Removal of As(V) from aqueous solution by Ce-Fe bimetal mixed oxide

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ABSTRACT

The objective of the present research is to investigate the removal efficiency of As(V) from synthetic arsenic solution by Ce-Fe bimetal mixed oxide. The Ce-Fe bimetal mixed oxide is synthesized by solvothermal process and is characterized by using SEM, EDX, XRD, FTIR and BET. The analysis of SEM and BET analyser data of the material shows that particles are in the range of 290–300 nm, average pore size and surface area of the material is 4.42 nm and 127 m^2/g respectively. Adsorption data are best fitted with the Langmuir isotherm with R^2 value of 0.9965. The maximum adsorption capacity is 32.12 mg/g at pH 3. Kinetics data revealed that the overall adsorption process followed pseudo-second-order kinetics. In the optimum conditions removal of As(V) using Ce-Fe bimetal mixed oxide is found to be 96%. The adsorption mechanism shows that the As(V) adsorption on the Ce-Fe bimetal mixed oxide is a complex mechanism including electrostatic attraction and the replacement of OH to form monodentate and bidentate complexes. The loaded adsorbent materials can be regenerated by using 0.5 M NaOH solution.

1. Introduction

A large number of pollutants invade into the water bodies due to different anthropogenic activities, which causes the depletion of water quality day by day [1]. The increase in pollution load in water affects adversely to both the aquatic life and other biological systems which makes ecological imbalance [2]. Hence, it is necessary to reduce the pollution load to water by the removal of the hazardous materials present in it for the benefit of the society [3]. Arsenic compounds are one of the priority hazardous materials in water due to their carcinogenic effect. The solubility of arsenic in water mainly depends on pH, redox conditions, temperature, and solution composition. Consumption of arsenic contaminated water for long period causes the diseases in skin, stomach, liver and kidney [4]. Due to toxicity of arsenic, World Health Organisation (WHO) prescribed the maximum permissible limit to be 0.01 mg/L in water.

In aquatic environment, arsenic exists in both organic and inorganic forms. The inorganic arsenic is more toxic than organic arsenic [5]. Inorganic arsenic exist in two forms As(III) and As(V), but oxidised As(V) form is mainly found in the water. Arsenate can be easily adsorbed on to the body protein with the help of sulfhydryl groups [6]. Various methods like coagulation-flocculation [7], ion exchange [8], reverse osmosis [9], membrane filtration [10] and adsorption [11]. have been used to remove As(V) from water but adsorption process is promising due to high removal efficiency in both at low and high concentration of arsenic [12,13].

Several adsorbents like zeolite [14], titanium dioxide [15], iron-containing mesoporous carbon [16], both Fe_2O_3 and Fe_3O_4 nanomaterials [17], magnetic wheat straw [18], ironoxide@carbon [19] and cellulose@Fe_2O_3 composites [20] etc. have been used for the removal of As(V) by the researcher. Due to strong affinity of iron toward arsenic, iron compounds or embedded iron materials are used in various methods for the treatment of arsenic contaminated water [21–23]. In the recent years, bi-metal oxides are used as adsorbent because of its small size, stability and high surface area. The bi-metal oxides possess both the properties of parental metal oxide and mixed oxide which increase the adsorption capacity significantly [15].

The removal of arsenic by Fe-Mn, Fe-Al, Fe-Zr oxides are well documented in literature [21,24,25]. However, hydrous cerium oxide is promising adsorbent owing to their strong affinity, but presently there is limited literature. Cerium oxide has high resistance to acid and does not elute during the removal process [26]. Also it has relatively low ionic potential and high basicity, so the OH groups present in its surface can easily forms hydroxyl ions and replace by other anions [27]. Owing to these properties, cerium oxide is capable of removing hazardous materials like fluoride, dichromate, anions of phosphorous and arsenic [26,28]. It had also

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been reported that Fe-Ce bimetal oxide [27,29], nano-structured iron(III)-cerium(IV) mixed oxide [30] and mesoporous cerium iron mixed oxide [31] etc. showed higher arsenic adsorption capacity promising us to design bimetallic combinations for the removal of arsenic from ground water.

Due to the tremendous adsorption properties of both iron oxide and cerium oxide, in this present study Ce-Fe bimetal mixed oxide is prepared by solvothermal process and used the material to investigate the adsorption efficiency of As(V) from aqueous solution. Different instrumental techniques were used to characterize the adsorbent. The effects of various parameter such as pH, initial arsenate concentration and contact time have been investigated to know the maximum uptake of arsenate. Finally, on the basis of these results, the mechanism for the adsorption of As(V) on the surface of the Ce-Fe bimetal mixed oxide is also proposed.

2. Materials and methods

2.1. Materials

All the chemicals are of analytical grade and used directly without any further purification. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium hydroxide (NaOH) and sodium dihydrogen arsenate heptahydrate ($NaH_2AsO_4 \cdot 7H_2O$) are purchased from Sigma-Aldrich (Germany) and cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) from Loba chemicals (India).

