

Kinetic modeling of AS(III) and AS(V) adsorption by a novel tetravalent manganese ferrioxyhyte



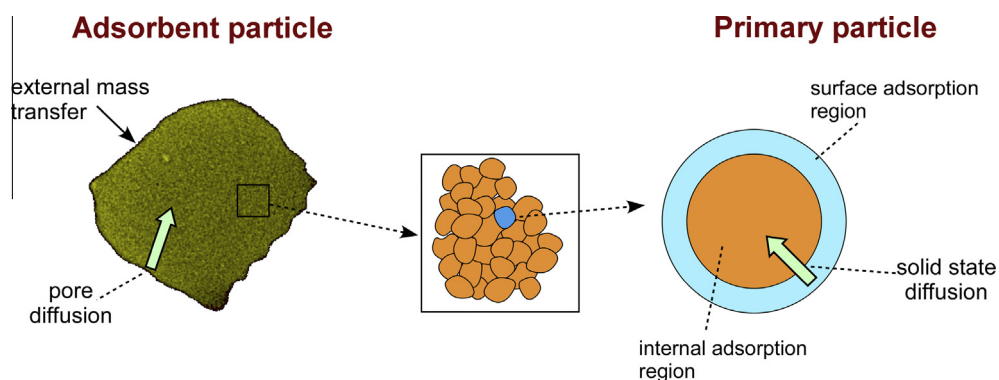
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GRAPHICAL ABSTRACT

Development of a structure based adsorption kinetic model for As adsorption on a novel tetravalent manganese ferrioxyhyte adsorbent.



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ABSTRACT

Hypothesis: The purpose of the present work is the development of a kinetic model for the adsorption of As(III) and As(V) onto tetravalent manganese ferrioxyhyte ($\delta\text{-Fe}_{0.75}\text{Mn}_{0.25}\text{OOH}$), which have been recently proved to be very efficient adsorbent for the particular species.

Experiments: In this respect equilibrium and adsorption kinetic experiments onto this type of adsorbent for As(III) and As(V) were performed. Two sizes of adsorbate particles are tested in order to acquire better insight to the adsorption process.

Results: The adsorption kinetic curves cannot be described by the well-known adsorption kinetic models so a detailed model that takes into account the structure of the adsorbent particle is developed. The model parameters were extracted by the requirement of agreement between model and experimental results. The batch model developed here is necessary for the development of models for fixed bed adsorption devices in order to exploit the commercial prospects of the particular adsorbent. This work constitutes the first attempt of kinetic study and adsorption model development for the specific very promising adsorbent.

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Nomenclature

A, B	fitting parameters	q	adsorbed solute quantity
b, n	parameters of isotherm equation	R_a	aggregate radius
c	liquid phase solute concentration	R_p	primary particle radius
D_p	effective pore diffusion coefficient in the adsorbed aggregate	V	solution volume
D_s	intra-primary particle diffusion coefficient	φ	fraction of adsorbed solute in surface region (region “1”)
D_{so}, k	parameters in relation for D_s	<i>Subscripts</i>	
h	external mass transfer coefficient	e	refers to equilibrium
m	adsorbent mass	1, 2	refer to the corresponding adsorption region

1. Introduction

Adsorption onto inorganic solids appears as one of the dominant methods among those proposed for drinking water treatment related to the removal of heavy metals [1]. Due to the combination of simplicity, compactness and easy waste handling, adsorption has become competitive to the low-cost chemical coagulation techniques [2]. The continuous effort to design novel adsorbents with high selectivity on specific contaminants or improve the properties of available ones favored important progress in the efficiency of such materials class. For instance, a large number of studies on the preparation and evaluation of arsenic adsorbents has been triggered by the reduction of the regulation limit worldwide [3], necessitated after arsenic implication with serious health problems [4]. The high affinity of low-crystalline iron oxy-hydroxides with As(V) rapidly expanded their application in arsenic treatment and many related products are now available in the market [5,6]. The potential of materials like activated alumina [7], zero-valent iron [8], TiO₂ [9], CeO₂ [10], ZrO₂ [11] and binary Fe/Mn oxide [12] to remove arsenic species from water has been also studied.

