



# Sorption of nalidixic acid onto micrometric and nanometric magnetites: Experimental study and modeling



M. Usman<sup>a,b,c,\*</sup>, S. Martin<sup>b,c</sup>, N. Cimetière<sup>b,c</sup>, S. Giraudet<sup>b,c</sup>, V. Chatain<sup>d</sup>, K. Hanna<sup>b,c</sup>

<sup>a</sup> Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad 38040, Pakistan

<sup>b</sup> Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

<sup>c</sup> Université Européenne de Bretagne, Rennes, France

<sup>d</sup> Université de Lyon, INSA-Lyon, Laboratoire de Génie Civil et d'Ingénierie Environnementale LGCIE, 20 avenue Albert Einstein, 69621 Villeurbanne, France

## ARTICLE INFO

### Article history:

Received 2 December 2013

Received in revised form 29 January 2014

Accepted 30 January 2014

Available online 6 February 2014

### Keywords:

Magnetite

Nalidixic acid

Sorption

Transport

Column

Modeling

## ABSTRACT

The sorption of nalidixic acid (NA) was studied onto three kinds of magnetite characterized by different particle sizes (from micrometric to nanometric) and surface properties. Experiments were performed under static batch and dynamic flow conditions. Obtained results indicate that kinetics and extent of sorption was strongly affected by the particle size of tested magnetites. Ionic strength effect was less significant suggesting that aggregation state of the magnetite particles did not affect the sorption. During kinetic sorption experiments, apparent rate constant normalized to solid mass was faster for nanosized magnetite while an opposite trend was observed for the surface area-normalized rate constants. Infrared data suggested the possibility of similar surface interactions on both micro-sized and nanosized magnetites. Transport of NA in magnetite-packed column was found associated to the instantaneous sorption without any significant effect of kinetic limitation. Breakthrough curves (BC) and sorption extent in columns were calculated by using Thomas, Yan and Yoon–Nelson models. Sorption capacities predicted by Thomas or Yan model were in good agreement with that determined by integrating total area above BC. However, Thomas model failed particularly to predict an accurate concentration at lower and higher time points of the BC. These findings have strong implications in relation to the transport and removal of environmental pollutants in natural and engineered systems.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

In environment, iron minerals are commonly found as ferric oxides including goethite, ferrihydrite, hematite and lepidocrocite [1]. Another form of iron minerals is the mixed Fe<sup>II</sup>–Fe<sup>III</sup> oxides including magnetite (Fe<sub>3</sub>O<sub>4</sub>) and green rust. Magnetite (Fe<sup>II</sup> Fe<sup>III</sup><sub>2</sub> O<sub>4</sub>) is very efficient in environmental remediation owing to its stability and presence of structural Fe<sup>II</sup> [2–5]. Magnetite is a ubiquitous iron oxide in soils and sediments. Existence of magnetite was reported in weathered clays, soils and in recent deposits of marine and freshwater sediments [6,7]. Recently, magnetite was identified as the main constituent of iron corrosion scale in drinking water distribution systems [8]. Top layers of corrosion scale were dominated by magnetite [8,9].

\* Corresponding author at: Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad-38040, Pakistan. Tel.: +92 419201220; fax: +92 419200764.

E-mail addresses: [muhammad.usman@uaf.edu.pk](mailto:muhammad.usman@uaf.edu.pk), [musmanch@yahoo.com](mailto:musmanch@yahoo.com) (M. Usman).

Magnetite can also be formed in laboratory by various abiotic and biotic procedures. Formation of biogenic magnetite was reported as a result of microbial reduction of ferric oxyhydroxides [10]. Abiotic procedures to form magnetite include co-precipitation of Fe<sup>II</sup> and Fe<sup>III</sup> salts in aqueous solutions or partial oxidation of hydroxylated Fe<sup>II</sup> solution [11]. Magnetite can also be formed by reacting aqueous Fe<sup>II</sup> with ferric oxides inducing their structural modifications and bulk phase transformations [12,13]. The morphology, crystallography and specific surface area of natural or synthetic magnetite can vary widely. Magnetite exists as micrometric and nanometric particles in many natural and engineered environments. Because of the larger specific surface area of nanosized particles, their surface reactivity is exalted and they play preeminent role in sorption of environmental pollutants.

