



Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Nano modification of NZVI with an aquatic plant *Azolla filiculoides* to remove Pb(II) and Hg(II) from water: Aging time and mechanism study

M. Arshadi ^{a,*}, M.K. Abdolmaleki ^b, F. Mousavinia ^c, S. Foroughifard ^d, A. Karimzadeh ^e^a Department of Chemistry, Shiraz Branch, Islamic Azad University, P.O. Box 71955-149, Shiraz, Fars, Iran^b Department of Chemistry, College of Arts and Sciences, University of Cincinnati, 404 Crosley Tower, Cincinnati, OH 45221-0172, United States^c Mehr Petrochemical Company, Phase (PSEEZ), Assaluyeh, Bushehr, Iran^d Department of Fishery, University of Guilan, P.O. Box 1144, Sowmesara, Iran^e Department of Chemical and Polymer Engineering, Yazd University, Yazd, Iran

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 June 2016

Revised 19 September 2016

Accepted 2 October 2016

Available online 4 October 2016

Keywords:

Azolla filiculoides

Lead

Mercury

NZVI

Aquatic plant

Nanobioadsorbent

ABSTRACT

This paper reports the preparation and stabilization of nano zero valent iron (NZVI) on a modified aquatic plant, *Azolla filiculoides*, and investigates its potential for the adsorption/reduction of Pb(II) and Hg(II) ions from aqueous media even after six months of storage in the lab condition. XRD, TEM and zeta potential results demonstrated that the *Azolla*-NaOH could be a good stabilizer of aged NZVI (six months) and the green support suppressed the oxidation and aggregation of immobilized NZVI. Kinetic and equilibrium models for lead and mercury ions uptake were developed by considering the effect of the initial Pb(II) and Hg(II) concentrations, contact time, adsorbent dosage, initial pH and effect of temperature. The contact time to obtain equilibrium for maximum uptake by *Azolla*-OH-NZVI was 20 min. The removal of toxic metal ions has been monitored in terms of pseudo-first- and -second-order kinetics, and the Freundlich and Langmuir isotherms models have also been utilized to the equilibrium uptake results. The uptake kinetics followed the mechanism of the pseudo-second-order equation for all systems studied, confirming chemical sorption as the rate-limiting step of adsorption mechanisms and not involving a mass transfer in solution. The thermodynamic results confirmed that the uptake of Pb(II) and Hg(II) ions were feasible, spontaneous and endothermic at 25–80 °C. XRD and zeta potential data displayed the existence of Pb(0) and Hg(0) on the *Azolla*-OH-NZVI surface. The nanobioadsorbent revealed high recyclability due to its reasonable uptake efficiency after 7th adsorption–desorption cycles. The proposed nano biocomposite could also be utilized to uptake Pb(II) and Hg(II) ions from the real water (*Anzali lagoon*

* Corresponding author.

E-mail addresses: mohammadarshadi@yahoo.com, moarshadi138@gmail.com (M. Arshadi).

water). However, coated NZVI with *Azolla filiculoides* as a green and environmentally friendly support suppressed rapid oxidation and aggregation of the immobilized NZVI, therefore vastly enhancing the probability of environmental transport and reducing the sedimentation and potential for toxicity.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Several traditional practical procedures which have been considered to sequester inorganic pollutants ions from various industrial outflows usually comprise membrane separation, ion exchange, chemical precipitation, flocculation, and evaporation, and are generally expensive, mainly in eliminating heavy metal ions from dilute solutions. Adsorption is mentioned reasonably appealing due to its effectiveness of cleaning from dilute aqueous media [1,2]. Because of the toxicity of heavy metals (Hg, Pb), the Agency for Toxic Substances and Disease Registry, of the U.S. Department of Health and Human Services, has classified these materials as priority inorganic pollutants [3]. Pb(II) and Hg(II) are highly toxic substances, exposure to which can cause a wide range of adverse health consequence for both adults and children at very low levels [4,5]. Nevertheless, vegetables, milk, hen's eggs and dairy products could most likely become polluted with metals ions either directly by food stuff and water or during packaging operation and manufacturing.

The aim of the present research is to search the feasibility of utilizing modified *Azolla filiculoides* as a low-cost bioadsorbent for inorganic contaminants removal from industrial wastewater. *Azolla filiculoides* was chosen because of its high cellulose content. *Azolla filiculoides* Lam. a small aquatic and planktonic fern is found buoyant on the surface of canals, Lakes, wetlands, ponds and slow-moving streams [6,7]. *Azolla* is propagated vegetatively and by spores; it is placed on US noxious weed list. Native range of *A. filiculoides* are observed in Africa, Madagascar, India, Southeast Asia, China and Japan, Malaya, the Philippines, the New Guinea mainland and Australia [8,9]. *Azolla* species can often grow on nitrogen poor water due to its ability to fix nitrogen.

