MAGNETIC CHRYSOTILE NANOTUBES MODIFIED WITH PH-SENSITIVE POLY(METHACRYLIC ACID) FOR ENHANCED UPTAKE OF CU(II) IONS

Shaojun Yuan,[a,*] **Yu Zheng,**[a] **Shengwei Tang,**[a] **Bin Liang,**[a] **Simo O Pehkonen**[b]
[a]Sichuan University, College of Chemical Engineering , Chengdu City, China, [b] University of Eastern Finland, Department of Environmental Sciences, Kuopio City, Finland.

yuanshaojun@gmail.com (S.J. Yuan), simo.pehkonen@uef.fi (S.O. Pehkonen)

Keywords: Magnetic chrysotile NTs; Hydrothermal synthesis; Atom transfer radical polymerization; Cu(II) ions; adsorption

Introduction

Magnetic nanomaterials have attracted much attention as a promising alternative adsorbent in purifying wastewater contaminated with heavy metal ions owing to their unique features of a large specific surface area, enhanced active sites, and magnetic properties for easy separation. Nano-magnetic iron oxides such as Fe_3O_4 and Fe_2O_3 have been used as novel sorbents for wastewater treatment, and have demonstrated their potential to effectively adsorb a wide range of heavy metal ions (Giraldo et al. 2013). However, nano-magnetic iron oxides only contain surface hydroxyl groups, which limit the chemical and physical reactivity towards interactions with other aqueous species (Mahmoud et al. 2014). In addition, nano-magnetic iron oxides are subject to agglomeration, and thus the high capacity and selectivity of these nanomaterials would be greatly reduced or lost (Mahmoud et al. 2013). Thus, an alternative magnetic nanomaterial is highly desired.

Chrysotile (i.e., $Mg_2Si_2O_5(OH)_4$) nanotubes (NTs) have been widely investigated to adsorb toxic metal ions from water (Zhuang et al. 2009). These naturally occurring nano-structured clay minerals are abundant in nature and are inexpensive as compared to carbon nanotubes (i.e., CNTs). More importantly, nickel chrysotile (i.e., $Ni_3Si_2O_5(OH)_4$), NTs have been found to be readily endowed with magnetic properties by *in situ* hydrothermal reduction (Yang et al. 2011). Accordingly, the purpose of this study is to develop magnetic poly(methacrylic acid) (PMAA)-grafted chrysotile NTs as a novel magnetic nanosorbent for effective uptake of Cu(II) ions from aqueous solutions.

Methods

$Ni_3Si_2O_5(OH)_4$ NTs were synthesized by a previously-reported hydrothermal reaction, and were further hydrothermally-reduced in a $NaBH_4$ solution at 180ºC for 12 h to obtain magnetic properties. The grafting of PMAA brushes onto the surfaces of magnetic chrysotile NTs was achieved by surface-initiated atom transfer radical polymerization (ATRP). The as-synthesized samples were characterized by TEM, XRD, FTIR, XPS, TGA, BET, zeta potential and VSM measurements. Batch adsorption experiments were carried out to determine the adsorption kinetics, isotherms, thermodynamic parameters and regeneration capacity of magnetic PMAA-grafted chrysotile NTs.

Results

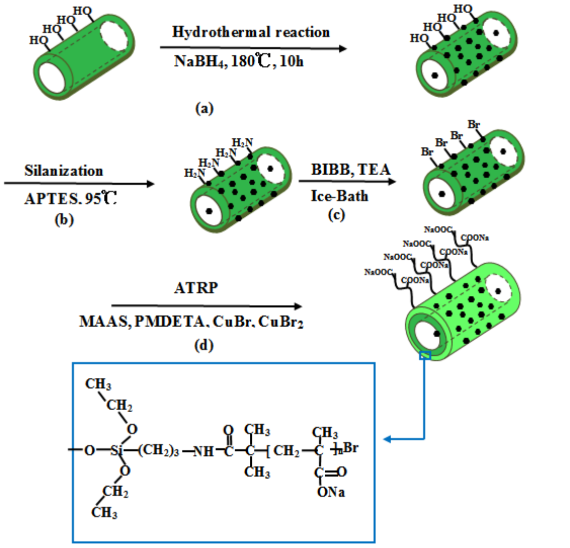

Fig. 1 Schematic illustration of a three-step synthesis process of magnetic PMAA-grafted chrysotile NTs

