



Adsorption studies of arsenic on nano aluminium doped manganese copper ferrite polymer (MA, VA, AA) composite: Kinetics and mechanism

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ABSTRACT

Aluminium doped nano manganese copper ferrite (average size of 13 nm) was synthesized by the chemical co-precipitation method and nanocomposite was prepared by doping this ferrite in methacrylate, vinyl acetate and acrylic acid polymer through slow heating process. This nanocomposite was used as an adsorbent for the removal of arsenic from aqueous solution. The equilibrium data was fitted to Freundlich, Langmuir, Dubinin Rudushkevich and Flory Huggins models. The maximum adsorption capacity (q_m) of arsenic on the nanocomposite was found to be 0.053 mg g^{-1} which is higher than that of many other adsorbents reported in literature. Mean sorption energy obtained from DR isotherm was $40.98 \text{ kJ mol}^{-1}$ indicating chemical nature of the adsorbate–adsorbent interactions. The pseudo-second order kinetic model gave a better fit to the experimental data indicating involvement of both the external as well as internal mass transfer. Bangham's model and intraparticle diffusion model were applied to investigate mechanism of the adsorption process. Non linear Bangham plot and significant value of intercept obtained from intraparticle diffusion model showed the film diffusion as well as pore diffusion to be the rate limiting steps.

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1. Introduction

Arsenic contaminated natural water is a world wide problem. Arsenic is present in water due to dissolution of minerals, the leaching of man-made arsenic compounds from smelting of metal ores, pesticides, wood preservatives and desiccants. Arsenic pollution has been reported recently in USA, China, Chile, Bangladesh, Taiwann, Mexico, Argentina, Poland, Canada, Newzealand, Japan, India and Pakistan [1–5]. The permissible limit set by World Health Organization (WHO) for safe drinking water now-a-days has been adopted as 10 ppb (0.01 mg l^{-1}). However, in Bangladesh, China, Mexico, Nepal, India and Pakistan earlier limit of 50 ppb (0.05 mg l^{-1}) has been retained [6–8].

Drinking water having arsenic beyond permissible limit is hazardous for human use. It causes skin, lung, bladder and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite and nausea [9–11].

Most remediation methods such as oxidation/precipitation method [12], coagulation/co-precipitation method [13], membrane method [14], ion exchange [15] and sorption method [16] remove

arsenic more effectively from water containing high initial arsenic concentration (usually $> 100 \text{ mg l}^{-1}$).

However, adsorption is evolving as a front line of defense due to its distinctive characteristics [17]. Selective adsorption utilizing biological materials, mineral oxides, activated carbons or polymer resins has generated increasing excitement [18]. Activated carbon and alumina remove arsenic with the adsorption capacity of 20 mg g^{-1} [19] and 15.9 mg g^{-1} [20], respectively but suffer from severe limitations of cost in case of former and low working pH in case of later adsorbent.

Free iron or iron compounds [iron oxides, oxyhydroxides and hydroxides including amorphous hydrous ferric oxide (FeO–OH), goethite ($\alpha\text{-FeO-OH}$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$), etc.] are the most widely used adsorbents, having higher removal efficiency at lower cost than many other adsorbents. Still iron based sorbents (IBS) constitute an emerging treatment technology for arsenic removal. IBS has a strong affinity for arsenic under natural pH conditions, relative to activated alumina and other adsorbents. This feature allows IBS to treat much higher bed volumes without the need for pH adjustment, unless the pH is > 8 [21].

In the present studies, a composite of nano ferrite with polymer (MA, VA, AA) has been used as adsorbent for the removal of arsenic under natural pH conditions. The kinetics and the interaction mechanisms have also been discussed.

The aluminium doped manganese copper ferrite has been synthesized by co-precipitation method. The synthesized sample

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is characterized by various techniques such as, thermogravimetric analysis (TGA), X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The nanocomposite was prepared by the addition of these nano ferrites during co polymerization of methylacrylate (MA), vinyl acetate (VA) and acrylic acid (AA) monomers using ethyleneglycoldimethylacrylate (EGDMA) and benzoyl peroxide (BPO) as cross linking agent and initiator, respectively.

2. Experimental

2.1. Chemicals

Chemicals used in the synthesis of nanocomposite were $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99%, Merck), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (97%, Riedel Dehaen Seelze Germany), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (98%, Merck), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%, Merck), NH_3 solution (33%, Merck), $\text{CH}_3\text{CH}_2\text{OH}$ (99%, Merck), CHCl_3 (99%, Merck), $\text{CH}_2\text{CHCOOCH}_3$ (99%, Merck), $\text{CH}_2\text{CHOCOCH}_3$ (99%, Fluka), CH_2CHCOOH (99%, Fluka), $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2-\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$ (100%, Fluka) and $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$ (100%, Merck). A 1000 ppm arsenic (III) As_2O_3 standard solution supplied by CPA LTD, Stara Zagora, Bulgaria (Ref. No. A003.2NP.L5) was used for the adsorption studies.

