Solid Phase Extraction of Hazardous metals from Aqua system by Nanoparticle-modified Agrowaste composite Adsorbents

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A B S T R A C T

This study reports for the first time the adsorption of Cd(II) and Hg(II) ions from simulated wastewaters onto Nauclea diderrichii agrowaste (NDS) modified with mesoporous SiO_2 (MND) and mesoporous SiO_2 + graphene oxide (GND). Modification of NDS with mesoporous SiO_2 and graphene oxide improved its adsorption capacity for Cd(II) and Hg(II) in aqueous solution with surface area increasing from 5.4 m^2/g (in NDS) to 209 m^2/g (in MND) and 267 m^2/g (in GND) respectively. The modification of NDS also improved its rate of uptake of both metal ions with uptake rate of Hg(II) being more than that of Cd(II). Kinetic data obtained gave better fit to the pseudo-second order kinetic model than to pseudo-first order, Elovich, modified pseudo-first order, ion exchange or Weber–Morris intraparticle diffusion kinetic models. Data obtained from the Weber–Morris intraparticle diffusion model suggests that pore diffusion mechanism may have played a significant role in the adsorption process. Thermodynamic data showed negative and positive values for $\Delta G°$ and $\Delta H°$ respectively for the adsorption systems, which supports the fact that the adsorption of both Cd(II) and Hg(II) by MND and GND adsorbents was feasible, spontaneous and endothermic in nature.

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Introduction

Global industrialization has led to an increase in the release of different pollutants into the ecosystems, many of which are non-biodegradable, thereby reducing the quality of the environment [1]. One of the most challenging issues in the globe today is that of environmental pollution caused by toxic heavy metals and their consequences on human life and ecology [1]. Contamination of various water bodies, land and biota by heavy metal ions has risen to levels that require urgent attention. Industrial activities are the major sources of cadmium {Cd(II)} and mercury {Hg(II)} ions including mining processes, metal plating, oil refining, electronic device manufacturing, printing, production of chemicals, dyes and paints, pulp and paper, textiles, petrochemicals, leather, fertilizers and pesticides [2,3].

Heavy metals are harmful to human health and to the environment due to their non-biodegradability. The World Health Organization (WHO) maximum tolerable limits for Cd(II) and Hg(II) ions in drinking water are 0.003 mg/L and 0.001 mg/L

respectively [4]. They accumulate in living organisms causing various disorders. Hence, it is necessary to remove them from the ecosystem [5]. For instance, Cd(II) is one of the heavy metal ions found at the top of the toxicity list [5]. Due to its non-biodegradability, Cd(II) accumulates in plants and its level increases along the food chain. At higher trophic levels, the toxic effect of cadmium is more pronounced in animals. Cadmium toxicity has been reported as one of the causes of cancer, hypertension, weight loss, bone lesions and Itai–Itai disease [1,6,7].

Cadmium is transferred through the food chain system of soil–plant–animal–human into animals and human beings, causing severe health implications. Its accumulation in organs through the ingestion of cadmium-contaminated food leads to the malfunction of such organ, for example, spilling of protein into the urine from cadmium contaminated kidney which disrupts protein metabolism [7].

Mercury is generally considered the most toxic metal in ecosystems [8]. Its different toxic forms are mainly elemental mercury, inorganomercurials and organomercurials. Its toxicity depends on temperature, pH and the presence of chlorine and sulphur. [9]. In particular, methyl mercury has been shown to be extremely detrimental to childhood growth at very low doses [10] and causes impairment of the kidney, chest pain and dyspnea [11,12].

Various researchers have used different agrowastes to remove these toxic metals from industrial wastewaters because they are cheap and readily available [1–18]. Literature has shown lately that various adsorbents such as dried *Opuntia ficus indica* [19], *Spirodela polyrhiza* L. [20], goethite [21], resin grafted coconut activated charcoal [22], dithiocarbamate chelating resin [23], chitosan and chitosan derivatives [24], ionic liquids modified palm shell activated carbon [25], charcoal immobilized papain [26], bamboo leaf powder [27], triton-X and sodium dodecyl sulphate modified bamboo leaf powder [27], sodium-zeolite tuff [28], porous glass beads/chitosan support [29], *Nauclea didderrichii* [13,14], *Zea mays* seed chaff [30], defatted *Carica papaya* seed [31], *Carica papaya* seed-Kaolinite [2], etc. have been used for cadmium and mercury adsorption.

However, recent advances in materials science have also shown that various materials synthesized from various nanoparticles, especially magnetic nanoparticles which are easily regenerated, chitosan (due to its multi-functionalities), biomaterials, activated carbons and polymers, have been used for adsorption purpose. These materials have also played the role of solid supports for various biosorbents and as functionalization substances, in order to increase their adsorption capacities. Some of the materials that have been used for adsorption of Cd(II) and Hg(II) ions in current times are sawdust and neem bark [32], activated alumina [33], rice husk ash [34], modified sludge [35], 3-hydroxybenzaldehyde modified bentonite and activated bentonite [36], lignocellulosic waste material [37], polymer modified Fe_3O_4 magnetic nanoparticles [38], SiO_2 and Fe_3O_4 modified with chitosan and EDTA [39], alginate modified pectin gel beads [40], sulphur impregnated activated carbon [41], carbonaceous rice husk [42], thiol functionalized mesoporous silica [43], mercapto-functionalized nanomagnetic Fe_3O_4 polymer [44], poly(c-glutamic acid) biopolymer [45], ground-up tree fern [46], thiourea modified magnetic chitosan [47], diethylene triamine modified silica gel [48], polyamidoamine functionalized chitosan [49], polyacrylonitrile-N-chlorosulphonated polystyrene [50], amidoxime modified silica gel [51], polyamine modified silica [52], sulphur-amidoxime modified silica gel [53], Schiff's base modified magnetic chitosan resin [54] and mercapto-modified Fe_3O_4 magnetic nanosorbent [55]. However, the use of adsorbents of agricultural origin has a draw back known as 'bleeding' [2]. This is due to their biodegradability in aqueous media after some hours. Some adsorbents of agricultural origin also have the disadvantage that they do not possess the appropriate bulk densities needed for industrial applications [2].

