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Optimization of the adsorption of Pb (II) from aqueous solution onto PAB nanocomposite using response surface methodology

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ABSTRACT

The present study reveals the synthesis of bentonite immobilized alginate grafted by polyacrylonitrile (PAB) nanocomposite by in situ chemical oxidation of acrylonitrile monomer in presence of alginate, bentonite and MBA as a cross linker. The material was characterized by FT-IR, XRD, SEM and TEM techniques. The influence of various adsorption parameters viz agitation time, pH of Pb (II) solution, adsorbent dose, Pb (II) ion concentration and temperature was optimized by central composite design (CCD) of the RSM using MINITAB 17. Based on the design suggested by MINITAB 17, experiments were performed and the optimum values were found as agitation time (172 min), pH 4.0, dose (0.06 g), Pb (II) ion concentration (55 mg L^{-1}) and temperature (44 °C) with 96.65% removal of Pb (II) ions with 0.99 desirability. The adsorption experimental data was applied to non-linear Langmuir, Freundlich and Temkin models at 30, 40 and 50 °C and based on the value of regression coefficient R^2 and χ^2, the experimental data was best followed by Langmuir model. The maximum monolayer adsorption capacity was found to be 45.63 mg g^{-1} at 30 °C, 47.41 mg g^{-1} at 40 °C and 47.38 mg g^{-1} at 50 °C.

1. Introduction

In the present scenario, environmental protection and energy supply are the two major crises exasperated by the world (Kebir et al., 2011; Bicáková and Straka, 2012). Discharge of heavy metals to the environment from various industrial activities such as metal plating, mining, refineries and agricultural leads to heavy metal poisoning in human health and damage to ecosystem (Wang and Chen, 2009; Hashim et al., 2011; Kavak, 2013). Among the various heavy metals, Pb (II) is found to be most toxic and have many applications in industries. According to bureau of Indian standard (BIS) for drinking water specification, a maximum permissible limit of 0.05 mg L^{-1} for Pb (II) is desirable (BIS, 2009) and maximum limit of 25 μg L^{-1} per kg body weight for all age group was established by WHO (FAO/WHO, 2011). Beyond this permissible limit, Pb (II) can cause serious health effect such as kidney failure, neurological damages, hypertension (Liang et al., 2011; Squadrone et al., 2013). Due to aforementioned reasons listed above, removal of heavy metals from natural as well as waste water is a subject of great interest in environmental science. Various techniques have been developed in recent years for treatment of heavy metal such as ion-exchange, adsorption, coagulation, precipitation and reverse osmosis (Ahmad et al., 2012; Srivastava et al., 2015a). Among these, adsorption has been recognized as the most promising technique due to its economical and ease in operation and ecofriendly nature (Jiang et al., 2015).

Recently nanocomposites based on bio-polymers grafted synthetic polymers have been used in various applications including waste water treatment. One of the biopolymer found in abundance in nature is sodium alginate having 1, 4-linked β-d-mannuronic acid residues and 1,4-linked α-l-guluronic acid residues (Zhu et al., 2014). Due to its biocompatible and biodegradable properties alginate is used in various scientific applications including drug delivery (Abd El-Ghaffar et al., 2012), adsorption (Jain et al., 2013) etc. Bentonite, one the member of smectite group primarily composed of montmorillonite (Savic et al., 2014) and can be substituted by biopolymers and various cationic surfactant to make it suitable for successful reinforcement in the hydrophobic polymeric material (Benhouria et al., 2015). Recently polyacrlonitrile (PAN) has been found to be a highly efficient material for removal of heavy metals (Neghlani et al., 2011). With ease of polymerization, low cost of monomer and high thermal stability polyacrlonitrile was used as a support for alginate and additionally providing a large matrix for bentonite nanoclay particles (Sharma et al., 2010). Response surface methodology combined with central composite design is most widely used technique applied in various fields such as biochemical engineering, food processing and adsorption for optimization of various variables (Gusain et al., 2014; Dotto and Pinto, 2011). The great advantage of using RSM is that it reduces the number of

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experimental replications required to evaluate the various parameters and their interaction (Rahimia et al., 2015; Amini et al., 2008). The statistical design can well explain the interaction of the various variables and find out the optimum condition of the variables for the adsorption of heavy metals (Xu et al., 2015). The CCD is ideal for sequential experimentation and provides a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points (Somayajula et al., 2012; Demirel and Kayan, 2012).

In the present study a novel nanocomposite material based on bentonite immobilized alginate grafted polyacrylonitrile has been synthesized and explored for the removal of Pb (II) ion from the aqueous solutions. The effect of various parameters were optimized using central composite design of response surface methodology.

2. Materials and methods

2.1. Chemicals and reagents

Sodium alginate powder, sodium bentonite clay, *N*, *N*-methylene bisacrylamide (MBA), Acrylonitrile (AN) 99% was purchased from Sigma Aldrich (India), Ammonium persulphate (APS) and Lead nitrate was purchased from Merck (India). Double distilled water was used throughout the experiments.

