Journal of Hazardous Materials 199–200 (2012) 9–14

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

Optimization of magnetic powdered activated carbon for aqueous Hg(II) removal and magnetic recovery

Emily K. Faulconer*, Natalia V. Hoogesteijn von Reitzenstein, David W. Mazyck

Department of Environmental Engineering Sciences, University of Florida, 217 Black Hall, P.O. Box 116450, Gainesville, FL 32611-645, United States

ARTICLE INFO

Article history:
Received 20 May 2011
Received in revised form 30 August 2011
Accepted 6 October 2011
Available online 3 November 2011

Keywords:
Activated carbon
Magnetic sorbent
Mercury adsorption

ABSTRACT

Activated carbon is known to adsorb aqueous Hg(II). MPAC (magnetic powdered activated carbon) has the potential to remove aqueous Hg to less than 0.2 μg/L while being magnetically recoverable. Magnetic recapture allows simple sorbent separation from the waste stream while an isolated waste potentially allows for mercury recycling. MPAC Hg-removal performance is verified by mercury mass balance, calculated by quantifying adsorbed, volatilized, and residual aqueous mercury. The batch reactor contained a sealed mercury–carbon contact chamber with mixing and constant N_2 (g) headspace flow to an oxidizing trap. Mercury adsorption was performed using spiked ultrapure water (100 μg/L Hg). Mercury concentrations were obtained using EPA method 245.1 and cold vapor atomic absorption spectroscopy. MPAC synthesis was optimized for Hg removal and sorbent recovery according to the variables: C:Fe, thermal oxidation temperature and time. The 3:1 C:Fe preserved most of the original sorbent surface area. As indicated by XRD patterns, thermal oxidation reduced the amorphous characteristic of the iron oxides but did not improve sorbent recovery and damaged porosity at higher oxidation temperatures. Therefore, the optimal synthesis variables, 3:1 C:Fe mass ratio without thermal oxidation, which can achieve 92.5% (±8.3%) sorbent recovery and 96.3% (±9%) Hg removal. The mass balance has been closed to within approximately ±15%.

1. Introduction

Mercury (Hg), a toxin that has been shown to bioaccumulate, can enter the environment from anthropogenic sources such as chlor-alkali wastewater and has severe health effects on humans, animals, and the environment [1]. The treatment of mercury-contaminated water remains a challenge, particularly due to the very low regulatory concentrations. Due to its listing as a toxic pollutant under section 307(a) of the Clean Water Act (CWA), site-specific technology-based aqueous Hg effluent limits are regulated through the National Pollutant Discharge Elimination System (NPDES) permitting system. Any discharge to impaired water must not exceed the Total Maximum Daily Load (TMDL), the maximum allowable amount of a pollutant that a particular body of water can receive and still meet water quality standards. States have the power to require lower effluent limits, as is the case in the Great Lakes region where the limit has been set to less than 1 μg/L. The EPA has determined the water quality criteria for the protection of wildlife and for the protection of human health to be 1.3 ng/L and 1.8 ng/L, respectively [2,3]. Adsorption can be used as a polishing technique to reach lower wastewater effluent concentrations [4].

Activated carbon is known to remove Hg(II) from aqueous solutions [5–10]. MPAC has the potential to lower wastewater effluent mercury concentrations from industries such as chlor alkali and coal-fired power plants utilizing flue gas desulfurization to less than 0.2 μg/L (the analytical detection limit using cold vapor atomic absorption (CVAA) spectroscopy) while being magnetically recoverable from solution. Traditional filtration methods to separate dispersed activated carbon from aqueous solution are susceptible to filter blockages and head loss. Magnetic recapture allows for simple separation of the sorbent from the waste stream and increases the ease of residuals management according to the cradle to grave responsibility of the Resource Conservation and Recovery Act (RCRA).

