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Synthesis and characterization of novel single-walled carbon nanotubes- doped walnut shell composite and its adsorption performance for lead in aqueous solutions

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ABSTRACT

In this study, first the adsorption potential of different synthesized carbon nanostructures, including single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes doped with iron (SWCNTs/Fe), and carbon nanofibers (CNFs), was compared in terms of their lead removal capacity. The results revealed that under similar conditions, SWCNTs have the most sorption capability for Pb(II) ions. A novel adsorbent, highly pure (~99%) single-walled carbon nanotubes-doped walnut shell composite (SWCNTs/WSh), was then prepared by immobilizing SWCNT particles on the surface of walnut shell. This adsorbent was examined to evaluate its potential to remove Pb(II) ions from aqueous solutions. SWCNTs and SWCNTs/WSh composite were characterized by TEM, FT-IR, SEM and BET measurements. The effects of several parameters, such as contact time, solution pH, adsorbent dose, metal concentration, and temperature, were studied in order to find the optimum adsorption conditions. The results showed that the adsorption kinetics could be explained well by means of the pseudo second order and intra-particle diffusion models. The equilibrium adsorption isotherm followed the Langmuir equation well. The maximum Pb(II) uptake predicted was 185.2 mg g^{-1}. In conclusion, the SWCNTs/WSh composite can be used as an effective adsorbent for the removal of Pb(II) ions from aqueous solutions.

Introduction

Heavy metals released into the environment as a result of different industrial activities pose a significant threat to the ecosystem and, consequently, human health because of their toxicity and persistence [1]. Thus, it is crucial that heavy metals be removed from wastewater effectively before being discharged into the environment. Conventional treatment technologies used for heavy metal removal mainly include ion exchange, filtration, chemical precipitation, reverse osmosis, solvent extraction, and membrane separation, etc. [2–6]. However, these technologies generally cannot perfectly follow the increasingly stringent regulations on the heavy metal discharge in a cost effective manner [5,7]. Therefore the identification of feasible technologies for heavy metal separation and removal from aqueous solutions has become all the more important.

Adsorption is an attractive method for the heavy metal removal due to its simplicity, ease of operation, regeneration capacity, sludge-free operation, and low cost for industrial application [8–10]. Various materials have been studied to determine their efficiency in heavy metal adsorption, including activated carbon [11–13], nut shells [14,15], agricultural by-products [16,17], biomaterials [18–20], and clay materials [21]. However, the adsorption performance of most of these materials has been, for the most part, unsatisfactory. To further improve adsorption efficiency, the discovery of application of more efficient adsorbents seems necessary.

Carbon nanostructures have been demonstrated to hold great potential as superior adsorbents in the removal of organic and inorganic contaminants from aqueous solutions in recent years [22,23]. The adsorption capability of carbon nanostructures can be attributed to their exceptional properties, such as their large specific surface area, light mass density, greater active sites, and highly porous, small, hollow, and layered structure [7,22,24]. However, nanomaterials usually exist as fine powders, which cannot be used in continuous flow systems unless they are of granular shape [10,25], thus severely limiting their wider

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industrial-scale applicability. Furthermore, the direct application of nanomaterial powders in water and wastewater treatment systems can lead to increasing emissions to the environment, which in turn may result in human contact risk to carbon nanomaterials [24].

In order to overcome these problems and improve heavy metal adsorption performance, in this research a novel adsorbent was concocted by immobilizing carbon nanostructures on the surface of a natural adsorbent. Using this new adsorbent, it is possible to benefit from the adsorption capacity of both the natural adsorbent and the nanostructure for heavy metal removal while also controlling nanomaterials emissions to the environment. Furthermore, natural adsorbent, as a supporting material, prevents the aggregation of nanomaterials, providing a larger surface area for Pb(II) sorption.

To achieve desirable adsorption characteristics, it is important to have a nano-composite adsorbent with high mechanical stability. Thus, it is necessary to find methods of immobilizing the carbon nanostructures on a suitable supporting material. Walnut shell, with its low cost, porous structures, excellent mechanical and physical properties, nontoxic nature, and its widespread availability, can serve as an ideal base material for immobilizing nanomaterials and has already been used as a heavy metal adsorbent in environmental protection [26]. Recently, calcium alginate beads [27], tea waste [28], activated carbon fiber [25], rice husk [29], sodium dodecyl sulphate [30], alginate [3,31], sawdust [32], and even sand [4,33] have been utilized in wastewater treatment for the immobilization of iron nanoparticles, nano-particles of hydrated ferric oxide, polyaniline and polypyrrole nanocomposites, magnetite nanoparticles, nanohydroxyapatite, nano-manganese and magnetic ferrite nanoparticles, $CuFe_2O_4$, and iron oxide nanoparticles, respectively. Despite sand's poor ability to remove heavy metals from water, Tian et al. (2012) utilized it as a base material for the deposition of carbon nanotubes (CNTs) in their research. The maximum sorption capacity of this new adsorbent for lead was 92.3 $\mathrm{m\,g\,g^{-1}}$ [24]. Considering the results obtained in previous research, it seems that a combination of carbon nanostructures and a material characterized by a significant metal adsorption factor can yield more effective adsorbents for the removal of these contaminants from wastewater samples. To the best of the authors' knowledge, there has been no published report on the application of carbon nanostructure-doped walnut shell composite (SWCNTs/WSh) for this purpose to this day.

