Colloids and Surfaces A: Physicochem. Eng. Aspects 444 (2014) 1–8

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Ions removal by iron nanoparticles: a study on solid–water interface with zeta potential

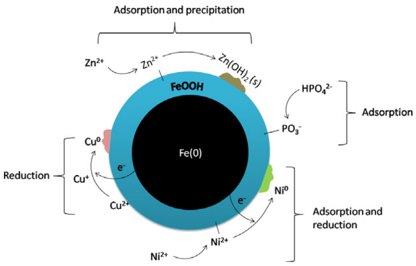
Ying Ji*

College of Environmental Science and Engineering, TongJi University, Shanghai 200092, China

HIGHLIGHTS

- A core–shell model based on XPS result and electrochemistry of interface reactions.
- Effect of concentration and oxygen on particles shown in XRD figure and IEP data.
- Surface change of iron nanoparticles in different aqueous solutions.
- Three mechanisms explain reactions between iron nanoparticles and ions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 September 2013
Received in revised form 7 November 2013
Accepted 7 December 2013
Available online 24 December 2013

Keywords:
Nanoscale zero-valent iron
Zeta potential
Core–shell model
Electric double layer
Heavy metals
Phosphate

ABSTRACT

In this study, nanosclae zero-valent iron (nZVI) reacted with three heavy metal cations and one anion in aqueous solutions. In different times of reaction and in particle concentrations, zeta potentials and isoelectric point (IEP) of reacted iron nanoparticles were measured. X-ray photoelectron spectroscopy (XPS) confirmed that nZVI particles had core–shell structure. nZVI particles also exhibited that FeOOH as sorbent and metallic iron as reductant. When nZVI particles were dosed into deionized (DI) water, IEP of nZVI shortly shifted to 7.3 and had kept stable during the next 3 h. The conclusion is that after contacting with water molecular, the nZVI surface presented more negatively than the surface of dry fresh nZVI (IEP = 8.3). Reactions which involved ions, water and iron nanoparticles resulted the change of IEP. Specifically, the peak-like trend of IEP in nZVI–Cu(II) pair indicated a possible reaction process as $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$, while Zn(II) removal was achieved via sorption on iron oxide shell followed by zinc hydroxide precipitation. Unlike nZVI–Cu(II) and nZVI–Zn(II), IEP of nZVI–Ni(II) closed to IEP of nZVI–water initially and finally up to 12. In the nZVI–PO_4(III) solution, P—O bonds on solid surface tended to adsorb protons so IEP remained increasing at whole reaction period. It was constantly lower than IEP of nZVI–water, though.

1. Introduction

Zero-valent iron (ZVI) has been widely used in various environmental applications for a long time as an excellent reducing agent, depending on its inexpensive and nontoxic characteristics [1,2]. Typical reduction equations of metal ions and organic components which are treated by ZVI are as follows:

$$Fe(s) + M^{n+} = Fe^{2+} + M^{(n-2)+} \quad (1)$$

$$H^{+} + Fe(s) + RX = Fe^{2+} + RH + X^{-} \quad (2)$$

In the last few years, nanoscale zero-valent iron (nZVI) caught more and more attention. This kind of nanosize material provides high reactivity, high efficiency in material use and enormous flexibility for in situ applications (e.g. groundwater treatment) [3,4]. Amount of research already demonstrated that nZVI is effective on remediation of many environmental contaminants [5,6] such as halogenated organic compounds, arsenic and chromium heavy metal ions.

nZVI has a core–shell structure, specifically, it contains a metallic iron core encapsulated by a layer of iron oxides[7,8]. The shell layer compositions vary according to synthesis methods and

---

* Tel.: +86 21 65985440.
E-mail address: 0jiy@tongji.edu.cn

0927-7757/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.12.031

Table 1
IEP and PZC of several iron oxides.

