Journal of Colloid and Interface Science 426 (2014) 241–251

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Nanoscale Zero-Valent Iron (NZVI) supported on *sineguelas* waste for Pb(II) removal from aqueous solution: Kinetics, thermodynamic and mechanism

M. Arshadi [a,*], M. Soleymanzadeh [b], J.W.L. Salvacion [b], F. SalimiVahid [b]

[a] Department of Science, Fasa Branch, Islamic Azad University, PO Box 364, Fasa 7461713591, Fars, Iran
[b] Mapúa Institute of Technology, Muralla St. Intramuros, Manila 1002, Philippines

A R T I C L E I N F O

Article history:
Received 6 March 2014
Accepted 6 April 2014
Available online 13 April 2014

Keywords:
NZVI
Adsorption
Sineguelas waste
Pb(II) ions
Isotherm
Kinetics

A B S T R A C T

In this study, the synthesis and characterization of a new adsorbent containing nanoscale zerovalent iron particles (NZVI) decorated sineguelas waste (S-NaOH-NZVI) from agriculture biomass was investigated for the adsorption/reduction of inorganic pollution such as Pb(II) ions. The combination of ZVI particles on the surface of sineguelas waste can help to overcome the disadvantage of ultra-fine powders which may have strong tendency to agglomerate into larger particles, resulting in an adverse effect on both effective surface area and catalyst performance. The synthesized materials were characterized with different methods such as FT-IR, BET, XRD, TEM and pH_{PZC}. Good dispersion of NZVI particles (ca. 10–70 nm) on the sineguelas waste was observed. The effects of various parameters, such as contact time, pH, concentration, adsorbent dosage and temperature were studied. The adsorption of Pb(II) ions has been studied in terms of pseudo-first- and second-order kinetics, and the Freundlich, Langmuir and Langmuir–Freundlich isotherms models have also been used to the equilibrium adsorption data. The adsorption kinetics followed the mechanism of the pseudo-second-order equation. The thermodynamic parameters (ΔG, ΔH and ΔS) indicated that the adsorption of Pb(II) ions were feasible, spontaneous and endothermic at 25–80 °C. XRD analysis indicated the presence of Pb(0) on the S-NaOH-NZVI surface. This study suggests that the modified sineguelas waste by NZVI particles can be prepared at low cost and the materials are environmentally benign for the removal of Pb(II) ions, and likely many other heavy metal ions, from water.

1. Introduction

Our environment is continually exposed to pollution by organic and inorganic compounds such as pesticides and metals. Essentially all industrial processes generate by-products that become waste materials. These waste materials have the potential of contaminating the environment. Heavy metals, solvents organic compounds, and petroleum products account for most of the contaminants. Heavy metals have been used in a variety of ways for many centuries. For the past three centuries, the production of heavy metals such as lead, copper, and zinc has increased exponentially [1].

According to the ranking of metal interested priorities referred by Volesky [2], Pb(II) is one of the most interesting heavy metal for removal and/or recovery considering the combination of environmental risk and reserve depletion. This metal is widely used in many industrial applications, such as storage battery manufacturing, painting pigment, fuels, photographic materials, explosive manufacturing, coating, automobile, aeronautical and steel industries [3,4]. This heavy metal is a highly toxic and cumulative poison and accumulates mainly in bones, brain, kidney and muscles. Lead poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain [5]. It is therefore essential to remove Pb(II) from wastewater before disposal.

The Philippines supply its water from different sources. These include rainfall, surface water resources, i.e. rivers, lakes, and reservoirs, and groundwater resources. Environmental Management Bureau (EMB) reports that heavy metals are parameters included in monitoring activities only for receiving water bodies where mining, electroplating, tanning, and other similar activities are operating. Annual average monitoring results of Meycauayan River in 2001, 2003, and 2004 show an excess (based on minimum criteria and value) for chromium (2001), cadmium (2001), and lead (2004). Monitoring results of Bocaue River indicate that the River met the criteria for chromium, copper, and cadmium. However, it

* Corresponding author.
E-mail addresses: m-arshadi@ch.iut.ac.ir, mohammadarshadi@yahoo.com (M. Arshadi).

http://dx.doi.org/10.1016/j.jcis.2014.04.014
0021-9797/© 2014 Elsevier Inc. All rights reserved.

showed high lead concentrations in all its sampling stations particularly during the dry season in 2004. The Marilao River showed similar excess (relative to existing standards) in lead and cadmium in its Class A and C waters. Potential sources of heavy metals are tanneries, electroplating, and other similar industries located in nearby area. The Marilao River was the subject of two Greenpeace reports in 1996 ("Lead Overload: Lead Battery Waste Trade and Recycling in the Philippines") and, again, in 2003 (Toxics Reloaded: Revisiting the Impacts of Lead Battery Waste Trade and Recycling in the Philippines) for lead contamination. Effluent samples taken from a discharge canal of the Philippine Recyclers, Incorporated (PRI) had lead levels of 190 ppm or 3800 times higher than the 0.05 ppm or mg/L standard set for lead in effluent from old and existing industries [6].

Many methods for treatment are available, including chemical and surface-chemistry processes such as precipitation, adsorption, membrane processes, and ionic exchange. However, these techniques have inherent limitations, such as poor efficiency, sensitive operating conditions, and the production of a secondary sludge requiring further costly disposal [7]. These disadvantages, together with the need for more economical and effective methods for recovering the metals, have resulted in the development of alternative separation technologies. One such alternative is biosorption, in which certain types of biomass are able to bind and concentrate metals from even very dilute aqueous solutions. The biosorption process offers a number of advantages when compared to the conventional methods currently used. One advantage is that the heavy metals can be recovered from the biomass [8].