The main objectives of the present work were to compare the adsorption capability of various carbon nanostructures for lead removal, prepare a novel adsorbent by immobilizing an appropriate carbon nanostructure on the surface of walnut shell, and determine the Pb(II) adsorption potential of this new adsorbent. The effect of various experimental parameters on uptake capacity was studied to understand the adsorption mechanism through various isotherms and their characteristic parameters. These parameters included contact time, solution pH, adsorbent dose, metal ion concentration, and temperature. The Pb(II) adsorption kinetics have also been discussed in this paper.

Experimental

Materials and methods

All chemicals used in this work were of analytical grade and purchased from Merck (Germany). The aqueous solutions were prepared using distilled water. Analytical grade lead nitrate was used to prepare 1000 $\mathrm{mg\,L^{-1}}$ stock solutions of lead ions, which were further diluted to the concentrations required for the investigation before use. All experiments were conducted at a constant temperature of 25 ± 0.1 °C.

Synthesis of carbon nanotubes (CNTs)

Various types of carbon nanostructures, including single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes doped with iron (SWCNTs/Fe), and carbon nanofibers (CNFs), were prepared by using the chemical vapor deposition (CVD) method at a temperature of ~1250 °C using acetylene, as the source of carbon, and ferrocene, as the source of iron nanoparticles, for the catalytic deposition of carbon vapor. For this purpose, acetylene, as the source of carbon, was bubbled via a solution of ferrocene and thiophene in benzene, mixed with hydrogen and argon, and then introduced to the line. The flow of all gases was automatically controlled using solenoid valves. The whole system is also controlled via custom computer software written in Visual Basic.

The synthesized CNTs were then directly purified end-opened and activated by means of purging oxygen in addition to using magnets, microwave radiations and ultraviolet (UV). This process resulted in highly pure CNT bundles (~99% purity percentage) with size distributions of 10–30 nm (SWCNTs), 40–60 nm (MWCNTs), 2–10 nm (SWCNTs/Fe), and 250–400 nm (CNFs).

Synthesis of SWCNT/WSh composite

Walnut shell was ground to give a fraction with uniform particle sizes of 0.6–2.0 mm. Afterwards, it was washed with distilled water several times to remove adhering dirt, and it was then dried at room temperature to evaporate the moisture. Next, the SWCNTs/WSh composite was synthesized by means of coating the purified SWCNTs on the surface of walnut shell using the CVD method, then purified via annealing the composite at ~500 °C for ~5 h, and finally cooled to room temperature with temperature ram equal to ~2 $\mathrm{°C\,min^{-1}}$.

Different percentages of SWCNTs/WSh composites ranging from 5 to 10 wt.% were prepared in this study. According to the preliminary adsorption experiments, the same Pb(II) adsorption percentage was achieved for all of the SWCNTs/WSh composite samples. Therefore, a ratio of ~5 wt.% was selected for doping walnut shell with SWCNTs.

Characterization and measurement tools

The morphological structure of the novel composite adsorbent was determined by means of scanning electron microscopy (SEM) using a Cambridge S360 scanning microscope. The surface functional groups of the prepared SWCNTs were studied using "Fourier-transform infrared" (FT-IR) spectrometry (Shimadzu 8000) with KBr as the background. The size and morphology of the SWCNTs were observed using a transmission microscope. The Pb(II) concentrations were measured using a Shimadzu A-A 680 (Japan), atomic absorption spectrophotometer. Total carbon (TC) analysis was performed by a total organic carbon analyzer (Shimadzu TOC-500, Japan). The specific surface areas of the raw walnut shell (RWSh) and SWCNTs/WSh composite were determined according to the technique described by Araujo and Jaroniec [34], using a lab-made thermogravimetric (TG) analyzer.

Adsorption experiments

The Pb(II) adsorption experiments were carried out by mixing the adsorbent in glass jars containing 250 mL of lead solution at an agitation speed of 65 revolutions per minute (rpm) and a temperature of 25 °C. Samples were withdrawn from the rotary shaker at appropriate time intervals and filtered using a 0.45-μm syringe filter to be analyzed for adsorption efficiency.