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Fast microwave-assisted sorption of heavy metals on the surface of nanosilica-functionalized-glycine and reduced glutathione

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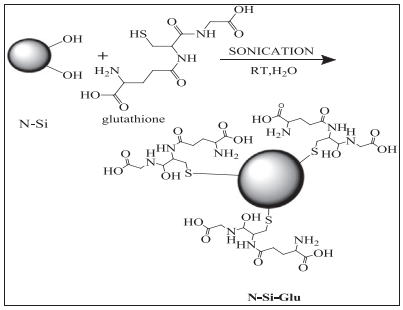
GRAPHICAL ABSTRACT



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ABSTRACT

Two eco-friendly nanosorbents have been designed and synthesized via surface crosslinking of nanosilica (N-Si) with glycine (Gly) and reduced glutathione (GSH) to produce (N-Si-Gly) and (N-Si-Glu) using crosslinking reagent and sonochemical reactions, respectively. An investigation was performed to search selectivity of nanosorbents via microwave-assisted removal of Ni(II)/Cu(II)/Cd(II)/Pb(II) to affirm green and fast technique. The microwave-assisted removal values of Ni(II), Cu(II), Cd(II) and Pb(II) were observed at 850, 2100, 3500 and 2150 μmol g^{-1}, respectively utilizing 10 mg of (N-Si-Glu) and 25.0 s heating, while those corresponded to 750, 1800, 2500 and 1850 μmol g^{-1}, respectively by using (N-Si-Gly). The microwave-assisted removal processes were more fitted to Freundlich compared to Langmuir isotherm except in case of Pb(II). The high percent removal of Cd(II) and Pb(II) ions exceed 95% from the second run in real wastewater samples indicating the efficiency of N-Si-Glu in the uptake of these metals utilizing microwave-assisted sorption technique.

1. Introduction

Heavy metal ions infection in water has to turn out to an international environmental subject and trouble. Mining operations, tanneries, batteries manufacturing, microelectronics, and petrochemical industries are the predominant assets for heavy metal ions contamination in water. These metals in excess quantity are dangerous to the human and biological system due to their lethality and accumulation within the flora and body (Gong et al., 2018; Wang et al., 2017a) The metal completing enterprises and electroplating are in particular accountable for Cu(II) contamination in water. Cu(II) makes keratinization, a dramatization of fingers, and itching. The kidney dysfunction and severe gastrointestinal irritation have occurred on account of the immoderate consumption of Cu(II). Inhalation of copper spray grows the risk of a lung tumor in uncovered people (Kong et al., 2011; Ghorbani and Eisazadeh, 2012; Pellera et al., 2012). Ni(II) has widely existed in

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surface water, and even in drinking water, discharged from cadmium-nickel batteries, phosphate fertilizers, pigments, sewage sludge and alloy industries. Nickel in additional amount makes emphysema and hypertension (Heidmann and Calmano, 2008; Fu and Wang, 2011).

Various technologies had been finished for heavy metallic containing wastewater remedy, consisting of electrocoagulation, chemical precipitation, ion-exchange, and so forth. Amongst these, adsorption strategy is broadly carried out because of excessive performance, low operation costs, and smooth operation (Akbal and Camci, 2011; Iqbal et al., 2009; Hossain et al., 2014; Yang et al., 2015).

Microwave-assisted sorption method was employed for extraction and expulsion of heavy metals from water samples. This system is recommended to work by the relocation of the adsorbate from solution and adsorption on the sorbent surface in a couple of seconds affected by microwave warming illumination to build up a harmony condition (Mahmoud et al., 2016b; Mahmoud et al., 2017a). This system is working in the invert heading of the microwave-assisted extraction (MAE) process (Chen et al., 2016). This strategy is basically mentioned to green and economical chemistry as it can expand productivity, upgrade wellbeing in a couple of various ways enhancing yields and keeping from waste generation through cleaner handling.

In most recent years, opportunity innovations utilizing nanomaterials have attracted enormous interest in natural remediation. The recently applied and implemented sorbents in this discipline are customarily in view of low-cost substances (Callery et al., 2016), polymeric compounds (Huang et al., 2016; Shen et al., 2015) and also derivatives of metal oxide (Rafiq et al., 2014; Hua et al., 2012).

Reduced glutathione (GSH, (ɣ-Glu-Cys-Gly)), plays a vital part in the human body by preventing damage to critical cell parts caused by reactive oxygen species, for example, heavy metals. It keeps up levels of reduced glutathione peroxidase and glutaredoxin. It maintains exogenous cancer prevention agents, for example, vitamins C and E in their reduced (active) forms. It has an ability to maintain sulfhydryl groups of proteins in the reduced shape and keep up thiol redox potential in cells. From the spearheading work, it is understood that GSH can adequately secure natural cells from the troublesome impacts that start from oxidizing substances and radiation harm (Maher, 2005; Cotgreave and Gerdes, 1998). In view of the literature survey, some research works have been centered around GSH uses in different fields of chemistry, for example, utilizing glutathione-stabilized gold bunches (GSH-Au NCs) as a fluorescent probe for particular determination of Cr (III) and Cr(VI) (Zhang et al., 2013). Glutathione-based nano-organocatalyst was used for microwave-assisted pyrazole, Paal–Knorr reaction and aza-Michael addition synthesis in water (Polshettiwar and Varma, 2010a). GSH immobilized nano iron oxide was reported for the expulsion of Pb(II) from wastewater (Xu et al., 2017). The utilization of glutathione (over other amino acids) as a dynamic catalytic moiety is favored because of its considerate nature and also the nearness of the exceedingly unique thiol gathering. The N-Si was arranged by sonochemical covalent bonding of glutathione atoms through coupling of its thiol group with the free hydroxyl groups of nanosorbent surfaces.