2.2. Synthesis of Ce-Fe bimetal mixed oxide

Ce-Fe bimetal mixed oxide is synthesized by solvothermal process. In a 100 mL conical flask containing 0.03 mol (5.210 g) of $FeCl_3 \cdot 6H_2O$ and 0.012 mol (2.605 g) of $Ce(NO_3)_3 \cdot 6H_2O$ are dissolved 40 mL ethanol and stirred to form a homogenous solution as reported in the literature [26]. 20 mL of alcoholic NaOH solution (1.6 g of NaOH dissolved in 20 mL ethanol) is added to the above homogenous solution. Then this mixture is vigorously stirred in a magnetic stirrer for half an hour and placed in a teflon-lined autoclave at a temperature of 180 °C for 5 h. The suspension is then kept in room temperature and pressure for 3 h. The precipitate was washed several times with double distilled water and ethanol to remove impurities. The material is dried at 80 °C for 24 h in a hot air oven and kept in an air tight container for characterization.

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \tag{1}$$

$$Ce^{3+} + 3OH^- \rightarrow Ce(OH)_3 \tag{2}$$

$$Fe(OH)_3 + Ce(OH)_3 \xrightarrow{Solvothermal\ process} Ce - Fe\ bimetal\ mixed\ oxide \tag{3}$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \tag{4}$$

$$Ce(OH)_3 \xrightarrow{Oxidation} CeO_2 + H_2O + H^+ \tag{5}$$

2.3. Characterization techniques

The XRD pecks were recorded by PHILLIPS X'PERT X-ray diffractometer model PW 1830 (Almelo, Netherlands) with Cu Kα radiation (35 kV and 30 mA) at a scan rate of 5° per minute and was analysed using standard software provided with the instrument.

FTIR study was taken to know the functional group present in the sample by FTIR spectrometer spectrum RX I (Perkin-Elmer Corporation, USA). SEM (JEOL, JSM 6390LV, Japan) with EDX (JEOL, JSM-6480LV) detection was used for determined surface morphology and the qualitative element composition of the material at an accelerating voltage of 20 kV. The surface area of the nanoparticles was determined by BET (Quantachrome Autosorb I, Boynton Beach, Florida) in N_2 atmosphere by adsorption technique. Zeta potential of the Ce-Fe bimetal mixed oxide at different pH was measured using Nano-ZS 90 (MALVERN, UK). The adsorption of As(V) was determined by using flame photometer technique of AAS (Elico SL 176, India).

2.4. Adsorption experiments

All the experiments are carried out by taking different concentration of As(V) solution in a series of 200 mL polylab plastic bottles fitted with cap. The reaction bottles are shaken in a thermostatic shaker (SELEC RC5100) with shaking rate of 250 rpm at temperature of 25 ± 5 °C. A fixed adsorbent dose of 1 g/L is taken for all experiments and pH is maintained by the addition of required amount of 0.1 N HCl and 0.1 N NaOH solution. After adsorption, the adsorbents are separated by centrifugation (REMI PR24) at a rate of 5000 rpm for 10 min. The concentration As(V) in the residual solution is analysed by atomic absorption spectroscopy. For isotherm study, experiment is conducted with initial As(V) concentration in the range of 1–60 mg/L at pH 3 with contact time for 60 min. Similarly for kinetic study experiments are conducted with a fixed initial concentration of 10 mg/L at pH 3 with a time interval of 10–120 min. The percentage removal and uptake capacity of As(V) is evaluated by using the following equation:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{6}$$

$$q_e = \frac{(C_0 - C_e)}{w} \times v \tag{7}$$

Where C_0 and C_e are the initial and equilibrium concentrations of As(V) in the aqueous solutions respectively and w (g) is the weight of the adsorbent and v (L) is the volume of the solution.

2.5. Isotherm study

The adsorption isotherm is an important parameter to know the maximum adsorption capacity and make an equilibrium relationship between the concentration of the adsorbate in the solid and liquid phase at constant temperature. In this study the equilibrium data are correlate with the theoretical Langmuir and Freundlich isotherm models.

A monolayer adsorption model can be represented in non-linearized Langmuir expression as follows: [32]

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{8}$$

Where q_m (mg/g) is the maximum adsorption capacity of the As(V) ion per unit weight of adsorbent to form a layer on the surface bound at high C_e, while C_e (mg/L) is the equilibrium concentration between adsorbate and adsorbent. b is Langmuir constant and q_e (mg/g) represents a particle limiting adsorption capacity when the adsorbent surface fully occupied by adsorbate.

For Langmuir isotherm a nonlinear model is fitted by taking the R_L value, which is a dimensionless quantity and is calculated to predict effectiveness of adsorption by using the following