However, the propagation of these adsorbents was inhibited by the relative high cost-to-efficiency ratio and their failure to remove the more toxic As(III) form. To face such issues, the synthesis of a single-phase Fe/Mn oxy-hydroxide with high positive surface charge density and an oxidative ability to turn As(III) into As(V), has been reported by our group [13]. The tetravalent manganese feroxyhyte is a low-cost adsorbent which presents a very high adsorption capacity against As(V) compared to the commercial iron oxy-hydroxides but furthermore appears similarly efficient to remove both As(III) and As(V). The competitiveness of this novel product is also promoted by the possibility for multiple reuse after its regeneration [14]. The design and optimization of continuous flow fixed bed adsorption devices required the knowledge not only of the adsorption capacity but also of the adsorption kinetics for the new material [15]. The purpose of the present work is to derive mechanisms and kinetics for the adsorption of As(III) and As(V) and to relate them to the structure of the novel material. Adsorption equilibrium and kinetics experiments were performed for two different sizes of adsorbent particles in order to acquire a better insight in adsorption mechanism by analyzing the corresponding experimental data.

2. Experimental

2.1. Material synthesis

The studied tetravalent manganese feroxyhyte adsorbent was synthesized according to the kilogram-scale in a continuous flow procedure described in [16]. In brief, the tetravalent manganese feroxyhyte (δ -Fe_{0.75}Mn_{0.25}OOH) was the product of the aqueous

co-precipitation of FeSO₄·H₂O and KMnO₄ in a two-stage reactor using a 1 h retention time under a constantly regulated pH value of 6 and redox potential of 650 mV. The collected solid suspension was thickened for 24 h, washed several times with water, centrifuged and dried. The dried product was ground and sieved to receive a fraction of small particles (<63 μ m) and granules in the size range 0.25–0.50 mm. By a combination of electron energy loss spectroscopy and transmission electron microscopy, as described in [13], the homogeneous distribution of Fe and Mn at the nanoscale level was verified. In addition, the presence of Mn(IV)-substituted crystal structure of feroxyhyte was identified through X-ray absorption fine structure analysis. The excess of positive charge is finally balanced by adsorbed ions in the surface of the material. The particles are aggregates with primary particles having diameters of the order of a few nanometers [16]. Specific surface area of the adsorbent at particle size <63 μ m and 250–500 μ m was measured to be 197 m²/g and 215 m²/g, respectively. Studied material consists of a low-crystalline Mn-feroxyhyte crystal structure with hexagonal symmetry and cell parameters 2.905–2.905–4.555 Å.

2.2. Adsorption data

Adsorption isotherms and kinetic data were recorded after batch experiments in arsenic solutions using smaller (<63 μ m) and large particles (0.25–0.50 mm). Stock solutions of As(III) and As(V) (1000 mg/L) were prepared by diluting NaAsO₂ and Na₂-HAsO₄·7H₂O, respectively, in distilled water. Working standards were freshly prepared by proper dilution of the stock solution in distilled water. A standard buffer of N,N-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES) was added in samples (2 mM) to facilitate pH control. The pH was adjusted to the value of 7 by adding either NaOH or HCl.

In order to obtain the adsorption isotherms of small particles, 20 mg of tetravalent manganese feroxyhyte were dispersed in 200 mL of 2.5–15 mg/L As(V) or 2–20 mg/L As(III) solutions inside conical flasks and shaken orbital for 24 h. For large granules, 80 mg of the material were equilibrated with 230 mL of the aqueous As(V) or As(III) solutions in 250 mL plastic containers and shaken rotational at 20 rpm for 3 days at 20 °C. Initial As(V) concentrations were 5–20 mg/L and As(III) 5–40 mg/L, respectively. It should be clarified that the modification of experimental setup for each case was a requirement in order to overcome issues related to variations in particles morphology, volume fraction into the water matrix and contact period to reach equilibrium.

Kinetics experiments for smaller particles were carried out by dispersing 20 mg of the material in 200 mL of 2.5 mg/L As(V) or 2 mg/L As(III) solutions inside conical flasks. Samples were taken for time intervals from 5 min up to 24 h. Similarly, 80 mg of particles sized 0.25–0.50 mm were dispersed in 230 mL of 5 mg/L As(V)

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