Many studies have been carried out to evaluate the magnetite adsorption capacity for different pollutants including heavy metals, oxyanions and radionuclides [14–18]. However, less information is available about the mechanism and extent of sorption of emerging organic contaminants especially pharmaceutical compounds. Therefore, it is important to consider the potential mobilization

risks of water pollution associated with these contaminants, and to investigate their interaction with magnetite.

Although large variability of magnetite is found in natural as well as engineered systems, sorption onto different magnetites has never been reported. The impact of particle size and morphology on magnetite sorption capability merits, therefore, to be investigated from both environmental and engineering aspects. Moreover, the interactions of environmental pollutants with magnetite were mainly investigated under batch conditions [16–18]; however transport of such contaminants in magnetite-packed column has scarcely been investigated under flow-through conditions. Contrary to batch tests, column experiments allow monitoring the effect of non-equilibrium sorption onto the transport of pollutants. Effect of hydrodynamic parameters (e.g. dispersion) on the solute breakthrough can also be evaluated in continuous flow through conditions. Estimation of field parameters could be more accurate in column tests which provide a suitable soil–aqueous phase ratio. Moreover, sorbate species can be flushed out of system in continuous flow conditions, ultimately affecting the kinetics and extent of reaction.

Present study was conducted to investigate sorption of NA (used as a model pharmaceutical pollutant), onto three kinds of magnetite. Sorption was evaluated vs. time, pH and ionic strength in batch experiments. Sorption isotherms were also recorded over a wide range of NA concentration. Fourier transform infrared in transmission mode (FTIR) was also used to recognize the main surface complexes structures. Flow through experiments were also conducted at two influent concentrations (50 and 200  $\mu\text{M}$  of NA) and at a relatively lower flow rate (i.e.  $0.2\text{ mL min}^{-1}$ ). Three different models (Thomas, Yan and Yoon–Nelson) were used to estimate the amount of NA sorbed in the column. Application of these semi-empirical models to determine the sorbed quantity of emerging organic pollutants in iron–mineral coated sand columns remains sparse.

## 2. Experimental procedures

### 2.1. Chemical reagents

Nalidixic acid (NA), sodium phosphate ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ), ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were provided by Sigma Aldrich. Fontainebleau sand (France) was purchased from Prolabo (grain size range =  $100\text{--}250\ \mu\text{m}$ ).

### 2.2. Formation and characterization of magnetite (M) and magnetite coated sand (MCS)

Experiments were conducted with three different kinds of magnetite ( $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$ ). Among them, two (M1 and M2) were prepared in lab, while third one (M3) was purchased from Prolabo. M1 and M2 were formed by mineralogical transformations of 2-line ferrihydrite and lepidocrocite ( $\gamma\text{-FeOOH}$ ), respectively, as previously reported [12]. Prior to reactivity tests, all magnetites were analyzed by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared spectrometer (FTIR) as described previously [2].

Magnetite coated sand (MCS) was prepared as described by Scheidegger et al. [19] and as explained previously [20,21] by using 1 g of each magnetite per 100 g of sand (1% w/w). Mineral characterization of sand was found to be exclusively quartz by XRD.

### 2.3. Sorption experiments

#### 2.3.1. Batch tests

Kinetic sorption was evaluated at  $200\ \mu\text{M}$  of NA concentration, at a fixed pH (6.5) and ionic strength ( $\text{NaCl}\ 10^{-2}\ \text{M}$ ) and at  $20^\circ\text{C}$

in the absence of light. The sorption isotherms were recorded at pH of 6.5 and wide range of NA concentration ( $2\text{--}200\ \mu\text{M}$ ). The sorption edge experiments were performed at a fixed NA concentration ( $50\ \mu\text{M}$ ) and ionic strength ( $\text{NaCl}\ 10^{-2}\ \text{M}$ ). Suspensions were centrifuged, filtered and the filtrate samples were subjected to analyses by UV–visible spectroscopy and depletion method was used to calculate the sorbed concentrations. Negligible quantity of dissolved Fe was detected by colorimetric method. The sorption tests are detailed previously [22,23].

