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Procedia Chemistry 19 (2016) 586 – 593

Procedia Chemistry

5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

The Assessment of Cr(VI) Removal by Iron Oxide Nanosheets and Nanowires Synthesized by Thermal Oxidation of Iron in Water Vapour

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Abstract

In this work, iron oxide nanosheets (NSs) and nanowires (NWs) were fabricated by thermal oxidation of iron foils at 500 and 800 ^{o}C in the presence of water vapour. Oxidation resulted in multi-scale oxide with the surface oxide comprising of α-Fe_2O_3 and inner oxide comprising of mostly Fe_3O_4. The mechanism of formation is discussed to be based on stress-driven mechanism and diffusion paths of iron ions. It was found that the NSs formed could adsorb 112 mg/L aqueous Cr(VI) and the NWs could adsorb 200 mg/L of Cr(VI). It is suggested that the Cr(VI) removal by the iron oxide NSs/NWs due to the electrostatic reaction between the adsorbent and adsorbate.

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: Iron oxide; thermal oxidation; nanowires; nanosheets; chromium; adsorption

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Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia
doi:10.1016/j.proche.2016.03.057

1. Introduction

Chromium in the form of soluble salts of Cr(VI) ions has been used in wide industrial process especially steel and plating industries for centuries. Despite its importance, experience of excessive exposure has shown that Cr(VI) acts as an acute irritant, can be allergen and carcinogen to human[1]. When Cr(VI) is digested, it can cause diarrhea, internal hemorrhage or kidney damage[2]. The World Health Organization (WHO) declared that the parameter limit of Cr(VI) effluent in water is 0.05 mg/L[3], hence discharge of Cr(VI) to the aquatic environment must be avoided or treatment is needed before it is safe to be discharged. Various methods have been employed to remove Cr(VI) from wastewater like membrane filtration, electrochemical treatment, chemical precipitation, ion exchange and adsorption[1]. Among those methods mentioned, adsorption is believed to be a rather efficient and cost effective to remove Cr(VI). Adsorption is a surface property of a certain solid material which has an ability to attract molecules/ions[4]. In this present work, the solid material reported is iron oxide film in a form of nanosheets (NSs) or nanowires (NWs) and Cr(VI) adsorption is expected to happen on these nanostructures.

Iron oxide exists typically in the form of magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and haematite (α-Fe_2O_3)[5]. Recently, iron oxide has attracted attention due to its capabilities on removing heavy metal such as Hg, As, Cu, Cd, Pb and Ni from contaminated or wastewater[6]. Its unique amphoteric properties offers the flexibility on shifting the surface charge of the iron oxide to be neutral, positive or negative, hence allowing either anion or cations adsorption from aqueous environment[5]. Normally Cr(VI) ions exist in either $HCrO_4^-$ or CrO_4^- form[1], hence it is anticipated the Cr(VI) adsorption will happen on a positively charge of adsorbent. Moreover, in the form of NWs/NSs, as the material is now consisted of structure in nanoscale, it is expected that the increase number of contact area for adsorption to occur would improve the adsorption performance. The NWs/NSs synthesized in this work are in the form of thin film on centimeter sized substrate (it is supported on Fe foil) thus it is expected that secondary pollution can be much avoided as the material can be easily sieved out from the treated water.

Oxidation of iron and steel has been studied for the past 50 years but with the focus on mostly kinetics, oxide scale stability and thermodynamic characteristic as well as the protective nature of the oxide to the underlying metal. When iron is oxidised at high temperature, it grows a scale containing multi phased oxides with an outer layer of α-Fe_2O_3. Haematite (α-Fe_2O_3) is known to have low toxicity and has been successfully applied in many chemical and biochemical applications[5]. α-Fe_2O_3 can be made to have unique morphologies for instance whiskers or plates by thermal oxidation of metal iron which in recent years have been termed as nanowires, nanobelts or nanosheets accodingly[7]. In fact, there have been a number of studies reported on the formation of iron oxide NWs in dry oxidising gas, in air or in wall-controlled environment containing certain gasses with controlled partial pressure[8,9]. Despite the success, the formation requires long oxidation time reaching 10 hours[10] to produce high aspect ratio and dense NWs (NWs covering the surface of the metal foil uniformly). Rapid synthesis of NWs can be achieved by using direct plasma oxidation[11], but the process seems to be more complex requiring precise control for plasma generation.

It has been reported that oxidation rate of iron can be increased when oxidation is done in the presence of water vapour reported by various authors for examples Pujilaksono et al.[12] and Yuan et al.[13]. Moreover, α-Fe_2O_3 NWs with so called “blades” morphology has been reported when iron is oxidised in the presence of small amount water[14]. Therefore, in this work we attempted on the formation of α-Fe_2O_3 nanostructures by oxidation in a furnace injected to it a flow of water vapour. Not only the process is simple, it resulted on the formation of NWs and NSs rapidly with high density. Then the potential of the nanomaterials as adsorbent of Cr(VI) was assessed. To the best of our knowledge, no work has been reported on the use of thermally oxidised iron as an Cr(VI) adsorbent. It is envisaged that, if oxidised iron can be used as an adsorbent, much of the iron or steel waste accumulated in the world can be reused as useful adsorbent for contaminated or wastewater treatment. Indeed this would be advantageous in reducing waste while providing cleaner water at the moment.