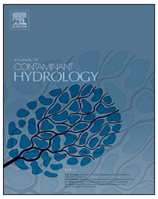
Journal of Contaminant Hydrology 203 (2017) 85–92

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd



Predicting the capability of carboxymethyl cellulose-stabilized iron nanoparticles for the remediation of arsenite from water using the response surface methodology (RSM) model: Modeling and optimization

Amir Mohammadi[a], Sepideh Nemati[b], Mohammad Mosaferi[c], Ali Abdollahnejhad[a], Mohammad Almasian[d], Amir Sheikhmohammadi[e,*]

[a] *Department of Environmental Health Engineering, School of Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran.*
[b] *Department of Environmental Health Engineering, School of Health, Urmia University of Medical Sciences, Urmia, Iran*
[c] *Department of Environmental Health Engineering, Tabriz Health Services Management Research Center, Tabriz University of Medical Sciences, Tabriz, Iran.*
[d] *Department of the English Language, School of Medicine, Lorestan University of Medical Sciences, Khorramabad, Iran*
[e] *Students Research Office, Department of Environmental Health Engineering, School of Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran*

ARTICLE INFO

Keywords:
Modeling
Response surface methodology
Carboxymethyl cellulose-stabilized iron nanoparticles
Arsenite
Optimization

ABSTRACT

This study aimed to investigate the feasibility of carboxymethyl cellulose-stabilized iron nanoparticles (C-nZVI) for the removal of arsenite ions from aqueous solutions. Iron nanoparticles and carboxymethyl cellulose-stabilized iron nanoparticles were freshly synthesized. The synthesized nanomaterials had a size of 10 nm approximately. The transmission electron microscope (TEM) images depicted bulkier dendrite flocs of non-stabilized iron nanoparticles. It described nanoscale particles as not discrete resulting from the aggregation of particles. The scanning electron microscopy (SEM) image showed that C-nZVI is approximately discrete, well-dispersed and an almost spherical shape. The energy dispersive x-ray spectroscopy (EDAX) and X-ray diffraction (XRD) spectrum confirmed the presence of Fe^0 in the C-nZVI composite. The central composite design under the Response Surface Methodology (RSM) was employed in order to investigate the effect of independent variables on arsenite removal and to determine the optimum condition. The reduced full second-order model indicated a well-fitted model since the experimental values were in good agreement with it. Therefore, this model is used for the prediction and optimization of arsenite removal from water. The maximum removal efficiency was estimated to be 100% when all parameters are considered simultaneously. The predicted optimal conditions for the maximum removal efficiency were achieved with initial arsenite concentration, 0.68 $mg\,L^{-1}$; C-nZVI, 0.3 ($g\,L^{-1}$); time, 31.25 (min) and pH, 5.2.

1. Introduction

Arsenic, a highly toxic element with carcinogenic health effects classified as a Class A carcinogen by the International Agency for Research on Cancer (Karagas et al., 2015; Nemati et al., 2014), is now recognized to be as a hazardous material for the environment threatening the health of several hundred million people (Bhattacharya et al., 2007; Han et al., 2016). Furthermore, due to its significant toxicity, World Health Organization (WHO) and Environmental Protection Agency (EPA) have recommended a maximum contaminant level (MCL) of 10 $\mu g\,L^{-1}$ and 5 $\mu g\,L^{-1}$ for total arsenic in potable water, respectively So, there is an urgent need to provide arsenic-free drinking water in the mentioned areas. As it is well known, arsenic can primarily be found in the water with neutral pH mainly in the non-ionic (arsenite (III)) and ionic (arsenate (V)) forms (Ociński et al., 2016). Both these forms are highly toxic and classified as class A carcinogens, although arsenite is more mobile and toxic than arsenate and most removal technologies such as coagulation (Kumar et al., 2004; Song et al., 2006), adsorption (Daus et al., 2004; Heshmatollah Nourmoradi et al., 2016), ion exchange (An et al., 2011), membrane filtration (Ning, 2002; Shih, 2005) and biological iron oxidation (Katsoyiannis and Zouboulis, 2004) are efficient in the removal of pentavalent arsenic (Mishra and Ramaprabhu, 2011; Triszcz et al., 2009); therefore, in this research arsenite was selected as a more hazardous form of arsenic for removal from water solutions. In comparison with other removal methods, zero-valent iron (ZVI, Fe^0) can remove As (III) with the sustained production of colloidal hydrous ferric oxides (HFO) (Fereshteh et al., 2006). Advantages of this method include no requirement of

