

Synthesis, characterization and application of iron (III) - loaded duolite C₂₆ adsorbent for arsenic removal

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ABSTRACT

Iron(III) was loaded onto the sulphonic acid sites of Duolite C26, a commercial cation-exchanger, and was then converted into hydrated ferric oxides (HFO) dispersed throughout the macropores of the ion exchanger beads. The resulting hydrated iron(III)-oxide loaded cation exchange resin (HFOLR) was tested for its ability to remove arsenate [As(V)] ions present in water by batch technology. The surface area and the pore size distribution of HFOLR were determined. Techniques like FTIR, SEM, XRD, and EDAX were utilized to describe the sorbent properties as well as adsorption mechanisms of As(V) ions. Maximum removal of arsenate (>99.0 %) onto HFOLR occurred at a solution pH range of 3.0–4.0. Isotherm studies revealed correlation with respect to Langmuir equation. Simulated groundwater samples were treated by HFOLR to demonstrate its efficiency in removing As(V) ions.

Key Words: Arsenic removal, adsorption, groundwater, Duolite C26.

INTRODUCTION

The removal of arsenic from water is of primary concern in many countries and research for the development of cost competitive technologies is urgent. The main treatment methods used for arsenic removal like precipitation–coagulation, reverse osmosis, nanofiltration or electro dialysis are not cost effective and possess many disadvantages¹⁻². Because of the ease of handling, sludge-free operation, and possibility of regeneration, the adsorption process appears to be the most promising one³. Iron oxide powders which are the common adsorbents used, are not effective as such for arsenic removal due to their low stability and poor hydraulic conductivity. The present work explored the synthesis of a hydrated ferric oxide–loaded macroporous cation exchange resin (HFOLR) and tested its suitability for the removal As(V) ions present in water and wastewater.

EXPERIMENTAL

A stock solution of As(V) was prepared using dibasic sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$). Ferric chloride was used for preparing Fe(III) stock solution. Working solutions were prepared by dilution of required volumes of stock solutions with deionised water. The concentrations of arsenic species were always given as elemental arsenic concentration in this study. The initial pH of the solutions was adjusted with either 0.1M HCl or 0.1M NaOH solution. The sulphonic acid type cation exchange resin Duolite C26 (bead size 520 μm) supplied by Sigma Aldrich, USA, was used to prepare the adsorbent.

Duolite C26 was first converted into Na^+ saturated form by washing several times with 0.1M NaOH and HCl. Loading of Duolite C26 with Fe was performed by batch equilibrium technique with varying iron(III) chloride solutions at pH 2.0 for 3 h

at 30°C and the maximum loading capacity for ferric ions calculated using isotherm data was found to be 56.10 mg/g. The iron loaded resin was washed with distilled water until the pH of the residual water was close to 5.0 and when no iron could be detected in the filtrate. The residue was then oven dried at 65°C for one day. It was then converted to HFOLR by treating with mixture of NaOH and NaCl solutions. The off white colour of Duolite changes to reddish brown due to the formation of hydrated ferric oxide (HFO).

The FTIR spectra of adsorbents were recorded between 4000 and 400 cm^{-1} using a KBr method with a Perkin Elmer IR-180 Spectrophotometer at 2 cm^{-1} resolution. Specific surface areas were determined using a Quantachrome NOVA Automated Gas Sorption System. N_2 adsorption/desorption experiments were carried out and pore size distributions were calculated using the Barret-Joyner-Halenda (BJH) model on the desorption branch of the isotherm. Potentiometric titration method was carried out to determine the surface charge density as a function of pH of the adsorbent. This allows the pH of point of zero charge (pH_{pzc}) to be determined. Hitachi Scanning Electron Microscope and Elemental micro-probe and elemental distribution mapping techniques were used for SEM analysis and analysing the elemental constitution of solid samples. The X-ray diffraction patterns were obtained with the help of Siemens D 5005 X-ray unit using Ni filtered Cu-K_α radiations.

Batch adsorption studies were carried out by agitating 50 mL As(V) solutions with HFOLR (0.1 g) in a conical flask after adjusting the pH with HCl or NaOH measured with a Systronic microprocessor digital pH meter (model μ 362). At the end of the predetermined contact periods, the mixtures were centrifuged and arsenic concentrations of the supernatants were determined using atomic absorption spectrophotometry (GBC Avanta A 4100). In order to ascertain the reproducibility of results, the experiments were performed in duplicate and the mean values were considered.