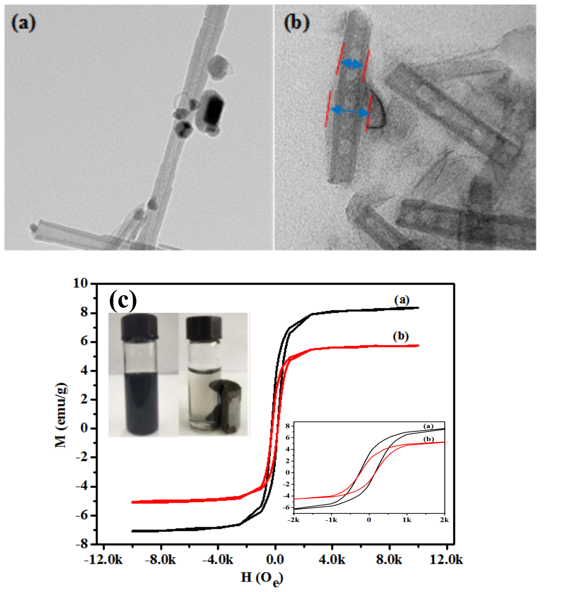

Fig. 2 TEM images of (a) magnetic chrysotile NTs and (b) PMAA-grafted chrysotile NTs, and (c) magnetization curves of magnetic PMAA-grafted chrysotile NTs from 1 and 2 h of reaction

Conclusion

$Ni_3Si_2O_5(OH)_4$NTs were synthesized by one-pot hydrothermal reaction, and further magnetized by *in situ* hydrothermal reduction. Subsequent grafting of pH-sensitive poly(methacrylic acid) (PMAA) brushes onto the surfaces of magnetic chrysotile NTs was achieved by surface-initiated ATRP to provide abundant adsorptive sites. The adsorption of Cu(II) ions was found to proceed rapidly, and the adsorption kinetics followed the pseudo-second-order model. The maximum adsorption capacity derived by the Langmuir isotherms was 1.28 mmol·g^{-1} at solution pH 5 and 25ºC. The calculated thermodynamics parameters revealed an endothermic and spontaneous adsorption process of Cu(II) ions on the PMAA-grafted chrysotile NTs. The adsorption-desorption cycle results demonstrated that the PMAA-grafted chrysotile NTs were readily regenerated, and kept high separation efficiency under an external magnetic field .

References

Giraldo, L., Erto, A. and Moreno-Pirajan, J.C. (2013) Magnetite nanoparticles for removal of heavy metals from aqueous solutions: synthesis and characterization. Adsorption 19(2-4), 465-474.

Mahmoud, M.E., Yakout, A.A., Hamza, K.H. and Osman, M.M. (2015) Novel nano-Fe_3O_4-encapsulated-dioctylphthalate and linked-triethylenetetramine sorbents for magnetic solid phase removal of heavy metals. J. Ind. Eng. Chem. 25, 207-215.

Mahmoud, M.E., Abdelwahab, M.S. and Fathallah, E.M. (2013) Design of novel nano-sorbents based on nano-magnetic iron oxide-bound-nano-silicon oxide-immobilized-triethylenetetramine for implementation in water treatment of heavy metals. Chem. Eng. J. 223, 318-327.

Zhuang, Y., Yang, Y., Xiang, G. and Wang, X. (2009) Magnesium silicate hollow nanostructures as highly efficient absorbents for toxic metal ions. J. Phys. Chem. C 113(24), 10441-10445.

Yang, Y., Liang, Q., Li, J., Zhuang, Y., He, Y., Bai, B. and Wang, X. (2011) $Ni_3Si_2O_5(OH)_4$ multi-walled nanotubes with tunable magnetic properties and their application as anode materials for lithium batteries. Nano Res. 4(9), 882-890.

Proceedings of the 18th International Conference on Heavy Metals in the Environment, 12 to 15 September 2016, Ghent, Belgium