



Short communication

New facile benign agrogenic-nanoscale titania material—Remediation potential for toxic inorganic cations



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ARTICLE INFO

Article history:

Received 3 September 2014

Received in revised form 9 January 2015

Accepted 14 January 2015

Available online 16 March 2015

Keywords:

Biomass

Kinetics

Agrogenic-nanoscale titania

Chromium

Lead

ABSTRACT

A new facile benign (eco-friendly) *Nauclea diderrichii* agrowaste-nanoscale titania hybrid adsorbent (TND) used in the sequestration of Cr(III) and Pb(II) ions is reported in this paper. Surface characterization techniques such as thermogravimetric analysis (TG), X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) surface area and porosimetric analyses indicated that *N. diderrichii* agrowaste (NDS) was successfully modified with nano-titania. TG analysis proved that modification of *N. diderrichii* agrowaste with nano-titania improved its thermal stability and rate of metal ion uptake. Pseudo-second order kinetic equation gave better fit to experimental data than pseudo-first order kinetic equation. The adsorption capacity of NDS and TND adsorbents for Cr(III) were 5.57 mg/g and 6.21 mg/g, respectively. Also, the amounts of Pb(II) sequestered by NDS and TND adsorbents were 6.82 mg/g and 7.49 mg/g, respectively. Also, the initial sorption rates of Cr(III) and Pb(II) by TND adsorbent was higher than for NDS adsorbent, making TND material a better adsorbent for toxic metal ions removal from aqueous effluents than NDS adsorbent.

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1. Introduction

Global industrialization has led to the release of toxic metal ions into the environment. Moreover, industrialization and urbanization have resulted in an elevation of the amounts of toxic metal ions present in the natural habitat, which comprises soils, lakes, rivers, ground-waters and oceans, thereby causing environmental pollution [1,2].

Environmental pollution from toxic metal ions (Ni(II), Cu(II), Cd(II), Cr(III) and Pb(II)) occurs in different industrial wastewaters, which are metal plating, mining operations, metallurgical engineering, battery manufacturing processes, production of paints and pigments, electroplating, nuclear power plants, ceramic industries

and glass industries [3–6]. These toxic metal ions are deleterious to the ecosystem [1,2]. Their non-biodegradable nature allows them bio-accumulate in living organisms, thereby posing precarious health challenges for the entire flora, fauna and human beings [6].

A long time exposure to Cr(III) species can cause skin allergies, cancer and DNA damage in human beings [7]. Lead is a known carcinogen and its bioaccumulation in living organisms causes disruption in the biosynthesis of the haemoglobin level, a rise in blood pressure, kidney damage in human beings, and then brain damage, miscarriages, abortions and diminished learning abilities of children [3–6].

The removal of these hazardous metal ions from water and wastewaters is essential for protecting human health and the ecosystem. The quest to remove these toxic metal ions from the environment has led to the use of various separation techniques. Metal ion uptake by biosorption may involve the contribution of diffusion, adsorption, chelation, complexation, and coordination or micro-precipitation mechanisms depending on the specificity of the biosorbent. The utilization of nanoscale materials has the merit

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of increasing the surface areas of biosorbents, and thus increasing their biosorptive applications [8].

Over the years, vast studies have been carried out on the adsorption of hazardous metal ions by different waste materials of biological origin such as sugarcane bagasse [9], waste orange peel [10], wheat bran [11], rice bran [12], Japanese cedars [13], *Thuja orientalis* [14], reed [15], *Carica papaya* [16,17], *Nauclea diderrichii* [18,19], clay [20], fly ash, guar gum-nano zinc oxide [21,22], natural clinoptilolite [23], Ca-alginate beads [24], lime fly ashes [25], bacteria exopolymer, gall nut, oak fruit [26], *Trichoderma harzianum* [27], *Anthrobacter* sp. biomass [28], *Zea mays* seed chaff [29], mesoporous silica and graphene oxide nanoparticles-modified *N. diderrichii* [30,31], biomass-derived fly ash [32], etc. The effects of these hazardous metal ions on the environment are fast growing and thus researchers have shown keen interest in using materials of biological origin (agrolignocellulosics) to develop selective adsorbents to combat this global menace [3].

Two major drawbacks of adsorbents of agricultural origin are that they easily degrade (bleed) in solutions after few hours and they are unable to withstand high temperatures during use [33]. These limit their industrial application. An attempt to overcome these challenges has been demonstrated by Unuabonah et al. [33,34] who made a *C. papaya*-kaolinite clay combo adsorbent with high efficiency for the removal of metal ions from aqueous solutions.

This study reports the development, characterization and application of a new facile environmentally-benign adsorbent prepared from *N. diderrichii* agrolignocellulosic waste (NDS) and nano-titania for the removal of Cr(III) and Pb(II) ions from aqueous solutions. The NDS-nano titania hybrid adsorbent (TND) prepared is expected to have high adsorption capacity and initial sorption rate for the toxic metal ions when compared with NDS. TND is reported for the first time to sequester Cr(III) and Pb(II) ions from aqua system.