RESULTS AND DISCUSSION

Since Duolite is a cation exchanger, under

acidic conditions Fe^{3+} will be exchanged with the H^+ ions of sulphonic acid groups. When NaCl/NaOH mixture is treated with the Fe loaded Duolite, the Fe(III) will be desorbed and will co-ordinate OH^- and H_2O to yield a suspension of hydrated ferric oxide (HFO).

Nitrogen adsorption–desorption isotherm of HFOLR revealed that the porosity was contained within the uniform channels of the templated framework. The nitrogen adsorption data were used to determine the BET surface area (1.51 m^2/g), the total pore volume (2.2277×10^{-3} mL/g), the average pore radius (60.31 Å) the micropore volume 4.441×10^{-4} mL/g of the HFOLR. The observed micropore area, having a value of 1.106 m^2/g , was much higher than the external surface area (4.042×10^{-1} m^2/g). The pH_{pzc} of HFOLR was found to be 8.4 which is in consistent with earlier values reported for HFO systems. Also it is seen that the pH_{pzc} value is higher than the naïve Duolite which is an advantage for the removal of arsenic systems.

Batch adsorption studies were conducted to ascertain the adsorptive power of HFOLR with respect to As(V). For an initial concentration of 10 mg/L, a maximum adsorption of 99.6 % of As(V) on HFOLR occurred in the pH range of 3.0–4.0. When the initial concentration was 25 mg/L, a maximum removal of 86.6 % occurred. At very low pH value, As(V) predominantly exists as a neutral species, H_3AsO_4 which is difficult to attach to exchange sites of the sorbent for anion exchange. The anionic form of H_2AsO_4^- can be adsorbed more easily on iron oxides, in this pH range, as the number of positively charged surface sites available for the adsorption like the cationic monomeric form [$\text{Fe}(\text{OH})_2^+$], is higher, and adsorption may be facilitated by coulombic interactions, but decreases with increasing pH. The maximum pH value for As(V) adsorption is found at lower pH values than expected from the $\text{p}K_{\text{a}1}$ of arsenic may indicate that immobilization of Fe(III) on this chelating resin produces a remarkable change in the Fe(III)–As(V) chemical interaction in comparison with other adsorbents.

The effect of ionic strength on As(V) adsorption onto HFOLR provided a measure of the relative bonding affinity of these ions for surface

hydroxyl groups. It was noted that the As(V) adsorption on HFOLR showed no dependence on ionic strength. Surface complex theory was successfully applied to explain the nature of interaction of As species with the surface functional groups of HFOLR. Positive identification of adsorbed arsenate species was provided using the FTIR and XRD techniques too. The XRD patterns for the adsorbent did not yield any crystalline peaks suggesting the amorphous nature due to the fact that the crystallization of iron oxides is strongly retarded by the presence of the anionic resin particles. Specific interaction with As(V) was noted from XRD patterns of As(V)-laden HFOLR. The surface morphology and microstructure of the samples HFOLR and As(V)-laden HFOLR were analysed by the SEM observation. Energy dispersive analysis of X-ray (EDAX) was used for characterizing the elements associated with the adsorbent before and after adsorption and prominent signals corresponding to As are observed for As(V)-laden HFOLR.

To establish the most proper relationship for the equilibrium curves, isotherm studies were performed using Langmuir isotherm equation. The maximal adsorption capacities of As(V) was found to be 36.2 mg/g at 30 °C, comparatively higher than that of other adsorbents reported in the literature. The simulated water samples based on groundwater of New Jersey, USA, which contained arsenic together with cations based on, Al, Mg, Fe, Ca and Mn as well as anions like, fluoride, chloride, sulfate

and carbonate, were treated by HFOLR to demonstrate its efficiency in removing As(V) ions (4). Arsenic content could be brought down from 1.0 mg/L to well below 0.01 mg/L, the maximum permissible level as per WHO norms, with an HFOLR dose of 2.5 g/L for As(V).

CONCLUSION

The present study investigated a possible strategy for the removal of arsenic by employing iron(III)-loaded macroporous resin as adsorbent by utilizing both the ion exchange nature of the cation exchanger Duolite C26 and the high affinity of Fe towards inorganic arsenic. The method is appropriate and advantageous to small communities, especially in developing countries because of the high arsenic removal efficiency, simplicity, and eases of construction, operation and maintenance and promises to be a competitive choice amongst the treatment systems available for arsenic removal.

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REFERENCES

1. Zeng L. *Water Res.*, **37**: 4351(2003).
2. Katsoyiannis I. A. and Zouboulis A. I., *Water Res.*, **36**: 5141(2002).
3. Zhang Y., Yang M. and Huang X., *Chemosphere* **51**: 945 (2003).
4. Bang S., Patel M., Lippincott L. and Meng X., *Chemosphere* **60**: 389 (2005).