Indigenous species of *Azolla* have not been observed in Iran. In 1986 the Ministry of Agriculture commenced the importation of *Azolla* from the Philippines into Anzali Wetland, in northern Iranian province of Gilan for investigations on its nitrogen fixation efficiency and *Azolla* was then diffused in North of Iran. In October–November 1991, the *Azolla* occupied the whole Wetland except for its western basin, where wind suppressed its growth. Currently nearly all sheltered open-water areas in the southern and eastern basins are covered by a dense mat of this fern which also pierced deeply into the *Phragmites* stands. Some channels of the southern basin are completely covered by *Azolla*, and in where it may be observed along the beach several kilometers eastward and westward from Bandar Anzali [10]. *Azolla* is distributed and has grown very fast in the three north provinces of Iran, for 20 years.

In recent years ZVI has been introduced as an engineered nano-materials and an efficient reducing agent for many toxic inorganic and organic pollutants [2,11–13]. ZVI is non-toxic and relatively low-cost in comparison with other zero-valent metallic nanoparticles. NZVI is singularly appealing for separation purposes because of their stunning surface area to weight ratio leading to a greater density of reactive sites and toxic metals removal efficiency. The magnetic characteristics of NZVI accelerated the easy filtration of NZVI from soil and water, through a magnetic field [11,12]. As-prepared NZVI has many advantages such as high reactivity and selectivity, where every single catalytic entity can act as a single active site. Notwithstanding their benefits, bare NZVI have not

been commercialized due to some issues occurring when the bare NZVI should be extracted and purified from the reaction mixture. In wastewater purification and groundwater treatment, NZVI could somewhat or totally transform from metal iron (Fe⁰) to non-toxic iron oxide/hydroxides commonly found in sediments and soils, which caused some significant variations in the nanoparticle structure and composition. However, many industrial problems such as corrosion and deposition on reactor wall are concerned with these bare NZVI. These problems would be suppressed if bare NZVI was stabilized on the insoluble solid supports with remarkable chemical and thermal stability and easily accessibility [2,12–14]. Stabilization is durable enough to undergo the harsh reaction conditions and the NZVI can be applied for many cycles [2,12].

In this paper the main object is to develop a recyclable cost-effective nanobioadsorbent (immobilized NZVI on an aquatic plant, *Azolla filiculoides*) in order to remove Pb(II) and Hg(II) ions from aqueous media. The effect of contact time, adsorbent dosage, initial concentration, temperature and pH on the removal of Pb(II) and Hg(II) has been studied. The results were analyzed by the Freundlich and Langmuir model. Furthermore, the proposed mechanisms for the removal of Pb(II) and Hg(II) ions from aqueous solutions onto the *Azolla*-OH-NZVI was elaborated.

2. Experimental section

2.1. Materials

All reagents (AR grade) were purchased from Merck or Fluka and used without further purification, except for solvents, which were treated according to standard methods.

2.2. Preparation of the modified *Azolla filiculoides*

Azolla filiculoides (*Azolla*) was obtained from Anzali lagoon and was cut and washed with water copiously. After that was put in the oven for 24 h in 70 °C, and after drying they were ground and were passed through different sieve size. The fraction of particle between 150 and 250 μm (geometric mean size: 200 μm) was selected. The powdered *Azolla* was washed thoroughly with hot distilled water and was dried at 65 °C. The sorbent thus obtained was designated pristine *Azolla*. Preliminary studies using *Azolla* treated with base was carried out in order to optimize the sorption of metal ions. Pristine *Azolla* was treated with 0.1 M NaOH solution at reflux for 2 h. A typical experimental procedure is as follows: 25 g of the pristine biomaterial is dispensed in 0.5 L of distilled water. Then a certain amount of 0.1 M NaOH is added and the suspension is subjected to mechanical stirring for 2 h on heater. The final material is separated by centrifugation and washed with distilled water. Excess of NaOH was removed with distilled water and the material was dried at 50 °C. NaOH treated pristine *Azolla* was designated as *Azolla*-OH.

2.3. Preparation of the *Azolla*-supported NZVI

The NZVI-biomaterial sample is synthesized based on the following procedure: FeCl₂·4H₂O (5.35 g) was dissolved in a 4/1 (v/v) ethanol/water mixture (72 mL ethanol + 18 mL deionized

Download English Version:

<https://daneshyari.com/en/article/4985494>

Download Persian Version:

<https://daneshyari.com/article/4985494>

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