Oxide	IEP	PZC	References
Goethite	–	7.5	Yates et al. (1975) [13]
	7.4	–	Tipping and Cook (1982) [14]
	8.5	8.9	Hsi and Langmuir (1985) [15]
		9.2	Lumsdon and Evans (1994) [16]
	9.4	9.5	Hiemstra and van Riemsdijk (1996) [17]
	8.4	–	Blesa et al. (1997) [18]
	9.4[a]	–	Boily et al. (2001) [19]
Lepidocrocite	–	7.45	Gupta (1976) [20,21]
	–	6.7	Waite and Morel (1984) [21]
		7.29	Zhang et al. (1992) [22]
Akaganéite	7.3	–	Matijevic and Scheiner (1978) [23]
	6.4	–	Rubio and Matijevic (1979) [24]
	7.2	7.2	Kanungo (1994) [25]
Ferrihydrite	–	7.9	Davis and Leckie (1979) [26]
	–	7.8	Charlet and Manceau (1992) [27]
Hematite	–	8.5	Parks and de Bruyn (1962) [28]
	–	9.48	Huang (1971) [29]
	7.0	–	Chang et al. (1983) [30]
	7.2 (synth.)	7.5	Hsi and Langmuir (1985) [15]
	7.0 (nat.)	7.8	Hsiand Langmuir (1985) [15]
	9.3	9.5	Penners et al. (1986) [31]
	8.5	8.5	Liang and Morgan (1990) [32]
	9.5	9.5	Schudel et al. (1997) [33]
		8.5–8.8[b]	Eggleston and Jordan (1998) [34]
Magnetite	6.8	–	Tewari and McClean (1972) [35]
	–	7.1	Astumian et al. (1981) [36]
	6.2	6.4	Ardizzone et al. (1982) [37]
	6.0	–	Sun et al. (1998) [38]
	–	6.3	Marmier et al. (1999) [39]
Maghemite	6.6	6.6	Garcell et al. (1998) [40]
$CoFe_2O_4$	8.2	8.2	Ardizzone et al. (1987) [41]
		6.5	de Vicente et al. (2000) [42]

[a] Measured with the Acoustosizer.

[b] Measured with the scanning force microscope.

environmental conditions [3,9,10]. In water, the surface layer possesses hydroxide groups which has a function as reactive sites and give rise to the surface charge:

$$\equiv FeOH = H^+ + \equiv FeO^- \quad (3)$$

$$\equiv FeOH_2{}^+ = H^+ + \equiv FeOH \quad (4)$$

The surface charge serves as an important indicator of reactivity and stability of nZVI. The surface charge influences on affinity between positively and negatively charged ions in solution, particle–particle interactions, stability and mobility in porous media and environmental conditions (e.g. ion strength, competitive contaminants). If two particles have the same surface charge in aquatic environment, repulsive forces will prevent them from approaching each other and adhering together in a long distance. By contrast, if two particles have opposite charge, attraction will happen. Once iron nanoparticles are introduced into pure water, they are charged. The "negative charge" means the surface of nZVI is able to sorb aqueous positively charged ions, e.g. metal cations (Cu^{2+}, Ag^+). Biodegradation and dissolution of carbon oxides may cause the decrease of environmental pH, thus turning surface charge of nZVI more positive, which is favorable to attract negatively charged ions, e.g. phosphate, metal oxyanions, arsenate.

To investigate electrochemistry properties of nZVI include surface charge, zeta potential (Fig. 1) measured from electrophoresis in this study, is a simple and direct parameter. From data of zeta potentials, values of IEP and point of zero charge (PZC) are gained. IEP is the pH value which the net proton charge is zero, viz. $\sigma_H = \sigma_{H^+} - \sigma_{OH^-} = 0$. PZC in which the charge on surface arising from all sources is zero, viz. $\sigma_{tot} = \sigma_H + \sigma_S = 0$. σ_H is the net proton charge, that is, the charge due to the binding of protons or the binding of OH^-. σ_S is the Stern layer surface charge density. IEP and PZC are equal if there is no specific adsorption. There are tons of literatures available concerned about zeta potential/IEP/PZC of various iron oxides, which is listed in Table 1 [11]. However, as for zero valent iron or nZVI, only few studies have been published [12].

In short, aqueous zero-valent iron can give rise to the surface charge. Therefore, the surface charge as well as surface potential is essential in predicting surface reactions, surface complex formation, ions transfer, etc. Zeta potential, which reflects the potential

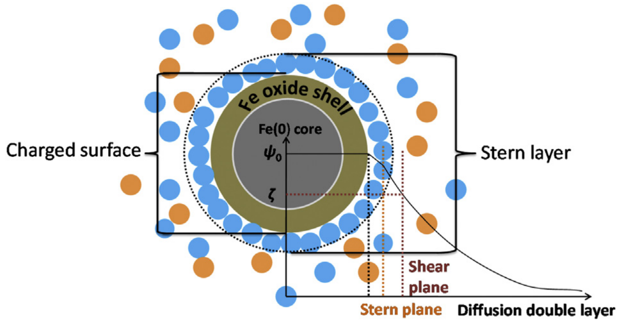


Fig. 1. Schematic electric double layer of a nZVI particle in water. Two colors present counter charge atoms. The surface potential, ψ decreases (Stern layer model) with distance-increasing from the surface. At the plane of shear (moving particle form bulk solution) a electric potential (the zeta potential) can be measured according to electrophoretic mobility.