Magnetic adsorbents are an attractive solution for metallic and organic aqueous pollutants, particularly due to the simple magnetic separation process. Magnetic iron oxides have been used to synthesize new adsorbents utilizing multiwalled carbon nanotubes for Pb, 1-napthol, Ni, Sr, and Eu adsorption [11–13], zeolites for Cr, Cu, and Zn adsorption [14], activated carbon for phenol, chloroform, and chlorobenzene adsorption [15], and dimercaptosuccinic acid for Hg, Ag, Pb, Cd, and Tl adsorption [16]. However, these adsorbents have been applied to only a limited number of contaminants and mercury has thus far been largely overlooked. The available

* Corresponding author. Tel.: +1 434 485 9021; fax: +1 352 392 3076.
E-mail addresses: emily.faulconer@yahoo.com, embem171@yahoo.com (E.K. Faulconer).

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doi:10.1016/j.jhazmat.2011.10.023

literature does not discuss the ratio of sorbent to iron oxide for either optimal adsorption or optimal magnetic recovery. Additionally, the potential for increased magnetic recovery from thermal oxidation of the iron oxides has not been investigated.

In this study, the adsorption of Hg(II) onto MPAC was studied in a batch system with respect to the synthesis variables of C:Fe mass ratio and thermal oxidation temperature and duration. Thermal oxidation was performed on the synthesized MPACs with the purpose of converting amorphous iron oxides formed during synthesis to magnetic iron oxides such as magnetite or maghemite. The goal of this study was to identify the synthesis variables for both optimal aqueous Hg removal and optimal sorbent recovery.

2. Materials and methods

2.1. Materials

Solutions were prepared using ultrapure Type I water with a resistivity of 18.2 MΩ and a conductivity of 0.055 μS. A commercially available bituminous coal-based powdered activated carbon (Calgon WPH) with a surface area of 1020 m^2/g was oven-dried at 100 °C for a minimum of 24 h prior to use. Hg(II) solutions were prepared by diluting 1000 mg/L stock $Hg(NO_3)_2$ (Fisher Scientific) in ultrapure water. The oxidizing purge trap to capture volatilized Hg was prepared using 4%, w/v potassium permanganate (Fisher Scientific) in 10% sulfuric acid (Fisher Scientific) solution. The total digestion of MPAC was performed using 400 μL aqua regia (3:1, v/v concentrated hydrochloric acid (J.T. Baker) to concentrated nitric acid (Fisher Scientific)), 2 mL of concentrated hydrofluoric acid (Acros Organics), and 20 mL of saturated boric acid solution (Acros Organics). According to EPA method 245.1, the heated digestion for Hg quantification was performed using concentrated nitric acid (Fisher Scientific), concentrated sulfuric acid (Fisher Scientific), 5%, w/v potassium permanganate (Fisher Scientific), 5%, w/v potassium persulfate (Fisher Scientific), and 12%, w/v sodium chloride–hydroxylamine sulfate solution (Fisher Scientific).

2.2. MPAC synthesis

MPAC composites were synthesized at room temperature by heterogeneous nucleation [17]. Fe(II) and Fe(III) salts (ferric chloride ($FeCl_3$) and ferrous-ferric oxide (FeO, Fe_2O_3)) were dissolved in ultrapure water with mechanical stirring. After carbon addition, rapid alkaline hydrolysis was induced by adding 5 M NaOH drop wise to the solution to reach pH 10. The hydrolysis products, $Fe(OH)^+$ and $Fe(OH)_2{}^+$, reacted to form ferrihydrite which preferentially precipitated onto the carbon surface but, due to thermodynamic instability, transformed into magnetite (Fe_3O_4) (Eqs. (1) and (2) [18]). In the presence of atmospheric oxygen, the magnetite is susceptible to oxidation to maghemite [19].

Generation of ferrihydrite intermediate:

$$2Fe(OH)_2{}^+ + Fe(OH)^+ + 3OH^- \rightarrow (Fe^{3+})_2(Fe^{2+})(OH^-)_8 \quad (1)$$

Dehydration of ferrihydrite, formation of magnetite:

$$(Fe^{3+})_2(Fe^{2+})(OH^-)_8 \rightarrow Fe_3O_4 + 4H_2O \quad (2)$$

The amount of activated carbon was adjusted to obtain 1:1, 2:1, and 3:1 C:Fe mass ratios. Samples were rinsed with ultrapure water to remove residual NaOH until a constant water contact pH was achieved and subsequently oven-dried at 100 °C overnight.

