequently used to determine the isotherm parameters. Error distribution gets altered by linearization of the non linear equation (Gusain et al., 2014b). Hence, scholars are using non linear equations. Current study deals with the use of both linear and non linear equations for their comparative analysis. Non linear analysis was also conducted using

* Corresponding author.
E-mail address: ysharma.apc@itbhu.ac.in (Y.C. Sharma).

http://dx.doi.org/10.1016/j.enmm.2016.07.002
2215-1532/

error analysis by Microsoft excel Solver add in (Gusain et al., 2014b) and Microcal origin curve fitting tool (Czinkota et al., 2002).

2. Material and methods

$K_2Cr_2O_7$, $ZrOCl_2{\cdot}8H_2O$, NH_4OH purchased from Merck India. Tubular Furnace (IKON), Analytical balance (VIBRA), pH meter (IKON) distilled water, X ray diffraction (MINIFLEX II, Desktop XRD, RIGAKU), DTA/TGA (Labsys^{TM} TG-DTA 16, SETARAM Instrumentation), Scanning electron microscope (Quanta 200 f, FEI), Transmission electron microscope (TECNAI G2, FEI) water bath shaker (Narang scientific), atomic adsorption spectrophotometer (Szhimadzu AA 7000), Fourier transform Infrared spectroscopy (PerkinElmer Version 10.03.05) were instruments used to characterize and perform the experiments.

2.1. Design of experiments

Conventionally experiments were conducted by variation of one variable at a time. Recently a number of experimental designs were used like ANN (artificial neural network) and RSM (response surface methodology) for adsorption. In the current study RSM is used to evaluate the effect of parameters on the percentage removal of cadmium. RSM contains two designs one is Box-Behnken design (BBD) and other one is Central composite design (CCD In the current experiment BBD) is used. The BBD have 3° of freedom (-1, 0, +1). The three parameters were studied in the BBD i.e. pH, Dose, Concentration.

The relationship between coded and non coded parameters is represented as follows (Montgomery, 2012):

$$\text{CODEDVALUE} = X_i - X_n/\Delta X \quad (1)$$

Here X_i is the value of uncoded value of i_{th} factor X_n is the midway average value of low and high, ΔX is the step change. The total number of experiments was 20.

A second order polynomial is used to explain the relationship between the response and input variables (Gusain et al., 2014a).

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

Y is the predicted response, i and j varies from 1 to the number of independent process variables. β_0, β_i, β_{ii}, β_{ij} were the offset term, linear effect, square effect and interaction effect calculated by the least squares method, ϵ_r is the error of prediction and X_i and X_j are coded independent process variables (Gusain et al., 2014a).

2.2. Batch experiments

Batch adsorption experiments were carried out to assess the removal efficacy of nano crystalline zirconia for cadmium removal from aqueous solutions. In the batch experiments, a stock solution of 1000 ppm of cadmium was prepared by dissolving $CdCl_2$ and standardizing it with atomic absorption spectrophotometer. Cadmium solution is further diluted in distilled water to make working solutions of desired concentrations. HCl and NaOH with a strength of 0.1 N used to maintain the initial pH of the solution. Experiments with conditions suggested by Box-Behnken with 50 ml volume conducted. Thereafter, the sample was separated from the solution by centrifugation (REMI PR 24) at 10000 rpm for 10 min. The residual concentrations of Cd in each aliquot were analyzed with atomic adsorption spectrophotometer.

Adsorbed amount of cadmium is calculated by following expression (Srivastava and Sharma, 2013)

$$q_e = (C_i - C_e) \times V/M \quad (3)$$

The q_e is the amount adsorbed on per unit mass of the adsorbent ($mg\,g^{-1}$), C_i and C_e (both in ppm) are the initial and the equilibrium concentration respectively; V and W are volume of adsorbate solution (L) and the weight of adsorbent (g) respectively. Percentage removal of Cd was calculated by applying following equation (Srivastava and Sharma, 2013)

$$\%\text{Removalofmetallicions} = (C_i - C_e/C_i) \times 100 \quad (4)$$

2.3. Regeneration experiments

Regeneration studies were performed at room temperature. First cadmium adsorption was conducted on adsorbent at following condition (initial concentration 5 ppm, pH = 7, Adsorbent dose = 8 g/l). Afterwards it has been stirred at room temperature for two hours. Adsorbent was then separated and dried in oven. Following this cadmium was desorbed by taking 1000 ml of regenerating solution in a beaker along with cadmium loaded adsorbent. It has been stirred at 350 rpm on magnetic stirrer and then dried and in oven

2.4. Process and parameter determination

Isotherm and parameter determination were executed linear and non linear methods. Error function analysis using solver add in (Gusain et al., 2014b) and curve fitting function of Microcal origin were used as non linear method. The sum of the square of the errors (ERRSQ), Hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), The average relative error (ARE), The sum of the absolute errors (EABS) were the error function employed in error function analysis. Non-linear curve fitting for isotherm and kinetic parameter determination using Microcal origin was done by customizing a non linear function for isotherm and kinetic model. The parameters in Microcal origin were estimated by reducing the difference between estimated values and experimental values using iteration by application of chi-square minimization method (Andrae et al., 2010). The initial parameters were initially set as 1. The Levenberg-Maquardt (LM) algorithm (Hagan and Menhaj, 1994) was used to adjust parameter values in iterative process.

The square of correlation coefficient is investigated as an indicator of isotherm and kinetic model suitability. The value of the square of correlation coefficient varied from 0 to 1 (Mendenhall et al., 2012).

$$r^2 = S_{(XY)}/S_{(XX)}S_{(YY)} \quad (5)$$

Here, $S_{(XY)}$ designates the sum of squares of X and Y, $S_{(XX)}$ as the sum of the squares of X and $S_{(YY)}$ as the sum of squares of Y.

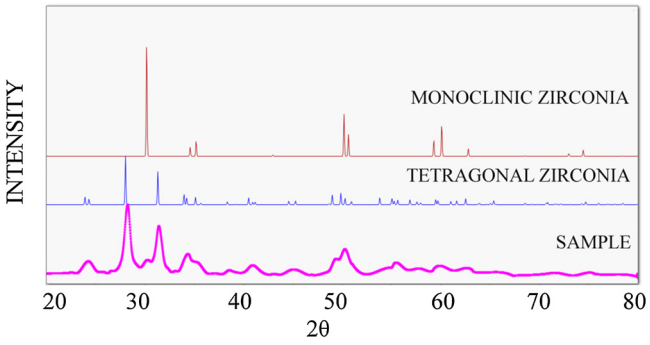

Fig. 1. XRD of sample, tetragonal zirconia (crystal diffract file), monoclinic zirconia (database_code_amcsd 0009231).