2. Materials and methods

2.1. Preparation of NDS, nano-titania and TND

N. diderrichii seeds were obtained from the Forest Research Institute of Nigeria (FRIN), in Ibadan (7° 23' 16" North, 3° 53' 47" East), Nigeria. After collection, it was heated in an oven at 60 °C for 3 h. Thereafter, it was pulverized and sieved to 450 μm particle size.

Nano-titania was synthesized using the sol-gel method by Choi et al. [35]. Transparent colloidal particles were formed immediately, which after evaporation led to a yellowish titania powder. This as-prepared yellowish titania powder was calcined at 550 °C for 6 h until the amorphous and low crystalline titania powder metamorphosed into highly crystalline titania powder.

Thereafter, the yellowish titania powder and NDS were placed in a 1 L beaker containing 700 mL ultra-pure de-ionized water from millipore water instrument in the ratio 0.5–1. The reaction mixture was agitated at 1000 rpm at 20 °C for 48 h. The NDS-nano titania hybrid adsorbent (TND) was also filtered by vacuum filtration and the wet TND material was placed in a heating crucible and dried at 100 °C overnight. The TND material was weighed into 3 mL plastic containers and kept for use in adsorption study.

2.2. Characterizations of NDS, nano-titania and TND

N. diderrichii seed agrolignocellulosic (NDS), nano-titania and TND were characterized using PerkinElmer Fourier Transform Infra Red (FTIR) spectrometer, Micromeritics Instrument Corporation, ASAP 2020 Model Analyzer (for Brunauer-Emmett-Teller (BET) nitrogen sorption-desorption multi-point analysis at 77 K), X-ray diffractometer (XRD) (D/Max-2500, Rigaku, Japan) with Cu Kα

radiation, PerkinElmer thermogravimetric analyzer (TG), F20 S-TWIN transmission electron microscope (TEM) (Tecnai G2, FEI Co.) and scanning electron microscope (SEM) (Hitachi S4800 Model).

2.3. Adsorption study

Fifty milligrams of NDS and TND adsorbents each were added to 20 mL of 20 mg/L of Cr(III) and Pb(II) aqueous solutions, prepared from Cr(NO₃)₃·9H₂O and Pb(NO₃)₂ salts, both of analytical grade, whose pH values were adjusted to 7.0 and 5.0, respectively, (pH values of maximum adsorption obtained from initial pH study {data not shown}) with either 0.1 M HNO₃ or NaOH.

For kinetic study, the suspensions under the same conditions above were agitated between 5 and 60 min, at 125 rpm and at temperatures of 303 K in a thermostatic shaker. Samples were withdrawn at various time intervals and filtered using filter papers. The supernatants obtained were analyzed for residual Cr(III) and Pb(II) ions using ICP-OES (inductively coupled plasma-optical emission spectrometer), PerkinElmer Optima 5300 DV Model. The amounts of Cr(III) and Pb(II) sequestered by NDS and TND adsorbents were calculated by difference using the equation;

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o is the initial concentration of metal ion (mg/L), C_e is the equilibrium concentration of residual metal ion in the solution (mg/L), V is the volume of the aqueous solution containing metal ions (L), W is the weight of adsorbent (g) and q_e is the amount of metal ion adsorbed by the adsorbent (mg/g).

Experimental data obtained from thermodynamic and kinetic studies described above were fitted into pseudo-second order [36], pseudo-first order [37], diffusion-chemisorption [38,39] and Weber-Morris intraparticle diffusion [18,40] models, respectively, which are written mathematically as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (2)$$

$$h_{\text{ads}} = k_2 q_e^2 \quad (3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t^{0.5}}{q_t} = \frac{t^{0.5}}{q_e} + \frac{1}{K_{\text{DC}}} \quad (5)$$

$$q_t = K_{\text{ip}} t^{1/2} + \psi \quad (6)$$

where k_1 , k_2 , h_{ads} , q_t , K_{ip} , ψ , K_{DC} are pseudo-first order rate constant (/min), pseudo-second order rate constant (g/mg min), initial sorption rate (mg/g min), amount of metal ion adsorbed at time t (min) by the adsorbent (mg/g), Weber-Morris intraparticle diffusion constant (mg/g min^{1/2}), the value film layer thickness and rate of mass transfer of adsorbate (mg/g t^{1/2}), respectively.

3. Results and discussion

3.1. FTIR analyses of NDS, nano-titania and TND

The FTIR spectrum of NDS has been previously described by Omorogie et al. [19]. Fig. 1 shows the FTIR spectra of nano-titania and TND. The FTIR spectrum of nano-titania showed a long shoulder peak at 1092 cm⁻¹ and short peaks at 3291 cm⁻¹, 2926 cm⁻¹, 1619 cm⁻¹ and 801 cm⁻¹ indicating -C-O stretch vibration from titania precursor (titanium isopropoxide), surface -O-H stretch, -C-H stretch vibration due to titania precursor, -C=O stretch vibration and -C-O in-plane deformation for Ti-O, respectively [41]. For TND, the surface -O-H stretch at 3291 cm⁻¹ in nano-titania became broadened and shifted to 3432 cm⁻¹. This may be due to the modification of nano-titania with NDS. Also, various

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