



Efficient arsenic removal by cross-linked macroporous polymer impregnated with hydrous iron oxide: Material performance



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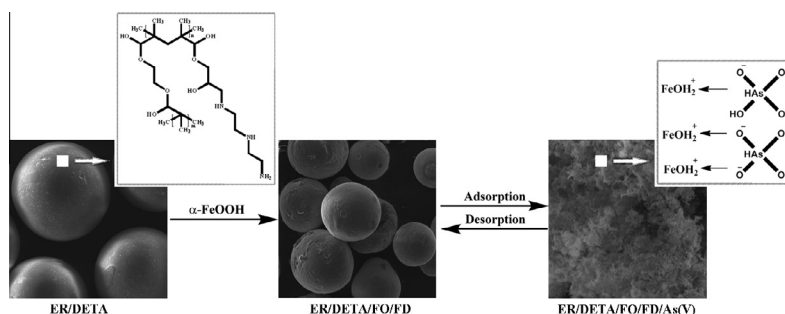
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HIGHLIGHTS

- Macroporous polymer impregnated with hydrous iron oxide is newly synthesized.
- High sorption ability of arsenic is obtained in non- and competitive conditions.
- Kinetic study predicts intra-particle diffusional transport as a limiting step.
- Safe disposal of exhausted adsorbents is indicated by TCLP test.
- Arsenic adsorption is study as economically favorable and efficient process.

GRAPHICAL ABSTRACT



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ABSTRACT

Optimization of the synthesis of cross-linked macroporous polymer impregnated with hydrous iron oxide and post-process of obtained material by application of freeze/drying technique, produces high performance adsorbent applicable for efficient arsenic removal. Characterization and analysis of adsorbent performances encompass material characterization, equilibrium and kinetic study, influences of interfering ions and modeling of adsorption data in ion free and competitive conditions. Kinetic study, i.e. fitting by Weber–Morris model and single resistance mass transfer model predicts intra-particle diffusion as a rate-controlling step. Thermodynamic parameters indicate endothermic, feasible and spontaneous nature of adsorption process. Competitive kinetic study in the presence of interfering ions shows low detrimental effect on both capacity and kinetic of arsenic removal. Visual MINTEQ modeling software was used for the prediction of adsorbent performances and interfering ion influences. Preliminary fixed-bed column study was accomplished by the use of Bohart–Adams, Yoon–Nelson, Thomas and Modified dose–response model. High arsenic removal capacity of 31.0 mg g^{-1} at 25°C , and multi-cycle reusability of ER/DETA/FO/FD, significantly affects the affordability of techno-economic indicators based on the operating costs of the process.

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1. Introduction

As a result of intensive economic growth and industrial development, inevitable natural imbalance leads to water pollution as a negative side effect that requires urgent action. In order to accomplish recommended maximal concentration level (MCL) of the pollutants of interest, numerous technologies and adsorbents were tested and applied for water purification. Adsorption has been identified as one of the most preferable and noteworthy solutions for application in purification treatment plants.

Various approaches have been applied in order to obtain abundant, cheap adsorbent with high surface area, porous structure and chemical stability. It is especially important for the adsorbent to be efficient and selective for specific pollutants with high regenerative capability. It has been proven that hydrous iron oxide (FO) has a crucial influence in mobility and transformation throughout the various compartments of the global ecosystem [1,2]. The high adsorption capacity and strong affinity of goethite toward anions (arsenate, arsenite, phosphate, silicate, etc.), cations (lead, nickel, cadmium, antimony, mercury, etc.), organic ions (glyphosate, acetate, citrate, malonate, etc.) and some gaseous contaminants shows a great potential in this area of research and application [2]. Since 2010, adsorption removal by goethite has been widely discussed and special attention was paid to arsenic [3–9]. On the basis of arsenic toxicity and cancer-related effect to human body, World Health Organization recommended that the MCL of arsenic in drinking water should not exceed $10 \mu\text{g dm}^{-3}$ [10]. Such trend of tremendous growth of interest in arsenic removal is in agreement with the result of study conducted in 2007 where was estimated that over 137 millions of people, in more than 70 countries, were affected by water polluted by arsenic [11].