2.2. Preparation of nano sized $\text{Mn}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.2}\text{Al}_{0.8}\text{O}_4$

The chemical co-precipitation method was used to synthesize the ferrite nanomaterial. Desired quantities of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2.131 g/250 ml), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (12.12 g/250 ml), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (2.474 g/250 ml), and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (7.502 g/250 ml) were dissolved in deionized water in each 250 ml measuring flask to make the solution. All solutions were mixed in 2000 ml beaker and this mixture was continuously stirred at 333 K on a hot plate with magnetic stirrer. Ammonia solution (4.0 M) was added dropwise as a precipitating agent and the pH of reaction mixture was kept between 10 and 11. The solution was stirred for 3 h at 333 K and then aged at room temperature for over night. The precipitates were filtered and washed with deionized water and then dried at 373 K for 15 h in an electric oven. The dried samples were annealed at 1073 K in a programmed furnace (PLF160/7) at heating rate of 5 K min^{-1} for 8 h to obtain single spinel phase.

2.3. Preparation of adsorbent (nanocomposite)

The synthesized sample of aluminium substituted manganese copper ferrite was doped in polymer (MA, VA, AA) to make the nanocomposite. Methylacrylate (MA), vinyl acetate (VA) and acrylic acid (AA) were used as monomers. Ethyleneglycoldimethylacrylate (EGDMA) and chloroform were used as cross linking agent and porogen, respectively. The monomers used were taken in the volumetric ratio of 2.5:1:2.5, respectively. Both the porogen and the cross linking agent were taken 50% (v/v) of the total monomers volume. All the chemicals were mixed in a 250 ml quick fit (double necked) flask equipped with condenser. Ethanol (50 ml) and benzoyl peroxide (1%, w/v of the total volume) were added to the reaction mixture as solvent and initiator, respectively. A 0.05 g of aluminium doped manganese copper ferrite ($\text{Mn}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.2}\text{Al}_{0.8}\text{O}_4$) was added to reaction mixture and the mixture was stirred for half an hour at room temperature to ensure thorough mixing. The polymerization (radical) reaction was carried out by following slow heating scheme. The temperature of the reaction mixture was increased gradually and for each 5 K rise in temperature, the temperature was maintained constant for at least 1 h with constant stirring up to 328 K. At 333 K and 338 K the temperature of the reaction mixture was maintained for 2 h.

The formation of the composite as precipitates began at 343 K and this temperature was maintained for 6 h to allow completion of the polymerization reaction. These precipitates were separated by filtration, washed with deionized water to remove unreacted material and dried in oven at 353 K for 2 h. The dried material was grinded to fine powder and was used for further investigations.

2.4. Fourier transform infrared spectroscopy

Incorporation of nano aluminium doped manganese copper ferrite into polymer matrix was detected by FTIR (FTIR-8400 Shimadzu Japan) spectra. The sample was prepared by grinding nanocomposite with potassium bromide and was pressed at pressure of 40 kN to form the transparent thin pellet. The FTIR spectrum was recorded at maximum resolution of 0.85 cm^{-1} in the range of $4000-400 \text{ cm}^{-1}$.

2.5. Thermogravimetric analysis

Thermal characterization of the synthesized nanocomposite was done using Perkin Elmer TG/DTA Diamond instrument. The sample was run from 298 K to 1073 K at a heating rate of 5 K min^{-1} .

2.6. Scanning electron microscopy

A scanning electron microscope (JEOL-JSM-6700F) was used to visualize the surface morphology of the nanocomposite before and after adsorption of arsenic from aqueous solution.

2.7. Adsorption studies

For adsorption studies, arsenic solutions of different concentrations (20–200 ppb) were prepared by diluting a 1000 ppb standard solution with deionized water. To each 25 ml conical flask having 15 ml of the solution of the given concentration, 0.05 g of the nanocomposite was added. All the adsorption experiments were carried out at natural pH 6.0. These solutions were shaken at 313 K in an orbital shaker at the rate of $120 \text{ strokes min}^{-1}$ for an optimized time of 90 min. The residues were separated by filtration and the filtrates were analyzed for arsenic concentration by atomic absorption spectrophotometer (Analytika Jena Vario – 6, Germany).

3. Results and discussion

3.1. Optimization of nano ferrite loading

Different quantities of aluminium doped manganese copper ferrites (0.2 g, 0.1 g, 0.05 g) were added during polymerization process but no composite was formed even at higher temperature except with 0.05 g (0.41% of the total polymer formed) of nano ferrite. This optimized quantity of the nano ferrite was therefore used to form its composite with polymer for further investigations.

3.2. XRD analysis of nano aluminium doped manganese copper ferrite

The powder X-ray diffraction (XRD) analysis is carried out to confirm the formation of single spinel phase by Philips X'Pert PRO 3040/60 diffractometer which uses $\text{Cu K}\alpha$ as a radiation source. The XRD pattern for nano aluminium doped manganese copper ferrite is shown in Fig. 1. All the diffracted peaks (220, 311, 422, 531 and 533) perfectly match with the standard pattern (ICSD 00-002-1392) confirming the formation of single spinel phase of the synthesized material. The calculated values of lattice constant (8.62 \AA) and cell volume (640.5 \AA^3) from the XRD pattern are also reflecting the cubic

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