

TO: Texas Hazardous Waste Research Center

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SUBJECT: Annual Progress Report

PROJECT NUMBER: 513LUB0024H

PROJECT TITLE: Novel Adsorbents: Carbon Nanocomposites towards Toxic Cr(VI) Removal

PROJECT PERIOD: 09/2013 ~ 05/2015

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Up to 5 pages of progress report including the following sections:

Project Description

The explicit purpose of this project is to chart a new direction for our research: grow functional nano-adsorbents on flexible electrospun fiber or cotton fabric substrates and to use these materials in filtration column units for continuous, fast and complete Cr(VI) removal. The carbon nanocomposite fibers/fabrics, consisting of carbon substrate and iron oxide nanoparticles, will be fabricated using the dip-coating and subsequent thermal annealing method developed recently by the PIs. The nanocomposite fibers/fabrics packing length, density and assembling configuration in the filtration column as well as flow rate and circulation time of polluted water will be systematically studied by using real industry polluted water. The open structure of the nanocomposite fiber/fabric is projected to remain high fluid flux during filtration. The decorated nanoparticles are expected to enlarge the Cr(VI) removal efficiency and capability. The Cr(VI) removal mechanisms will be exploited by studying the Cr valence state change on the carbon nanocomposites surface with X-ray photoelectron spectroscopy and magnetization change before and after treatment.

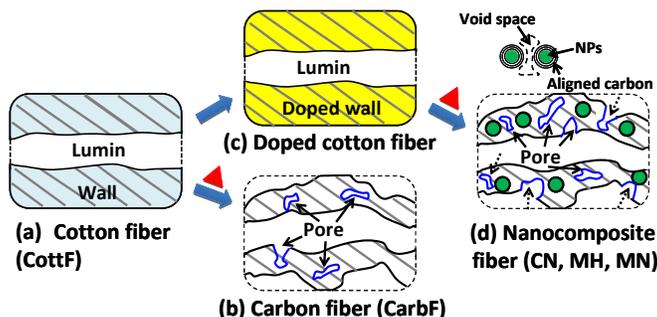
Objectives

The objective of this project is to (1) develop facile and cost effective processes to manufacture carbon nanocomposite fibers/fabrics; (2) investigate the Cr(VI) removal from polluted water by the created nanocomposite fibers/fabrics in a filtration column system; (3) determine the Cr(VI) removal mechanisms. In this report, the magnetic carbon nanocomposite fabrics were synthesized and their performances on Cr(VI) removal from polluted solution were investigated. Meanwhile, the mechanisms involved in the Cr(VI) removal processes were discussed.

Methodology

Synthesis of magnetic carbon nanocomposite fabrics

Three major steps were involved for the synthesis of magnetic carbon nanocomposites. First, the cotton fabric (CottF) was dried at 80 °C in a regular oven for 6 hours; second, the dried CottF was cut into pieces and immersed in a beaker containing 40 mL 1.0 M $\text{Fe}(\text{NO}_3)_3$ solution. After 2 hours, the beaker was moved to vacuum oven and subjected to 700 mmHg vacuum for additional 4 hours at room temperature. After that, the $\text{Fe}(\text{NO}_3)_3$ doped CottF was dried at 80 °C in regular oven overnight; finally, the $\text{Fe}(\text{NO}_3)_3$ doped CottF was annealed to fabricate magnetic carbon nanocomposites. Three different annealing conditions were used to compare the process dependent material property: (a) conventional annealing, the doped CottF fabrics was loaded in a tube furnace and heated to 850 °C with a heating rate of 10 °C/min in N_2 atmosphere. The obtained product was named CN. Using 5% H_2/Ar mixture as purging gas in a conventional process, the samples ignite immediately once exposed to air; (b) the doped CottF was annealed at ~850 °C using microwave assisted heating system within 5% H_2/Ar and high purity N_2 atmosphere for 2 hours and the resulting products were name as MH and MN, respectively. For comparison, carbon fabrics (CarbF) were also fabricated from a conventional annealing in N_2 atmosphere.



Scheme 1. (a) hollow structure of cotton fibers with fiber wall and lumin, (b) porous structure of carbon fiber after annealing at 800 °C, (c) iron nitrate doped cotton fabric, (d) nanocomposite fibers doped with nanoparticles and some extra pores have been created as marked by the dash arrow.