Glycine and reduced glutathione are known as green chemical compounds that are characterized by the presence of some donor atoms such as nitrogen, oxygen and sulfur. Surface modification of nanoosilica with glycine and reduced glutathione using crosslinking reagent and sonochemical reactions provided ecofriendly nanosorbents for removal of heavy metals from water. In this work, reduced glutathione has been used as a surface modifier for N-Si surface by sonochemical reaction to produce N-Si-Glu. In addition, the N-Si surface was aimed to immobilize with glycine via glutaraldehyde as a crosslinking agent for the preparation of N-Si-Gly. The two nanosorbents are compared via optimization of the microwave-assisted sorption technique as a green and efficient protocol for removal of Ni(II), Cu(II), Cd(II) and Pb(II) from real samples under different test controlling parameters. It is also aimed to apply and investigate the microwave-assisted sorption technique to confirm its capability of higher sorption behavior and faster operating time.

2. Materials and methods

2.1. Characterization of N-Si-Glu and N-Si-Gly

Thermal gravimetric analysis (TGA) of nanosilica and the other immobilized nanosorbents were examined by utilizing a Perkin–Elmer TGA7 Thermobalance. The selected operating conditions were the temperature warming reach 20–600 °C, heating rate 10 °C min^{-1}, flow rate 20 mL min^{-1} pure N_2 atmosphere. The infrared spectra of nanosilica and immobilized nanosilica sorbents were recorded from KBr pellets by using a BRUKER Vertex 70 Fourier transform infrared spectrophotometer in the degree of 400–4000 cm^{-1}. SEM (JSM-6360LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.), an ion sputtering coating device (JEOL-JFC-1100E) and HR-TEM images were taken by a (JEOL-JEM2100F, Japan) at 200 kV to examine the surface morphology and determine the particle size of all nanosilica sorbents.

The crystalline structures of the nanosorbents were inspected utilizing X-ray diffraction (XRD) by Shimadzu XRD-6100, X-ray diffractometer utilizing target Cu-Kα. Surface area analysis was performed by using (BELSORP –mini II nitrogen physisorption, Japan) in order to measure the surface area of nanosorbents. The concentrations of analyzed metals were dictated by utilizing a Perkin Elmer atomic absorption spectrophotometer, model 2380.

Samsung microwave oven (ME732K, Korea) was utilized for nanosilica modification and equipped with the following specifications. The power source = 240 V–50 Hz, operating frequency = 2.450 MHz microwave input power = 1150 W, microwave energy output = 800 W.

2.2. Chemicals

Nanosilica (10–20 nm), L-Glutathione reduced (F.W. 307.32) were purchased from Aldrich Chemical Company, Milwaukee, WI, USA. Different concentrations of Ni(II), Cu(II), Cd(II) and Pb(II) solutions were prepared from a stock solution of (0.01 M) by dissolving 3.58 g of $Ni(SO_4)_2{\cdot}6H_2O$,1.70 g of $CuCl_2{\cdot}2H_2O$, 1.83 g of $CdCl_2$ and 3.79 g of $Pb(CH_3COO)_2{\cdot}3H_2O$, respectively in double distilled water (DDW) to form 1.0 L solution and the accurate concentrations of these ions were examined by complexometric titration with standard 0.01 M EDTA utilizing the fitting buffer and indicator.

2.3. Functionalization of NSi with glycine

Nanosilica sorbent was activated following the protocol previously described by our group (Mahmoud et al., 2016c). Adding 2.0 g of glycine, 150 mL ethanol, and 7 mL of glutaraldehyde were mixed with 2.0 g of activated nanosilica. This mixture was refluxed for 12 h. The produced nanosorbent (N-Si-Gly) was then separated by filtration washed with water and ethanol and dried in an oven at 60 °C.

2.4. Anchoring of glutathione (reduced form) on nanosilica sorbent

3 g activated (N-Si) was dispersed in (30 mL ethanol + 90 mL DDW) and sonicated for 20 min. 2.4 g L-glutathione reduced form dissolved in 30 mL DDW was mixed with the above solution and again sonicated for 2 h. This mixture was stirred for 12 h at room temperature. Then the glutathione-functionalized nanosilica (N-Si-Glu) was isolated by centrifugation at 15,000 rpm for 20 min and purified through triplet washes with (75 mL of ethanol +25 mL DDW) and dried under vacuum.

2.5. Microwave-assisted sorption of metal ions by N-Si-Gly and N-Si-Glu

2.5.1. Heating time impact on the microwave-assisted sorption values

10.0 ± 1.0 mg of the selected nanosorbent, (N-Si-Gly) or (N-Si-Glu) was transferred in a test tube and mixed with a 10.0 mL aliquot of 0.01 M divalent metal ion. This mixture was warmed for the selected time period (5, 10, 15, 20 and 25 s) inside a microwave at 800 W. The