Mesoporous materials have been applied in surface processes like catalysis and adsorption [56–59]. In recent times functionalities have been grafted to the surfaces of various types of mesoporous materials to selectively adsorb various pollutants of interest from aqueous media [60–62]. This study reports for the first time the adsorption capacities of a new class of adsorbent-nanoparticle modified agrowaste adsorbent, using *Nauclea didderrichii* agrowaste (NDS) modified with mesoporous SiO_2 and mesoporous SiO_2 + graphene oxide for the adsorption of Cd(II) and Hg(II) ions from simulated wastewater system.

As a follow up to our previous research work [13], this modification is aimed at improving the surface textural properties and functionalities of NDS and thus increasing its adsorption capacities and uptake rates for Cd(II) and Hg(II) ions.

Experimental

Preparation/characterizations of samples and adsorption study

Nauclea didderrichii agrowaste (NDS) was 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. Mesoporous SiO_2 was prepared by liquid templating method as described by Kresge et al. [56]. One gram of CTAB (Cethyl Trimethyl Ammonium Bromide) was weighed and dissolved in 480 mL deionized water. A 3.5 mL of 2 M NaOH was added to CTAB/H_2O solution. This was heated with an electric heater to 80 °C and the beaker containing the CTAB/H_2O solution was immersed in a silicone oil bath. The reaction mixture was agitated continuously at 1000 rpm for 1 h. Thereafter, 6 mL of TEOS (tetra ethyl ortho silicate) was added dropwisely to the reaction mixture and heated at 80 °C for 2 h. After cooling, the white precipitate formed was separated from the suspension using a separating funnel under vacuum. The white precipitate obtained was dried in an oven for 3 h at 100 °C before being calcined for 5 h at 550 °C [56].

The mesoporous SiO_2 prepared initially was subsequently added to NDS (in the ratio of 1:2, w/w) in 500 mL deionized water from Millipore water instrument. This reaction mixture was agitated at 1000 rpm at 20 °C for 48 h and the NDS + mesoporous SiO_2 (MND) was filtered via vacuum filtration. The wet MND was placed in an oven and dried at 100 °C overnight and kept for further use.

Graphene oxide was synthesized by chemical oxidation of natural graphite flake according to methods described by Hummers and Offeman [63]. Concentrated sulphuric acid and orthophosphoric acid (400:50 mL) were added to a mixture of $KMnO_4$ (30 g) and graphite (5 g). It was heated to 50 °C and stirred for 24 h. The resulting mixture was poured into ice (250 mL) and H_2O_2 (30%, 50 mL) and then filtered using a polycarbonate membrane. The solid product, graphene oxide was washed with water, 30% HCl, and ethanol two times before vacuum drying for 12 h using vacuum dessicator. The NDS + mesoporous SiO_2 + graphene oxide (GND) was also prepared by subsequently adding NDS, mesoporous SiO_2 and graphene oxide (in the ratio of 1:0.5:2, w/w) in 700 mL deionized water from Millipore water instrument. The reaction mixture was agitated at 1000 rpm at 20 °C for 48 h. The GND was also filtered by vacuum and wet GND was placed in a heating crucible and dried at 100 °C overnight. The GND was kept for further use. Thereafter, various surface characterizations of NDS, mesoporous SiO_2, graphene oxide, MND and GND were carried out using Perkin Elmer Spectrum 1 Fourier transform infra red (FTIR) spectrometer, Perkin Elmer Thermogravimetric analyzer (TG), X-ray diffractometer (XRD) D/Max-2500 (Rigaku, Japan) with Cu Kα radiation, λ = 0.154056 nm, Multipoint technique of nitrogen adsorption–desorption {Brunauer–Emmett–Teller (BET)} at 77 K by Micromeritics Instrument Corporation, ASAP 2020 Model analyzer, scanning electron microscope (SEM) (Hitachi S4800 Model) and transmission electron microscope (TEM), F20 S-TWIN, Tecnai G2, FEI Co.), at 200 kV accelerating voltage.

Adsorption experiments were carried out with fifty milligrams of MND and GND adsorbents were added to 20 mL of 20 mg/L Cd(II) and Hg(II) aqueous solutions, prepared from $Cd(NO_3)_2 \cdot 4H_2O$ and $Hg(NO_3)_2 \cdot \frac{1}{2}H_2O$ of analytical grade, whose pH values were adjusted to 7.0 and 4.0 respectively (pH values of maximum adsorption were obtained from initial pH study {Data not shown}) with either 0.1 M HNO_3 or NaOH.

One thousand milligrams per liter of Cd(II) and Hg(II) aqueous solutions (simulated wastewater) were prepared by dissolving accurately weighed amounts of $Cd(NO_3)_2 \cdot 4H_2O$ and $Hg(NO_3)_2 \cdot \frac{1}{2}H_2O$ (analytical grade) in 1 L of deionized water from Millipore water instrument. Furthermore, 20 mg/L of simulated wastewater containing Cd(II) and Hg(II) ions was prepared from 1000 mg/L by serial dilution.

For kinetic study, the suspensions under same conditions above were agitated in a rotary shaker. Samples were withdrawn at