Accomplishments/Problems

1. Characterizations

The fibers exhibit an average diameter of about 10-15 μm and the length can be easily extended to several centimeters without breakage. It is interesting to observe a hollow tube structure decorating with nanoparticles either on the fiber surface or within the fiber body matrix (Fig. 1A). This result confirms the successful conversion from inorganic salt $\text{Fe}(\text{NO}_3)_3$ to nanoparticles as well as cotton to hollow carbon fibers. However, from this conventional annealing process, the nanoparticle size is not uniform and significant amount of large particles were observed. In this study, microwave assisted annealing was also applied in current study to fabricate uniformly sized iron nanoparticles. Both 5% H_2/Ar and N_2 were used as purging gases during annealing and the properties of the products were comparatively investigated. The nanoparticle size and dispersion were well controlled as expected and no apparent agglomeration was observed (Fig. 1B), while the tube structure of the carbon fibers seems collapsed due to the twisting of the fibers during annealing. After replacing the purging gas with N_2 , the surface of MN became much rougher with some debris adhering to the fiber, Fig. 1C. XRD characterization

was conducted to reveal the crystalline information in bulk, Fig. 1D. Comparing the XRD profiles of CN and MH/MN, the particles in CN have been heavily oxidized into Fe_2O_3 that most of the oxide crystalline peaks are observed, Fig. 1D(a). In MH and MN, fewer oxide peaks were observed indicating the as-synthesized nanoparticles were better protected from oxidation via the graphitized carbon shell.

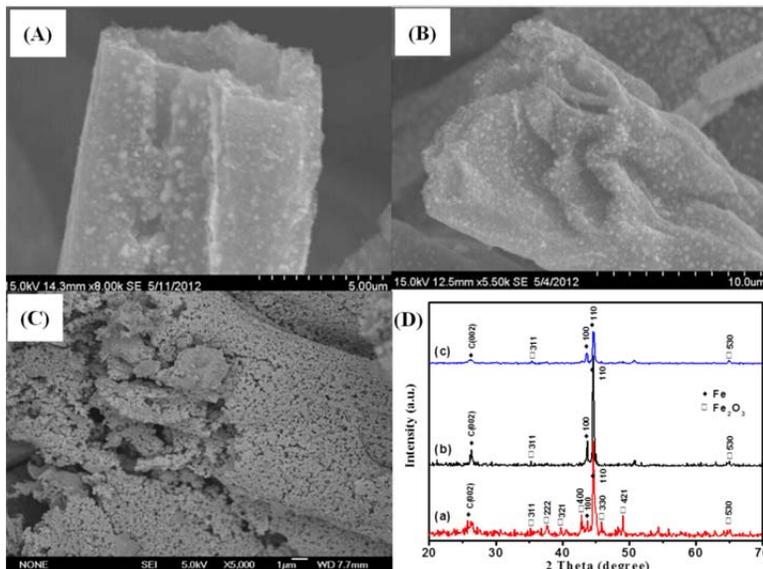


Fig. 1 SEM images of (A) CN, (B) MH, and (C) MN, and (D) XRD profiles of (a) CN, (b) MH, and (c) MN.

2. Cr(VI) removal

Both MH and MN show complete Cr(VI) removal with an initial concentration of 1.5 mg/L, while CN only shows 68.7% removal percentage and even lower for CottF (21.3%) and CarbF (30.7%) (Fig. 2A). This result reveals the superior Cr(VI) removal performance of MH and MN than that of CottF, CarbF and CN. However, it is not able to determine the specific removal capacity of MH and MN, since both of them reach a complete removal. Then MH and MN were further tested in higher concentrated Cr(VI) solution of 4.0 mg/L. It is obvious that removal percentage of MN (88.9%) is relatively higher than that of MH (61.9%). Therefore, MN will be used as model compound to systematically study the Cr removal kinetics and mechanisms. The effect of initial Cr(VI) concentration on the removal efficiency of MN at neutral solution is shown in Fig. 2B. A maximum removal percentage of 100% was achieved for the initial Cr(VI) concentrations of 1.5, 2.0 and 2.5 mg/L. Then, it decreased with increasing the initial Cr(VI) concentration. Keeping the highest Cr(VI) concentration of 4.0 mg/L with the same contact time of 10 min, different loading of MN is applied to investigate the Cr(VI) removal performance, Fig. 2C. It is observed that the removal percentage increases with increasing the MN loading due to the increased adsorption sites with larger amount of MN. The maximum removal percentage of ~100% could be achieved at the MN loading of 2.0 g/L. Fig. 2D shows the adsorption data of Cr(VI) over MN at different time intervals of 5, 10 and 15 minutes. Different kinetic models including pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion have been used to fit the experimental results and correlation coefficient (R^2) is introduced to evaluate the suitability of different models. The higher R^2 value indicates a more applicable model to the

Cr(VI) adsorption kinetics. Among these models, pseudo-second order obtains the highest correlation coefficient of $R^2=0.999$.

