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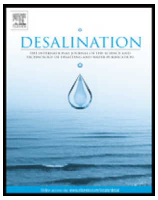

Carbon nanocages as heavy metal ion adsorbents

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ABSTRACT

Heavy metal ion contamination in drinking water poses a major risk to human health, whilst contamination in wastewater streams can cause damage to the wider environment. In this study carbon nanocages, synthesised using a supercritical fluid deposition method, were examined as adsorbents of Pb^{2+} ions from aqueous solutions. Through careful selection of the catalyst and the carbon deposition temperature and pressure, high yields of nanocages with surface areas up to 1175 $m^2\ g^{-1}$ were synthesised. These high surface area materials were subsequently tested for their ability to absorb Pb^{2+} ions, as a function of pH, from simulated wastewater. The nanocages were found to be effective at removing the Pb^{2+} ions at levels of 11.1 $mg\ g^{-1}$, compared to 7.6 $mg\ g^{-1}$ for commercially available activated carbon. The kinetics of metal ion adsorption by the nanocages and activated carbon can be described by a pseudo-second-order kinetics model, with a rate coefficient (k_2) of $4.8\times10^2\ g\ mg^{-1}\ min^{-1}$.

1. Introduction

Heavy metal ion contamination in waste and drinking water is harmful to human health and the wider environment. Heavy metal ions are listed as high priority contaminants by both the 2007 CERCLA Priority List of Hazardous Substances compiled by the US EPA (ATSDR, 2007) and the European Union Restriction of Hazardous Substances Directive (RoHS, 2003) [1,2]. Directives have been enforced by both agencies restricting the use of these materials in manufacturing and also limiting the acceptable level of these contaminants in drinking water. Classification of hazardous substances takes into account a combination of factors including frequency, toxicity and potential for human exposure. The accumulation of heavy metal ions in the human body can lead to many debilitating effects, such as joint and muscle pains to digestive problems and learning difficulties [3–5]. Removal of metal ions from drinking water in treatment centres has become a major issue and several methods are generally used such as ion exchange [6,7], electrochemical [8,9], membrane separation [10] and adsorption [11–13]. Adsorption is currently the cheapest and most effective means of removing metal ions from wastewater. The most commonly used materials are activated carbons [11,14,15], zeolites [13], clays [12] and biomaterials [16,17]. Activated carbons can be produced from cheap carbon precursors by pyrolysis at high temperatures (generally 400–900 °C). Pyrolysis will burn off any biomass and other volatile contents of the material which in turn produces carbon structures with high surface areas, a high degree of porosity and the potential for abundant adsorption sites with pre- or post-chemical and/or physical processing. Activated carbons for lead removal have been produced from diverse and abundant supplies of raw materials. High surface area carbon matrices have been produced from coconut shells [18,19], cattle manure [20] and eucalyptus bark [21] to name just a few. Functional groups can be introduced onto the surface of activated carbons using oxidative chemical reagents. The activation of carbon surfaces can take place before pyrolysis by soaking or impregnating the raw materials (carbon precursors) with highly oxidising acids, bases or salts [22–24]. Babel et al. have shown that nitric acid is a more effective oxidising acid than sulphuric acid for treating granular activated carbon for Cr ion removal [22]. Physical activation can also be used by introducing steam and/or CO_2 into the pyrolysis process. Girgis et al. carried out a comprehensive study using peanut hulls, H_3PO_4, steam and KOH over a range of different impregnation compositions, temperatures and pyrolysis times [23]. Carbons with high surface areas and pore volumes, up to 1177 $m^2\ g^{-1}$ and 0.597 $cm^3\ g^{-1}$ respectively, were obtained by impregnating peanut hull with 85% H_3PO_4 in a 1:1 weight ratio followed by pyrolysis at 500 °C for 3 h. Consequently this sample also exhibited the highest adsorption capacity when tested for the removal of methylene blue. However, post processing with acids to introduce functional groups onto the surface of the pyrolysed products can often lead to a reduction in surface area, resulting from the collapse of the carbon structure due to oxidation [25]. This oxidative surface functionalisation process, whilst reducing the surface area, also causes pore widening which can result in a more kinetically favourable uptake of metal ions [26].

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Carbon nanocages (CNCs) are hollow graphitic cages similar to fullerene structures, but can be multilayered and have irregular shapes unlike the traditional fullerene spheres, and are often produced as a by-product of carbon nanotube (CNT) growth [27,28]. CNTs themselves have shown excellent adsorption capacities and desorption is facile by simple acid washing without compromising the structure of the CNTs [29]. The surface area of pristine CNTs, which is typically below 100 $m^2\ g^{-1}$, can be increased to 830 $m^2\ g^{-1}$ through post processing by chemical activation or heat treatment [30–32]. Exfoliation of carbon layers and the introduction of defects in the carbon lattice by acid treatment contribute to the increasing surface area of CNTs. In this study, CNCs synthesised by the supercritical deposition of *p*-xylene over Co/Mo/MgO catalysts, using a method previously reported by Li et al. [33], were examined as adsorbents of lead ions (Pb^{2+}) from aqueous solutions. A comparative study was carried out with commercial activated carbon purchased from Fluka Chemika to gauge the performance and viability of CNCs.

