Journal of Hazardous Materials 289 (2015) 210–218

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Modified natural diatomite and its enhanced immobilization of lead, copper and cadmium in simulated contaminated soils

Xinxin Ye[a,*], Shenghong Kang[a], Huimin Wang[a], Hongying Li[b], Yunxia Zhang[a], Guozhong Wang[a,*], Huijun Zhao[a,c]

[a] Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, PR China
[b] Institute of Soil and Fertilizer, Anhui Academy of Agricultural Sciences, Hefei 230031, China
[c] Centre for Clean Environment and Energy, Gold Coast Campus, Griffith University, Queensland 4222, Australia

HIGHLIGHTS

- We modify natural diatomite using the facile acid treatment and ultrasonication.
- Modification add pore volume, surface area and electronegativity of natural diatomite.
- Modified diatomite is superior to natural diatomite in soil heavy metal remediation.
- Modified diatomite can be promising for in-situ immobilization of heavy metal in soil.

ARTICLE INFO

Article history:
Received 5 November 2014
Received in revised form 13 February 2015
Accepted 17 February 2015
Available online 20 February 2015

Keywords:
PTEs
Natural diatomite
Modified diatomite
Soil remediation

ABSTRACT

Natural diatomite was modified through facile acid treatment and ultrasonication, which increased its electronegativity, and the pore volume and surface area achieved to 0.211 $cm^3 g^{-1}$ and 76.9 $m^2 g^{-1}$, respectively. Modified diatomite was investigated to immobilize the potential toxic elements (PTEs) of Pb, Cu and Cd in simulated contaminated soil comparing to natural diatomite. When incubated with contaminated soils at rates of 2.5% and 5.0% by weight for 90 days, modified diatomite was more effective in immobilizing Pb, Cu and Cd than natural diatomite. After treated with 5.0% modified diatomite for 90 days, the contaminated soils showed 69.7%, 49.7% and 23.7% reductions in Pb, Cu and Cd concentrations after 0.01 M $CaCl_2$ extraction, respectively. The concentrations of Pb, Cu and Cd were reduced by 66.7%, 47.2% and 33.1% in the leaching procedure, respectively. The surface complexation played an important role in the immobilization of PTEs in soils. The decreased extractable metal content of soil was accompanied by improved microbial activity which significantly increased ($P < 0.05$) in 5.0% modified diatomite-amended soils. These results suggested that modified diatomite with micro/nanostructured characteristics increased the immobilization of PTEs in contaminated soil and had great potential as green and low-cost amendments.

1. Introduction

Soil pollution is a worldwide problem. The accumulation of PTEs in soils detrimentally affects soil quality, food safety, environment and human health. The in-situ immobilization of PTEs has been widely applied to the remediation of contaminated soils due to lower cost and reduced soil disturbance [1,2]. Repair materials play a crucial role in the in-situ immobilization of contaminants. Therefore, many studies have focused on the selection, modification and production of low-cost materials with good metal-binding capacities [3,4].

Morphologies, structure and surface state of the materials have obvious influences on their adsorption properties. Although nanostructured materials have higher specific surface areas than micro-scale materials, they tend to aggregate, which decreases the effective surface states and leads to a reduction in their adsorption capacity for pollutants. Micro/nanostructured materials, constructed by integrating nano-units into micro-scale materials, have superior properties due to their large surface area, high activity, anti-aggregation properties and good stability,

* Corresponding authors. Tel.: +86 551 6559 5616; fax: +86 551 6559 1434.
E-mail addresses: xxye@issp.ac.cn (X. Ye), gzhwang@issp.ac.cn (G. Wang).

http://dx.doi.org/10.1016/j.jhazmat.2015.02.052
0304-3894/

compared to individual nano-scale and micro-scale materials [5]. Recently, there have been some reports on the removal of PTEs using micro/nanostructured materials in wastewater treatment [6,7]. However, there have been few studies into the application of micro/nanostructured materials in the remediation of contaminated soils.

Diatomite is a low-cost, environment-friendly and natural micro/nanostructured material derived from sedimentary silica, and has cylindrical and plate morphologies with well-developed mesoporous/macroporous structures [8]. Many studies have revealed that naturally occurring diatomite has a strong adsorption affinity for PTEs in aqueous solution, such as Ni [9], Cr [10], Pb [11,12], Cd [12], Cu [13] and Th [14]. However, diatomite, during its formation, is inclined to associate and combine with other mineral impurities that mix and wrap around diatomite shell and reduce the original micro/nanostructured characteristics. The impurities in diatomite structure significantly impact on the adsorption of PTEs from contaminated environments [15]. Therefore, it is very important to modify natural diatomite via the purifying and activating technique in an attempt to optimize the PTEs immobilization process and improve the structurally enhanced absorption of PTEs [16]. Different modification methods for diatomite have been described, such as thermal treatment [15], acid treatment [17], ball milling [18] and surface functionalization [19]. Compared with other methods, the acid soluble and ultrasonic treatment methods can be readily applied to the large-scale production of modified diatomite because of simple technology and low cost. However, there has been little research into remediation efficiency and the mechanisms behind the improvements in modified mineral materials, such as natural diatomite, when applied to contaminated soils.

