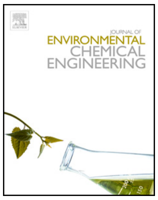
Journal of Environmental Chemical Engineering 4 (2016) 398–404

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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



A novel bio-compatible sorbent based on carbon nanostructure modified by porphyrin for heavy metal separation from industrial wastewaters

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ARTICLE INFO

Article history:
Received 11 August 2015
Received in revised form 25 October 2015
Accepted 25 November 2015
Available online 27 November 2015

Keywords:
Heavy metal separation
Industrial wastewater
Bio-compatible sorbent
Carbon nanostructure

ABSTRACT

A novel method for heavy metal separation has been developed using a carbon nanostructure material. This nanostructure material has been synthesized by hydrothermal condensation of Fructose and modified by porphyrin as a bio-compatible ligand. The formation of this nanostructure was confirmed by infrared spectroscopy (IR), N_2 adsorption, thermal analysis (TG/DTA), X-Ray powder diffraction (XRD), elemental analysis (CHN) and high resolution transmission electron microscopy (HRTEM). The application of this bio-compatible sorbent was investigated in Cd(II), Ni(II), Cu(II) and Fe(III) separation from aqueous solutions. Several parameters such as sample pH, sample flow rate and temperature were analysed through this study. Finally, in order to investigate the applicability of this sorbent, the sorbent was applied for heavy metals separation in industrial wastewater and natural samples.

1. Introduction

Heavy metals are toxic and harmful to people and other living creatures and exposure to them through ingestion or uptake of drinking water and food products can lead to its accumulation in plants and animals [1]. With the rapid development of modern industries, the concentration of heavy metals in wastewater is increasing rapidly [2,3]. These heavy metal ions like cadmium, copper, iron, and nickel ions in the environment (specifically in the food chain) can cause serious health problems [4]. So heavy metal removal is both a very pertinent and also challenging issue for environmental engineering.

Various removal methods including precipitation [5]; ion exchange [6]; coagulation and flocculation [7]; and membrane filtration [8] have been developed in the past for the removal of heavy metals from wastewater. These methods often require large quantities of organic solvents, many of which are harmful to health and can cause serious environmental problems [9–11]. They also have low reusability and in some cases have challenging disposal issues and are often of a very high cost [12].

On the other hand, adsorption is one of the most economical and widely used techniques for heavy metal removal in wastewater and offers several advantages such as low cost, ease of use, high removal capacity and flexibility in design and operation [13–15]. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by a suitable desorption process [16]. In this regard, various ranges of sorbents such as alumina [17], zeolite [18], Fe_3O_4 [19], nanoporous materials [20] and carbon nanotubes [21] have been used for heavy metal removal.

Recently, the synthesis of carbon derivatives as bio-compatible materials has attracted scientific attention for use in heavy metals removal [22]. In addition to being bio-compatible, the nanostructure materials are also attractive due to their high thermal and chemical stabilities, large specific surface areas and convenient modifications [23]. Although these materials have lots of aforementioned advantages, their applications have been restricted without modification as there is no strong interaction between ions and sorbents [24]. Also non-modified sorbents do not act selectively and are not suitable to be used in natural samples.

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http://dx.doi.org/10.1016/j.jece.2015.11.034

Based on abovementioned situations and since bio-compatible materials are safe to be used in the living bodies, developing bio-compatible sorbents is vital for removing heavy metal ions from living cells. In this work, a biocompatible nanostructure carbon material was synthesized by fructose hydrothermal condensation in the presence of a surfactant in water. This sorbent was modified with amine groups and subsequently modified by porphyrin, as a bio-compatible ligand. After characterization this novel biocompatible sorbent was used for heavy metal removal from various aqueous solutions. In this heavy metal removal study, the effects of several parameters such as the sample pH, have been measured. Furthermore, the sorbent reusability and maximum adsorption capacities for each metal ion were calculated. Finally, in order to investigate the applicability of this sorbent, the sorbent was applied for heavy metal removal in industrial wastewater samples and several artificial samples.

2. Experimental

2.1. Reagents and materials

For this study, D-Fructose (Fru), 3-aminopropyltriethoxysilane, CH_2Cl_2, Ethanol, HNO_3, HCl and $HClO_4$ were of analytical grade and purchased from Merck Company (Darmstadt, Germany). The template (Pluronic® F127 triblock) ($M_w = 12600$, EO106–PO70–EO106) copolymer and stock solutions (1000 mg L^{-1}) of cadmium, nickel, copper, and iron ions were purchased from Sigma–Aldrich Company (Steinheim, Germany). All materials were used as received without any purification. To adjust pH of solutions to pH of 1.0 to 4.0, a mixture of $Na_3C_3H_5O(CO_2)_3$/HCl (trisodium citrate/hydrochloric acid) was used. A solution of $CH_3COOH/NaCH_3COO$ was used to adjust pH values in the range of 4.0–6.0 while a buffer solution containing Na_2HPO_4/NaH_2PO_4 was used for pH values in the range of 6.0–8.0.