---

* Corresponding author.
E-mail address: asheikh1359@gmail.com (A. Sheikhmohammadi).

http://dx.doi.org/10.1016/j.jconhyd.2017.06.005
Received 27 November 2016; Received in revised form 12 June 2017; Accepted 16 June 2017

previous oxidative treatment and the use of additional chemical products. The rate of ZVI reactions and the mass of the sludge produced can be improved using Fe^0 in nano form (nZVI) (Fereshteh et al., 2006). The main disadvantage of nZVI is that it aggregates rapidly in water in the absence of an effective stabilizer (He and Zhao, 2007; He et al., 2010), resulting in the alteration of the mobility of the nanoparticles in an aquatic environment (Dickson et al., 2012; Fereshteh et al., 2006). Surface modification of nZVI by water soluble polysaccharides as stabilizer (due to their low cost, environmental compatibility, nontoxicity and biodegradability) has been reported in some studies (Cao et al., 2011; Fereshteh et al., 2006; Raychoudhury et al., 2010).The stabilizers improve nZVI transport in porous media to provide steric and electrostatic stabilization against the particle-particle attractive forces (Alidokht et al., 2011; Raychoudhury et al., 2010). So, in this study, a chemical derivative of cellulose with carboxylate and hydroxyl groups, known as carboxymethyl cellulose, was used as a stabilizer to enhance the reactivity and to prevent the aggregation of Fe^0 nanoparticles. Another important reason for selecting carboxymethyl cellulose was because of the presence of highly biodegradable −OH, −CO–, and −COOH groups that cause a food-grade ingredient, nontoxic and biodegradable compound. In order to improve process efficiency, minimize operational costs and time, and take into account the most important factors, it is essential to use the optimization techniques in application of carboxymethyl cellulose-stabilized nZVI (C-nZVI) on an industrial scale. In classical method of studying a process, one factor is changed while others are fixed which because it does not depict the interactive effects of all the involved factors, requires many experimental runs to determine optimum levels, is labor-intensive and time-consuming, so the optimization is not as precise as expected and unreliable. Hence, statistical experimental design such as response surface methodology (RSM) may be considered as an efficient way for elimination of the classical method limitations (Bandpei et al., 2017; Khayet et al., 2011; Wang et al., 2011).

2. Experiments and methods

2.1. Chemicals

All chemicals were of reagent grade. Ferrous sulfate ($FeSO_4·7H_2O$), sodium borohydride ($NaBH_4$) and sodium arsenite stock solution ($NaAsO_2$, 0.05 mol L^{-1}) were provided by Merck Co. (Germany).The water-soluble carboxymethyl cellulose was purchased from Sigma-Aldrich. Deionized water was used to prepare all the solutions. The pH of the arsenite solution was adjusted to the desired values by adding 0.1 M NaOH (BDH chemicals Co, UK) and/or HCl (37%, Merck Co).

2.2. Synthesis of zerovalent iron nanoparticles and C-nZVI

Fe^0 and C-nZVI were freshly synthesized using method reported by Alidokht et al. (2011). A key advantage of this method is its simplicity. It can be safely done in most chemistry labs with simple chemical reagents. Conventionally, these nanoparticles can be synthesized by both $FeSO_4·7H_2O$ and $FeCl_3·6H_2O$ in reaction to $NaBH_4$ aqueous solution. Significant and stoichiometric differences were observed for two different aqueous solution salts during the reaction with the borohydride solution. $FeSO_4·7H_2O$ is a better option for nZVI synthesis, because it tends to be less oxidized in the solution. This feature makes the required time for the reaction nZVI with Borohydride is reduced (Alidokht et al., 2011; Cao et al., 2011; Fereshteh et al., 2006). For the preparation of C-nZVI, first an aqueous solution of 0.14 M $FeSO_4·7\ H_2O$ (100 mL) and 0.2% (w/w) Na-carboxymethyl cellulose as a stabilizer were stirred with an electric rod in a flask (500 mL) for 15 min to enable the formation of C-nZVI. To remove dissolved oxygen, the mixture was purged with nitrogen gas. Then in order to the reduction of the Fe^{+2} to Fe^0, 100 mL of 0.5 M sodium borohydride solution was added drop-wise into the mixture and stirred for 30 min. Ferrous iron was reduced to zerovalent iron by borohydride according to the following reaction (Alidokht et al., 2011):