The remediation of polluted soils should not only be assessed by soil chemical characteristics using conventional analysis and extraction procedures, but also by the restoration of soil-based ecosystem functions [20]. Some microbial and enzyme activities are deemed as promising tools for assessing the remediation and recovery of PTEs contaminated soils using various amendments [21,22]. Furthermore, the influence of the repair material on basic soil properties is also an important factor when judging whether or not a material can be used to rehabilitate contaminated soils. Therefore, the influence of natural and modified diatomite on soil physicochemical and biological properties should be considered.

We characterize the differences of properties for natural and modified diatomite in detail, and investigate systematically the immobilization capacity of Pb, Cu and Cd by natural and modified diatomite in two upland soils with different properties. Pb, Cu and Cd were selected as targets for PTEs due to their extensive existence in contaminated farmland in China. The remediation effectiveness was evaluated by determining the change in Pb, Cu and Cd concentrations based on $CaCl_2$ extractions, the toxicity characteristic leaching procedure (TCLP), and the response of biological indicators to natural and modified diatomite. The mechanisms responsible for the immobilization of PTEs were elucidated by comparing the differences of the binding energy of Pb in soils before and after the addition of natural and modified diatomite using the X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

Natural diatomite sample came from Chengzhou County (Zhejiang Province, China). A modified diatomite sample was obtained according to the following procedures: natural diatomite (50 g) and 4 mol L^{-1} HCl (250 mL) were mixed in a 500 mL beaker and then placed in the groove of an ultrasonic dispersion instrument. The diatomite samples were treated by the agitation and low-speed ultrasonic process for 3 h. Finally, the sample was filtered and washed repeatedly with ethyl alcohol and deionized water until the pH was neutral and then dried to a constant weight.

Table 1
Basic physico-chemical properties of the soils.

Soil	pH	OC[a]	CEC[b]	Clay	Total concentration (mg kg^{-1})		
		(g kg^{-1})	(cmol kg^{-1})	(%)	Pb	Cu	Cd
TC	6.30	12.3	12.6	21.8	29.8	21.2	0.17
GC	4.68	14.8	10.2	16.1	13.3	11.6	0.13

[a] OC: soil organic carbon.
[b] CEC: cation exchange capacity.

2.2. Characterization of natural and modified diatomite

The phase structure of natural and modified diatomite was analyzed by an XRD (X-ray diffractometer) (Philips X'Pert, Netherlands). The morphology and microstructure examinations were conducted using a field emission scanning electron microscope (FESEM) (Sirion 200 FEG, USA). The Fourier Transform Infrared Spectroscopy (FT-IR) measurements were mounted on a Nexus spectrometer (Thermo Nicolet Corporation, USA) in a KBr pellet at room temperature. The N_2 adsorption-desorption isotherms were determined by Ommishop 100cx equipment (Coulter, USA). The Zeta potential of the obtained suspension was determined using a Zeta potential analyzer (Zetasizer3000HSa, Malvern, UK). XPS spectra were recorded on soil powders with a thermo ESCALAB 250 spectrometer.

2.3. Soils

Two uncontaminated soils used for maize cultivation were collected at a depth of 0–20 cm from Guichi County (GC), Chizhou City, China (30°19′N, 117°47′E) and Tongcheng County (TC), Auqing City, China (31°07′N, 116°53′E). Soil pH was measured using a glass electrode with a soil/water ratio of 1:2.5; organic carbon (OC) was determined by wet digestion following the method of Nelson and Sommers [23] and cation exchange capacity(CEC) was measured by NH_4OAC leaching, as described by Lu [24]. Soil texture was analyzed using Bowman and Hutka's method [25]. Total soil Pb, Cu and Cd contents were determined by graphite furnace atomic absorption spectrometry (GFAAS) (SpetrAA 220Z, Australia) with mixed acid digestion (HNO_3–$HClO_4$–HF) [26]. A certified sediment reference material (GBW07455 from the National Research Center for Standard Materials in China) was used to evaluate the validity of our analyses in the soil digestions. Table 1 lists the basic soil physico-chemical properties.

To simulate the combined pollution of PTEs, two soil samples were placed in polythene pots. Pb, Cu and Cd nitrates were added at 1000 mg kg^{-1}, 800 mg kg^{-1} and 5 mg kg^{-1}, respectively. The addition of Pb and Cu doubled the three-grade environmental quality standard for soils in China (GB 15,618–1995) (i.e., 500 mg kg^{-1} for Pb and 400 mg kg^{-1} for Cu) and the amount of Cd added was five times as much as the three-grade standard (i.e., 1 mg kg^{-1} for Cd). The addition amount of PTEs based on the soil environmental standard was commonly considered to study the behavior of PTEs in contaminated soils in China which were reported in some literature [27,28]. The soil mixed with PTEs was placed in pots and incubated at constant humidity (70% water holding capacity). The pots were then covered by a plastic lid with some small holes to allow gaseous exchange and minimize moisture loss and incubated for three months at room temperature in order to balance the concentration of PTEs between solid and liquid phase in soils.