Adsorption properties of nano-scale materials have attracted great interest in the last decade. Generally, nanometer sized FO results in a large specific surface area, high porosity and bulk adsorption site density, while acceptable environmental impact makes it an attractive option for heavy metal removal. The underlying role of FO based adsorbent can be explained *via* double pair of oxygen electrons together with dissociable hydrogen, which regulates the mobility of species in various parts of the ecosystem. When FO interacts with arsenic, oxygen donor atom of the surface hydroxyl group can interact with protons, whereas the metal ion acts as a Lewis acid and exchanges the hydroxide group for other ligands to form surface complexes. However, in the design of adsorbent with target properties, some drawbacks of nanomaterials such as agglomeration and poor mechanical strength, i.e. inability of application in flow-through systems, should be considered [12]. In that respect, applicability of nanoscale FO demands the right choice of solid support which is amenable for functionalization with electron donor groups capable of iron coordination.

A large diversity of host adsorbent materials was presented in literature, wherein macroporous copolymers based on glycidyl methacrylate present an adequate choice due to the use of suspension polymerization as an alternative for production of spherical beads of different geometry, design of textural properties and possibility of ring-opening reaction of pendant epoxy group [13,14]. Up to this moment, functionalized macroporous glycidyl methacrylate copolymer has been studied as adsorbent for chromium [13,14], copper [15], arsenic [16], indium [17], uranium [18] and Reactive Black 5 [19]. Some recent studies have specifically investigated arsenic removal by anion exchange fibers and resins from water [20–24]. Based on our best knowledge, data about glycidyl methacrylate copolymer loaded with FO or studies devoted to adsorption performance of such adsorbents with respect to arsenic were not found in literature.

In this work, research was focused on the development of new hybrid adsorbent, based on cross-linked copolymer modified with FO mainly in the goethite form. The optimization of process was achieved by multistep synthesis carried out by fabrication of amino functionalized copolymer, controlled oxidative precipitation of FO in three successive steps, and followed by vacuum/drying and freeze/drying treatment. Specific objectives of this study were focused on: (1) the improvement of textural properties of chemically modified adsorbent; (2) the increase of sorption capacity; (3) the evaluation of equilibrium, kinetic and thermodynamic aspect of process; (4) the estimation of limiting step of the whole process, and (5) the cost effectiveness of multi-cycle process. Some aspects of comparative analysis with As(III) were presented.

2. Experimental part

All chemicals and reagents used for modification, characterization of adsorbents and arsenic determination, statistical criteria, adsorption, kinetic and thermodynamic parameters determination, surface complexation modeling and modeling of adsorption data in a fixed bed column study is provided in [Supplementary material](#).

2.1. Adsorbents preparation

Specific topic of this study was aimed at the definition of optimal parameters for novel hybrid adsorbent synthesis to be applicable for effective arsenic removal. Few studies describe synthesis of the macroporous resin [25,26]. Growing interest in macroporous resin, based on glycidyl methacrylate, GMA, and ethylene glycol dimethacrylate, EGDMA, is due to innumerable possibilities for subsequent chemical transformation of pendant epoxy group. The resin synthesized in that way is used as a versatile support for subsequent modification/-impregnation with high affinity material for arsenic removal. In this work, the synthesis procedure was conducted in three successive steps. The optimal conditions were selected according to the adsorption maximum in relation to variable experimental parameters: amount of diethylenetriamine (DETA) and synthesis method in the second step, concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and drying technique in the third step, which was performed in the following way:

- Macroporous poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) cross-linked resin was prepared by a radical suspension copolymerization as described in the work of Vukoje et al. [27]. In brief, the monomer mixture (24.2 g GMA and 10.3 g EGDMA), initiator (0.800 g AIBN) and inert component (porogen agent) (36.5 g of cyclohexanol and 9.10 g of hexadecanol) were suspended in the aqueous phase (238 cm^3 water and 2.40 g poly(*N*-vinyl pyrrolidone)). The copolymerization was carried out at 70 °C for 2 h and at 80 °C for next 6 h with a stirring rate of 200 rpm. The obtained copolymer was washed with water and ethanol, kept in ethanol for 12 h, vacuum dried at 40 °C and purified by Soxhlet extraction with chloroform. The fraction with average particle diameter in the range 0.20–0.50 mm was used in subsequent reactions and was named **ER**.
- The **ER** (10 g) was dispersed in tetrahydrofuran (THF) (100 cm^3) and sonicated for 30 min. The dispersion was transferred on magnetic stirrer and 10, 20 or 30 cm^3 of diethylenetriamine (DETA) in 50 cm^3 of THF was added drop-wise for 30 min. Reaction took place at 25 °C for 1 h, and after the increase of dispersion temperature to 60 °C the mixing continued for next 1, 2 and 4 h. Analogous experiments were performed under ultrasound treatment. Product, **ER/DETA**, was filtered, washed twice with ethanol

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