2. Experimental

2.1. Synthesis and characterisation of CNCs

CNCs were synthesised using a supercritical fluid deposition method previously reported by Li et al. [33]. Briefly 0.5 g of Co/Mo/MgO catalyst was placed in a reaction cell which was heated to 700 °C at a rate of 5 °C min^{-1} under a flow of argon (200 ml min^{-1}). The catalyst was reduced in 10% H_2/Ar for 30 min at a flow rate of 200 ml min^{-1}. 3 ml of *p*-xylene was placed in the front part of a delivery cell, separated by a piston, in a water bath at 40 °C. The front part of the cell was then charged with CO_2 up to the desired reaction pressure using an ISCO pump. The contents of the supercritical fluid cell were flowed over the catalyst material in the reaction cell and CO_2 was applied to the back of the piston in the delivery cell to maintain a constant pressure throughout the course of the reaction. After the reaction was complete, the cell was depressurised and allowed to cool to room temperature under a flow of argon (200 ml min^{-1}). The catalyst material was removed by stirring in 3 M HNO_3 for 4 h, then filtered and washed with deionised water until the acidity of the filtrate was at pH 6, and finally dried at 60 °C in an oven for 24 h.

2.2. Characterisation

Transmission electron microscopy (TEM) of the CNCs was performed on a JEOL 2000FX microscope operating at 200 kV, and high-resolution TEM images were obtained on a JEM 2010 microscope operating at 200 kV. Samples were prepared for TEM analysis by dispersing the material in ethanol and dropping onto copper grids. Scanning electron microscopy (SEM) analysis of CNCs and commercial activated carbons, to identify their morphologies, were conducted on a JEOL 5510 SEM. The powder samples were placed on carbon tape and then adhered to a brass stub. The surface areas of the carbon sorbent materials were measured using a Micromeritics Gemini 2375 volumetric analyser. Each sample was degassed for 5 h at 200 °C prior to measurement. The surface area was calculated using the Brauner Emmett Teller (BET) method based on the adsorption data in the relative pressure (P/P_0) region of 0.01–0.99. Single-point pore volume was evaluated by converting the amount adsorbed at $P/P_0 = 0.99$ to the volume of liquid nitrogen [34]. Characterisation of CNCs by X-ray photoelectron spectroscopy (XPS) was carried out on a VSW Atomtech system using a non-monochromated Al X-ray source. Survey spectra were an average of 5 scans captured at a pass energy of 100 eV, a step size of 0.7 eV and a dwell time of 0.1 s. Level spectra were an average of 30 scans captured at a pass energy of 20 eV, a step size of 0.2 eV and a dwell time of 0.1 s. The final concentration of Pb ions in solution after adsorption was measured on a Perkin–Elmer 2280 Atomic Adsorption Spectrophotometer (AAS). The solutions were aspirated and mixed with acetylene before being ignited in a flame. A single element hollow cathode lamp was used which adsorbs light at the most dominant characteristic wavelength, which was at 217.0 nm for Pb.

2.3. Determination of zero point charge

The point of zero charge (pH_{pzc}) of CNCs and commercially available activated carbon (AC) was measured using a batch equilibrium technique. 50 ml of 0.1 M $Na(NO_3)$, used as an inert/background electrolyte, was placed in a beaker and the initial pH of the solution was adjusted using 0.01 M NaOH and/or 0.01 M HNO_3. 50 mg of the adsorbent material was then added to the solution and stirred for 24 h to allow the pH of the suspension to equilibrate. The mixture was filtered and the final pH of the solution was measured using a pH meter. Experiments were completed for initial pH values ranging between 3 and 11, at an interval of approximately 1.0 pH unit. This equilibrium time allows for a plot of $pH_{initial}$ vs pH_{final} and the plateau that emerges can be taken as the pH_{pzc} of the material.

2.4. Dispersability of sorbent materials in aqueous media

The dispersability of CNCs and activated carbon was observed by mixing 15 mg of sorbent in 15 ml of deionised H_2O (concentration of 1 g dm^{-3}) and sonicated for 20 min to form a homogeneous suspension. The suspensions were then left to stand and pictures were captured on a Samsung S630 digital camera at regular intervals to observe the time taken for the materials to agglomerate.

2.5. Flowability of aqueous media through sorbent materials

A comparative test was used to examine the ease of flow of an aqueous solution through a fixed bed of CNCs and activated carbon. The system was set up by packing a fixed mass of cotton wool into a glass pipette and 20 mg of sorbent materials placed on top to form the sorbent bed. Another fixed mass of cotton wool was then packed above the sorbent bed to prevent dispersion of the sorbent powders into the aqueous media. An aqueous solution of methyl blue (used as a colourant) was then flowed through the system and timed from when the aqueous solution was added to the system to the instant the first drop exited the system.

2.6. Adsorption of Pb ions from aqueous solutions

CNCs were tested as an adsorbent material for heavy metal ions from aqueous solutions using a batch adsorption technique. Parallel batch adsorption tests were carried out using activated carbon (AC) purchased from Fluka Chemika to compare with the CNCs. A 1000 mg dm^{-3} stock solution of Pb^{2+} was made by dissolving $Pb(NO_3)_2$ in deionised water.

2.6.1. Varying the pH

25 mg dm^{-3} stock solutions of Pb^{2+} ions were prepared by diluting 1000 mg dm^{-3} stock solutions described above in deionised water and adjusting the pH of the solution using 0.01 M NaOH or 0.01 M HNO_3. Typically 20 ml of a 25 mg dm^{-3} of the Pb^{2+} ion solution and 10 mg of the adsorbent material were placed in a beaker and stirred for 4 h to allow for adsorption equilibrium in accordance with previous publications [15]. The final concentration of metal ions in solution that was not adsorbed by materials was measured on an AAS and the adsorption efficiency was calculated using Eq. (1) below:

$$q_e = (C_0 - C_e) \times V/m \qquad (1)$$

where q_e is the metal uptake on the adsorbent under equilibrium conditions (mg g^{-1}); C_0 and C_e are the initial and final concentrations