$$2Fe^{2+}_{(aq)} + BH^{-}_{(aq)} + 3H_2O_{(1)} \rightarrow 2Fe^{0}_{(s)} + 3H_2BO^{-}_{3(aq)} + 4H^{+}_{(aq)} + 2H_{2(g)}$$

The product was an aqueous black suspension. Iron nanoparticles were separated by centrifuge (5000 rpm for 5 min) and then were washed with absolute ethanol to remove excess borohydrate. The prepared particles were dried under vacuum overnight and then gently crushed into fine powders. The synthesis procedure of nonstabilized Fe^0 nanoparticles was the same as stabilized Fe^0 nanoparticles without using carboxymethyl cellulose (Alidokht et al., 2011; Cao et al., 2011; Fereshteh et al., 2006). Cellulose consists of a linear molecular chain structure known as a beta linkage and a series of hydroglucose units that are interconnected by an oxygen linkage. The carboxymethyl cellulose can easily be created by replacing the native CH_2OH group in the glucose unit (present in cellulose) with a carboxymethyl group.

2.3. Batch experiments

Arsenite removal experiments were carried out using glass Erlenmeyer 250 mL flasks containing 150 mL arsenite solution at room temperature (25 ± 1 °C). The adsorption experiments were conducted according to the design developed by RSM. The experiments were conducted under in the absence of oxygen and dissolved carbon dioxide gas (because the presence of oxygen and dissolved carbon dioxide gas would help to remove arsenite through oxygen-induced corrosion products of iron) (Tanboonchuy et al., 2011).The flasks were shaken with an orbit incubator shaker (200 rpm) for time periods up to 35 min. Parallel experiments were conducted in the absence of nanoparticles (blank samples) and no significant change was observed. The initial pH of the solution was adjusted in the desired amount and the required dosage of C-nZVI was added inside Erlenmeyer flasks with a certain concentration of arsenite. Suspensions were withdrawn from the reactors at certain reaction time intervals and centrifuged at 3000 rpm for 5 min. Samples were filtered through 0.22 μm syringe filters for analysis.

2.4. Characterization and analytical methods

Fresh Fe^0 nanoparticles were examined under a transmission electron microscope (TEM) (Sohbatzadeh et al.) at 180 kV. Scanning electron microscopy (SEM) characterization was performed by a Hitachi S 4160, 15.0 kV (Japan) instrument to identify morphological features and surface characteristics of the Fe^0 and C-nZVI (Kumar, 2011). In this study, the chemical composition and crystallographic structure of natural and manufactured materials studied by X-ray diffraction (XRD) method that is based on constructive interference of monochromatic X-rays and a crystalline sample. XRD pattern for C-nZVI was identical using a Siemens D5000 (Germany) diffractometer that contained characteristic peaks at $2\theta = 20°$ to 85° with a step time of 0.3 s and a step of 0.02° (2θ) with monochromatic Cu-Kα radiation (40KV, 30 mA, $\lambda = 0.15418$ nm). Energy dispersive X-ray spectroscopy (EDAX) analysis applied to investigate the presence of Fe^0 and any other iron mineral in the C-nZVI composite. All samples were analyzed for residual arsenite concentration using a graphite furnace atomic absorption spectrometer (GFAAS, Buck Scientific, Inc. 210VGP model, USA) (Fereshteh et al., 2006).

2.5. Factorial experimental design and optimization of parameters

RSM using central composite design (CCD) was used as an experimental technique for predicting and modeling the complex relations among input independent factors (initial arsenite concentration (x_1), C-nZVI dose (x_2), time (x_3) and pH (x_4)) and one dependent output response (arsenite removal efficiency (ϒ)). The R software for windows