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Zirconium-Loaded Mesostructured Silica Nanoparticles Adsorbent for Removal of Hexavalent Chromium from Aqueous Solution

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EXTENDED ABSTRACT

Chromium is one of the heavy metals present in effluents produced from the aerospace, electroplating, leather, mining, dyeing, fertilizer, and photography industries [1]. In the aqueous phase, chromium mostly exists in two oxidation states, namely, trivalent chromium (Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, or $\text{Cr}(\text{OH})_2^+$, etc.) and hexavalent chromium (HCrO_4^- , CrO_4^{2-} , or $\text{Cr}_2\text{O}_7^{2-}$, etc.). Most of the hexavalent compounds are considered to be more hazardous due to their carcinogenic properties, which can cause severe health problems in humans. Therefore, it is essential to reduce the Cr(VI) content of wastewater to below the tolerance limit before it is discharged into the environment [2]. Several research groups have developed technologies to reduce the Cr(VI) content from aqueous media, such as adsorption, electrochemical precipitation, ion exchange, and reverse osmosis techniques [2-5]. Among these technologies, adsorption has been regarded as an easy and efficient method to remove Cr(VI), owing to its relatively low cost and simplicity of design and operation. The conventional adsorbents for adsorption of organic and inorganic metal compounds have been studied widely, and include activated carbon, zeolite, natural clay, and biomaterials [6-9]. However, the inherent drawbacks associated with most of these adsorbents leads to relatively low adsorption capacity and selectivity, mechanical and thermal instability, or the need for a longer equilibrium time, even though the adsorbents may be cheap, to some extent, in practice. Therefore, the development of an adsorbent with a good Cr(VI) removal ability would be desirable.

Recent studies have shown that mesoporous powder materials, such as MCM-41, SBA-15, FSM, and HMS, which have a large surface area and a meso-scale pore size, promise a high adsorption capacity for removal of toxic compounds and/or heavy metals from aqueous solutions [10]. Nevertheless, these materials possess a neutral framework that limits their application as a catalyst, support, and adsorbent. Recently, efforts have been made to modify the mesoporous molecular sieve in order to increase the active sites for catalysis or adsorption and to enhance their practicability. Several studies have been reported on the modification of mesoporous silica with organic compounds, such as amino groups and

organosulfur for the removal of Cr(VI) [11-13]. Sepehrian and co-workers, however, prepared mesoporous silica incorporated with several inorganic metals such as Zr(IV), La(III), Al(III), and Ce(IV) to study the adsorption behavior for certain heavy metals [14]. In addition, Zhang et al. reported the introduction of Ti into the framework of pure MCM-41 by direct synthesis and a post-synthetic impregnation method [2]. They concluded that inorganic metals, such as Zr(IV), Al(III), and Fe(III), have affinity toward inorganic anions, including fluoride, phosphate, arsenic, and chromium.

Our research group studied MCM41-type mesostructured silica nanoparticles (MSN) for removal of Cr(VI). Recently, MSN have drawn a great deal of research attention, especially regarding adsorption, due to the excellence properties of MSN, such as high surface area, small particles, presence of intraparticle and interparticle pores, and easily modified silica framework. In this study, MSN was modified with zirconium ion in order to increase the ability of MSN to attract Cr(VI). The adsorption of Cr(VI) was carried out in a batch system. The interaction of Zr and Cr(VI) ions with MSN was observed by FTIR, XPS, and solid-state NMR studies. Adsorption kinetics of Cr(VI) on Zr/MSN were investigated at 303–323 K.

The difference adsorption capacity of Cr(VI) on MSN, 1Zr/MSN, 5Zr/MSN, and 10Zr/MSN showed that the adsorption capacity of Cr(VI) was proportionally promoted by introducing zirconium ions onto the MSN. The maximum adsorption capacity was 1.2, 5.1, 8.4, and 9.8 mg g⁻¹ for MSN, 1Zr/MSN, 5Zr/MSN, and 10Zr/MSN, respectively. These changes may be due to the modification of the siliceous framework with heteroelement (Zr), which apparently increased the active sites and subsequently increased the capacity of the adsorbent to adsorb Cr(VI). Pure silica-based mesostructured nanoparticles show a limited application value due to the lack of active sites in the silica walls. It was believed that, with an increase in zirconium loading, the adsorption rate should also be increased owing to a higher number of hydroxyl groups generated on the siliceous framework. Thus, there will be more Cr(VI) ions attracted to the surface of Zr/MSN.

From the characterization results, the proposed adsorption mechanism of Cr(VI) onto MSN and Zr/MSN is proposed. FTIR spectra showed possible interactions of the silanol groups with the metal ions and the disappearance of hydroxyl groups in defect sites. Furthermore, the XPS spectrum of Zr_{3d} confirmed the chemical oxidation state of the Zr⁴⁺ ions, which indicates that the Zr in the MSN may be in the form of Zr⁴⁺ connected to four O atoms, i.e., (Zr(O)₄)⁴⁺. The O_{1s} XPS spectrum illustrated the presence of a Si-O-Zr bond. As a result, it can be concluded that the available structural defect sites interacted with Zr ions to form the structure shown in Scheme 1. Modification with Zr ions increased the active sites on the surface, which led to an enhanced adsorption capacity of the MSN.

Keywords: Mesostructured Silica Nanoparticles, Zirconium, Chromium, Pseudo-second-order Kinetic model, Endothermic.

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