Although maghemite is likely the predominant iron species present on the MPAC surface due to the synthesis technique used, small amounts of non-magnetic iron oxides (e.g. hematite, amorphous iron oxides) may occur. Thermal oxidation may convert some of these amorphous iron oxides to magnetic iron oxides such as magnetite or maghemite [19]. To compare the initial synthesis product to one having undergone thermal oxidation, representative portions of the original MPAC were subjected to oxidation in a box furnace with air flow with varying temperatures (250 °C, 350 °C, and 450 °C) and durations (0, 3, and 6 h).

2.3. MPAC characterization

The surface area was measured by a surface area analyzer (Quantachrome Instruments NOVA 2200e). Each sample was outgassed at 110 °C for 24 h before being placed in a 77 K liquid nitrogen bath with nitrogen gas adsorbate. The surface area of each sample was calculated by the Brunauer–Emmett–Teller (BET) equation [20]. Using the adsorption isotherm, the pore size distributions over the mesopore region were calculated using the Barrett–Joyner–Halenda (BJH) equation [21].

The X-ray diffraction (XRD) patterns of the MPAC were recorded using a Philips APD 3720 X-ray unit. XRD patterns were analyzed to identify the iron speciation on the MPAC surface. Compounds were identified using the powder diffraction identification number according to the International Center for Diffraction Data.

The MPAC, easily dispersed in aqueous solution, can be retrieved using a strong magnet such as neodymium, a rare-earth magnet. The recovery (%) of MPAC from aqueous solution and sorbent mass balance was determined using the dry mass captured by the magnet, the dry mass retained by a 0.45 μm nitrocellulose filter after vacuum filtration, and the mass of the initial MPAC dose. The contact time (5 min) and carbon dose (1 g/L) were held constant while the MPAC species varied based on synthesis variables. Preliminary experimentation indicated the use of a 5 min contact time because the results were not significantly different than a 10 or 30 min contact time while a 1 min contact time produced considerably lower magnetic sorbent recovery from aqueous solution. Iron effluent levels were quantified using a spectrophotometer (Hach DR/4000 Spectrophotometer and TPTZ powder pillow method 2190).

2.4. Adsorption experiments

In order to ensure future experiments were performed at adsorption equilibrium, the contact time required to reach Hg adsorption equilibrium onto MPAC was investigated. A 1 g/L dose of MPAC was applied to 100 μg/L Hg solution for 0–180 min.

MPAC Hg-removal performance was verified by integral mass balance of Hg. Based on published aqueous Hg(II) mass balances, acceptable mass balance closure was determined to be within approximately ±15% [22,23]. This was achieved by quantifying the residual aqueous Hg, adsorbed Hg extracted from MPAC by HF digestion, and volatilized Hg captured in the $KMnO_4$ trap. Trace levels of Hg, 0.125 μg Hg/g virgin activated carbon, were determined via aqua regia and hydrofluoric acid digestion and these values considered in the mass balance. The MPAC dose (1 g/L), Hg concentration (100 μg/L), and contact time (180 min) were held constant.

The batch reactor contained a sealed Teflon mercury–carbon contact chamber with 0.8 L/min headspace N_2 flow through an inlet/outlet port to an oxidizing purge trap. The MPAC was applied at a 1 g/L dose to 100 μg/L Hg-spiked ultrapure water ($Hg(NO_3)$) and magnetically mixed for 180 min contact time at room temperature. After the specified contact time, the adsorbent was separated via filtration using 0.45 μm nitrocellulose filter and the reactor rinsed with 20% (v/v) HNO_3 in ultrapure water. Metal concentrations were measured using EPA digestion method 245.1 and cold vapor atomic adsorption spectroscopy (CVAA).