2.2. Apparatus

Infrared spectroscopy (IR spectrum) was recorded on a BOMEM/MB series spectrometer. The samples preparations were performed by grounding KBr and the solid powder and making KBr pellets. The elemental analysis was performed with a Thermo Finnigan Flash-2000 microanalyzer (Italy). Metal ions determination were performed on a radial view Varian Vista-Pro simultaneous inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Springvale, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD). The instrument conditions were as follow: Ar coolant gas flow rate: 15.0 L min^{-1}; Ar carrier gas flow rate: 0.7 L min^{-1}; Ar auxiliary gas flow: 1.0 L min^{-1}; RF power supply: 1.3 kW. The wavelengths for copper, cadmium, nickel, and iron were 324.8, 228.8, 232.0 and 248.3 nm, respectively. In cases where ion concentrations were found to be higher than the linear calibration range of ICP-OES, the solution was diluted with deionized water and reanalyzed. The thermal analysis (TG/DTA) was carried out on a Bahr STA-503 instrument under air atmosphere (flow rate: from room temperature to 580 °C at a rate of 5 °C/min). All pH measurements were recorded at 25 ± 1 °C with a digital WTW Metrohm 827 Ion Analyzer (Herisau, Switzerland), equipped with a combined glass-calomel electrode. A peristaltic pump was obtained from Leybold (Cologne, Germany), and an adjustable vacuum gauge and controller were obtained from Analytichem International (Harber City, CA, USA). The adjustable vacuum gauge allowed for control of the flow rate during removal analysis. Specific surface area was measured by nitrogen adsorption technique (BET) using a Micrometritics ASPS 2010 analyzer. Sample tube was loaded with 500 mg of prepared sample and then sealed. Samples were degassed at 150 °C for 10 h and then transferred to the analyzer. Adsorption isotherms were measured at 77 K in a liquid-nitrogen bath. The HRTEM micrograph was recorded by a Philips EM420 transmission electron microscope. The samples were prepared by dispensing one microliter of diluted solution of prepared sample in methanol on Holey carbon grids and allowed to dry. The grids were then placed in a single tilt holder and TEM was operated at 120 keV.

2.3. Preparation of Tetraphenylporphyrin ($TPPH_2$)

Tetraphenylporphyrin ($TPPH_2$) was prepared according to the Lindsey method and its formation was confirmed by IR spectroscopy [25]. To obtain this compound, benzaldehyde, pyrrole and triethyl orthoacetate (1 mmol each) were dissolved in CH_2Cl_2 under nitrogen atmosphere. To this solution, 10 mL of boron trifluoride etherate solution (0.001 mol L^{-1}) was added and stirred

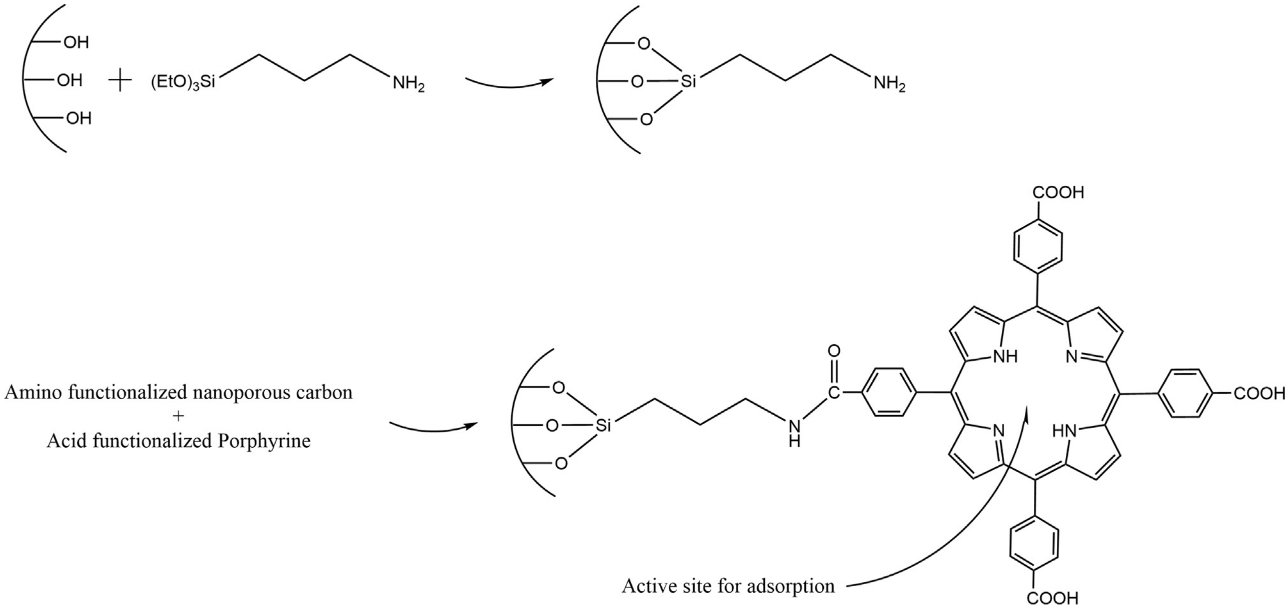

Fig. 1. A schematic diagram for sorbent synthesis.