For this reason, the use of low-cost materials as adsorbent for metal-ion removal from wastewater has been investigated. Using agricultural waste products for metal removal not only has the same advantages as other adsorption materials, but it also uses what was once a waste product. A number of biological adsorption materials have been investigated for their potential to remove toxic metals, including apple waste [9], corn cobs [10], and banana peels [11]. These materials were successful in removing heavy metals to varying degrees. One of the best ways of using bioproduct effectively is to be affected by nanozerovalent iron. Extensive laboratory studies have demonstrated that nanoscale iron particles are effective for the transformation of a wide array of common environmental contaminants such as various organic compounds [12–15] and metal ions such as As(III), Pb(II), Cu(II), Ni(II) and Cr(VI) [12,14,16,17].

The aim of the present research is to explore the feasibility of utilizing sineguelas waste as a low-cost bioadsorbent for metal removal in industrial wastewater. Sineguelas waste was selected because of its high cellulose content. Although other agricultural products have been investigated, this is the first study to investigate metal adsorption on sineguelas. Sineguelas is a fruit that grows in tropical climate like the Philippines. The fruit is indigenous to Southern Mexico and the Northern part of Peru. Some of its species is believed also to originate from tropical parts of America. Sineguelas grows in shrub and does not actually require delicate cultivation [18]. This paper reports the preparation of zerovalent iron nanoparticles immobilized on sineguelas waste as a low-cost active nanoadsorbent and its application in removing Pb(II) ions from aqueous solution at various conditions. The effect of contact time and initial concentration, temperature and pH on the removal of Pb(II) ion has been studied. The results were analyzed by the Freundlich, Langmuir and Langmuir–Freundlich model.

2. Experimental

2.1. Materials and analytical techniques

All reagents (A.R.) were purchased from Merck or Aldrich and were used without further purification, except that solvents were treated according to the standard methods. The pH of solution was adjusted using 0.1 M HCl/NaOH using a pH meter (Metrohm, 827 pH Lab). The concentration of Pb(II) solution was measured by atomic absorption spectrophotometry using a Perkin–Elmer 3030 instrument. The pH at the point of zero charge (pH_{PZC}) of different adsorbents was obtained by the solid addition method [19]. IR spectra (Jasco FT/IR-680 plus spectrophotometer and KBr pellets) were used for the characterization of the adsorbents. XRD (Philips X'PERT MPD diffractometer) was performed for the crystalline structure of the adsorbents. The XRD patterns were recorded in the 2θ range of 10–100°. Transmission electron microscopy (TEM) was carried out on the powder samples with a Tecnai F30 TEM operating at an accelerating voltage of 300 kV. The specific surface areas were calculated using BET method [20].

2.2. Preparation of the modified sineguelas

Sineguelas was obtained from a local store and was cut and then its pit (seed) was removed. An easy way to do this is to slice into the sineguelas and cut it all around the seed to remove its flesh cleanly. After separating the seeds and their flesh, all seeds were put in the oven for 72 h in 70 °C and after drying; they were ground and were passed through different sieve size. The fraction of particle between 250 and 400 μm (geometric mean size: 305 μm) was selected. Fresh sineguelas was washed thoroughly with hot distilled water and was dried at 65 °C. The sorbent thus obtained was designated pristine sineguelas (S). Preliminary studies using sineguelas treated with base was carried out in order to optimize the sorption of metal ions. Pristine sineguelas was treated with 0.1 M NaOH solution at reflex for 2 h [21]. 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 washes with distilled water. Excess of NaOH was removed with distilled water and the material was dried at 50 °C. NaOH treated pristine sineguelas was designated as S-NaOH.

2.3. Preparation of the biomaterial-supported NZVI (S-NaOH-NZVI)

The NZVI-biomaterial sample is synthesized based on the following procedure: $FeCl_2{\cdot}4H_2O$ was dissolved in a 4/1 (v/v) ethanol/water mixture (72 mL ethanol + 18 mL deionized water), then the S-NaOH is added to this solution and the mixture is left in an ultrasonic shaker for 25 min in order to disperse the biomaterial grains. Meanwhile, sodium borohydride solution is prepared by dissolving $NaBH_4$ in 100 mL of deionized water. The borohydride solution is then added dropwise to the aqueous Fe(II)–S-NaOH mixture while stirring continuously on a magnetic stirrer. Black solid particles of NZVI appeared immediately following the addition of the first drop of NaBH4 solution. After the full addition of the borohydride solution, the mixture is left for a further 20 min of stirring and then filtered. Immobilization of NZVI on the S-NaOH was designated as S-NaOH-NZVI.

2.4. Adsorption measurements

Different Pb(II) ion concentrations were freshly prepared in a solution of deionized water. Sorption experiments were carried out in batch conditions: 0.1 g of nanoadsorbent was shaken up with a 30 mL of the inorganic pollutant of different concentrations (from 5.0 to 1000 mg L^{-1}) in a controlled temperature box 25 °C. The time required to work in equilibrium condition was determined by preliminary kinetic measurements. The kinetic tests of all Pb(II) ions showed no significant variation in sorption after 24 h. After centrifugation at 3000 g for 5 min, the liquid phase were