To investigate the effects of ionic strength and that of phosphate, batch sorption experiments were carried out at various molar concentrations ( $10^{-4}\text{--}10^{-1}\ \text{M}$ ) of NaCl, and of phosphate ( $10^{-5}\text{--}10^{-2}\ \text{M}$ ). In order to determine the mass balance, solid phase extraction was conducted using acetonitrile as an organic solvent.

The sorption tests were performed in triplicate and their standard deviation was found to be less than 5%.

#### 2.3.2. Column experiments

Dry MCS (50 g) was packed into glass columns having internal diameter of 2.6 cm providing bed length of 6.3 cm and bulk density of  $1.49\ \text{g cm}^{-3}$ . Each column contained 0.5 g of the reactive material, i.e. magnetite.

The column was then saturated with a  $10^{-2}\ \text{mol L}^{-1}$  NaCl solution at a fixed flow rate ( $0.2\ \text{mL min}^{-1}$ ;  $q = 0.037\ \text{cm min}^{-1}$ ). The hydrodynamic parameters were determined by a bromide tracer experiment (using a  $10^{-2}\ \text{mol L}^{-1}$  KBr solution) and using classical Convection Dispersion Equation (CDE) as explained previously [22,24,25]:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad (1)$$

where  $c$  is the water solute concentration ( $\text{ML}^{-3}$ ),  $t$  denotes time (T),  $x$  is the spatial coordinate (L),  $D$  represents the dispersion coefficient ( $\text{L}^2\ \text{T}^{-1}$ ),  $q$  is the flow velocity ( $\text{L T}^{-1}$ ),  $\theta$  is the volumetric water content ( $\text{L}^3\ \text{L}^{-3}$ ), and  $v$  is the Darcian velocity =  $q/\theta$  ( $\text{L T}^{-1}$ ). The breakthrough curve of bromide exhibited a slight asymmetrical shape with little tailing (data is not presented). The bromide concentration was analyzed using CDE to estimate the values of  $\theta$  and  $D$  which represents flow homogeneity, as explained previously [23,25,26]. NA solution ( $200\ \mu\text{M}$ , pH = 6) was then injected in a continuous mode into the column at the same constant flow rate ( $0.2\ \text{mL min}^{-1}$ ), under  $\text{O}_2$ -free controlled atmosphere.

## 3. Results and discussion

### 3.1. Characterization of tested magnetites

Three kinds of magnetite were analyzed by XRD and their diffractograms are shown in Fig. 1a. Five different peaks are represented in XRD diffractograms at  $2\theta = 21.2^\circ$ ,  $35^\circ$ ,  $41.2^\circ$ ,  $50.4^\circ$  and  $62.8^\circ$  which could be assigned to magnetite in all diffractograms. These main peaks have  $d$ -space values of 2.53, 2.96, 2.09, 4.85 and  $1.71\ \text{\AA}$  which may correspond to the more intense lines 311, 220, 400, 111 and 422, respectively of magnetite.

Morphology of three kinds of magnetite is shown by TEM images (Fig. 1b). M1 is characterized by smaller particles with non-uniform size or shape. But, shape of M2 particles is between hexagonal to octahedral while M3 exhibits non-uniform size and shape. Particle size of tested magnetites was in following order;  $\text{M1} < \text{M2} < \text{M3}$  while a reverse order was found for BET surface area ( $\text{M1} > \text{M2} > \text{M3}$ ) (Table 1). If particles are considered to be spherical, the radius of these particles ( $\rho = 5.15 \times 10^6\ \text{g m}^{-3}$ ) could be correlated to the surface area as  $\text{SSA}_{\text{Geo}} = 6/(\rho d)$ . A good agreement between SSA determined by BET and  $\text{SSA}_{\text{Geo}}$  was observed except for M1. The disagreement observed for M1 might be caused by the existence of

Download English Version:

<https://daneshyari.com/en/article/5361909>

Download Persian Version:

<https://daneshyari.com/article/5361909>

[Daneshyari.com](https://daneshyari.com)