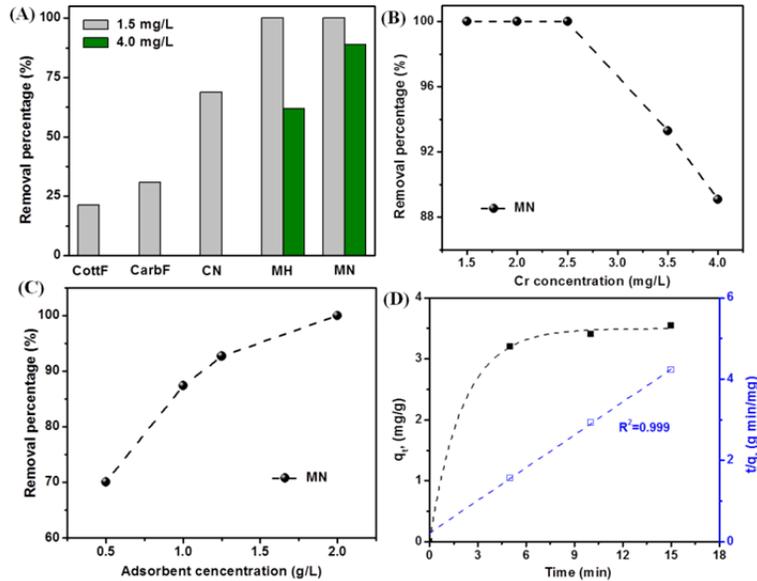


Fig. 2 (A) Cr(VI) removal performance of different materials; effect of (B) initial Cr(VI) concentration and (C) adsorbent concentration on Cr(VI) removal performance; and (D) Kinetic adsorption data plots of Cr(VI) by MN.

3. Cr(VI) removal mechanisms

Fig. 3 shows the magnetic hysteresis loops of MN and MN after treatment in different pH solutions. It is obvious that the saturation magnetization of MN at each pH condition decreases significantly after the treatment process. The magnetization loss in acidic or basic solutions is even more serious than that in neutral solution. In low pH solutions, the protons provide positive charge to adsorb the HCrO_4^- and thus a high removal percentage is observed. Besides the adsorption, redox reaction also occurred at the interface of magnetic nanoparticles and Cr(VI) species. Redox reaction proceeds faster in acidic solutions due to the dissolution of nanoparticles as revealed by the magnetization loss, which well explains the larger magnetization loss in low pH solutions. In basic solutions, the magnetization loss of nanoparticle is mainly due to the oxidation rather than dissolution.

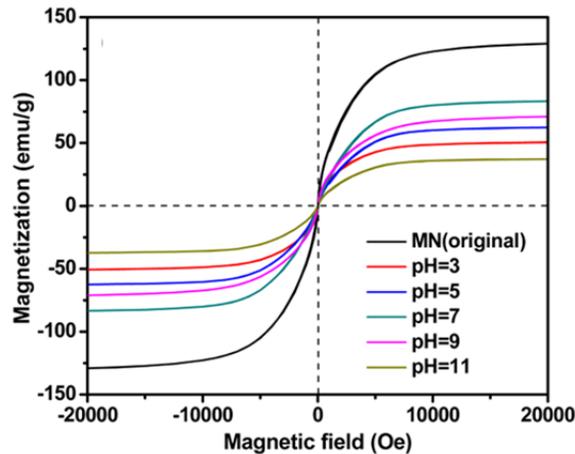


Fig. 3 Magnetic hysteresis loop of the MN (original) and MN after treatment in Cr(VI) solution of different pH values.

Future Work

A continuous flow system packed with the carbon nanocomposites will be setup and used to filtrate the Cr(VI)-containing wastewater. The fluid flow rate, residence time, removal rate and percentage, polluted water treatment capacity will be determined.

List of Publications and Presentations

1. J. Zhu, H. Gu, J. Guo, M. Chen, H. Wei, Z. Luo, H. A. Colorado, N. Yerra, D. Ding, T. C. Ho, N. Haldolaarachchige, J. Hopper, D. P. Young, Z. Guo and S. Wei. Mesoporous Magnetic Carbon Nanocomposite Fabrics towards Highly Efficient Cr(VI) Removal. *Journal of Materials Chemistry A*, 2014, 2, 2256-2265.
2. C. Xu, B. Qiu, H. Gu, X. Yan, H. Wei, X. Huang, Y. Wang, D. Rutman, D. Cao, S. Bhana, Z. Guo and S. Wei. Synergistic Interactions between Activated Carbon Fabric and Toxic Hexavalent Chromium. *ECS Journal of Solid State Science and Technology*, 2014,3 (3), m1-m9.
3. B. Qiu, C. Xu, D. Sun, H. Wei, X. Zhang, J. Guo, Q. Wang, D. Rutman, Z. Guo and S. Wei. Polyaniline Coating on Carbon Fiber Fabrics for Hexavalent Chromium Removal. *RSC Advances*, 2014, 4, 29855-29865.
4. B. Qiu, H. Gu, X. Yan, J. Guo, Y. Wang, D. Sun, Q. Wang, X. Zhang, B. Weeks, M. A. Khan, D.P. Young, Z. Guo and S. Wei. Cellulose Derived Magnetic Mesoporous Carbon Nanocomposites with Enhanced Hexavalent Chromium Removal. *Journal of Materials Chemistry A*, 2014, DOI: 10.1039/C4TA04040F.