2.2. Synthesis of PAB

The detailed procedure for the synthesis of nanocomposite material reported elsewhere (Mittal et al., 2014) has been given with some modifications. 2 g of dried sodium alginate powder was taken in 100 mL of double distilled water in a typical round bottom flask and stirred on magnetic stirrer at 40 °C with agitation rate of 800 rpm until complete dissolution. 1.0 g bentonite was taken in 50 mL of double distilled water and sonicated for 1 h at 30 °C. The suspension of bentonite was mixed to the above solution of alginate at continuous stirring at 40 °C for 2 h. Now to the above colloidal solution of bent-alg, 10 mL of AN monomer was mixed with 0.75 g *N*, *N*- methylene bisacrylamide and temperature was set to 65 °C for 1 h. The polymerization process was carried out by slow addition APS solution. After polymerization reaction the mixture was allowed to sit for 3 h at room temperature. The process was terminated by 0.1 M ferrous ammonium sulphate. The coagulated product was filtered and purified by washing with double distilled water. The product was dried at 50 °C for 3 h in oven and crushed into fined particles and stored for further characterization and adsorption experiments.

2.3. Instrumentation

To investigate the type of bond formation and groups involved in adsorption reactions the nanocomposite was characterized by a Perkin Elmer 1800 model IR spectrophotometer operating at frequency range from 400 to 4000 cm^{-1}. To obtain the information about the crystalline structure of the nanocomposite X-Ray diffraction (XRD) technique was used using Siemens D 5005 X-Ray unit Cu Kα (λ = 1:5406 Å) radiation, generated at a voltage of 40 kV and a current of 40 mA. Scanning electron microscopy (SEM) analysis were done using GSM 6510LV Scanning electron microscope. The particle size and distribution of nanoclay in the polymer matrix of the synthesized nanocomposite were observed by using JEM 2100 transmission electron microscope (TEM). The concentration of metal ion in the solution was measured by Atomic Absorption Spectrophotometer (AAS) model GBC-902. Elico Li 120 pH meter was used to adjust the pH of the solutions.

2.4. Design of experiments (DOE) for the Pb (II) adsorption parameters

Central composite design of RSM was used to optimize the five independent variables viz. contact time (X_1), pH (X_2), adsorbent dose (X_3), Pb (II) concentration (X_4) and temperature (X_5) for the adsorption of Pb (II) on PAB. The experimental design as recommended by MINITAB 17 for five variables with the experimental and predicted response in 52 runs are given in Table 1. The adsorption behaviour of Pb (II) on PAB for five variables can be expressed by quadratic regression model as follows (Savasari et al., 2015);

$$y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{1 \le i < j}^{n} b_{ij} x_i x_j + \varepsilon \quad (1)$$

where y is the response, b_0 is the model constant, b_i, b_{ii} and b_{ij} are the linear, quadratic and interaction terms respectively. x_i and x_j are the independent variables, n is the amount of variables and ε is the residual term.

2.5. Adsorption isotherms

The adsorption experiments are performed using Batch techniques in a 100 mL conical flask. For adsorption isotherm, 0.055 g of adsorbent was taken with various Pb (II) concentration at pH 4 and at the temperature of 30, 40 and 50 °C for 172 min. The obtained equilibrium data was applied to non-linear form of Langmuir, Freundlich and Temkin model. The amount of metal ion adsorbed on PAB and%metal removal is calculated as;

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

$$\%removal = \frac{C_o - C_e}{C_o} \times 100 \quad (3)$$

where q_e is the amount of metal ion adsorbed per unit weight of the adsorbent (mg g^{-1}); C_o and C_e are the concentrations of the metal ion in the initial solution (mg L^{-1}) and after adsorption respectively; V is the volume of the adsorption medium (L); m is the amount of the adsorbent (g).

2.6. Desorption and regeneration

The desorption and regeneration of PAB was done with 0.1 M HCl solution using 0.05 g of adsorbent with 20 mL of 55 mg L^{-1} Pb (II) ion solution. The mixture was agitated for 172 min and the desorbed amount of Pb (II) was calculated by the following formula;

$$\%des = \frac{C_D V}{q_e m} \times 100 \quad (4)$$

where q_e is the adsorption capacity of adsorbent, C_D is the concentration of the desorbed metal ion, V is the volume of the adsorption medium (L); m is the amount of the adsorbent (g).

3. Results and discussion

3.1. Characterization of the synthesized adsorbent

Fourier Transform Infrared is a widely used technique to analyse the various functional groups in the samples formed during chemical synthesis. Fig. 1 constitute the FT-IR spectra of bentonite, alginate, PAN and PAB. While looking at the spectra of bentonite the peak at 3420 and 3622 cm^{-1} corresponds to —OH groups at the inner surface of the bentonite and peak at 1030 cm^{-1} is due to Si—O bending vibration and peak at 916 cm^{-1} corresponds to the Al—O bending vibrations (Parolo et al., 2014). The FT-IR spectra