REMOVAL OF Co\textsuperscript{2+}, Ni\textsuperscript{2+}, AND Pb\textsuperscript{2+} BY MANGANESE OXIDE-COATED ZEOLITE: EQUILIBRIUM, THERMODYNAMICS, AND KINETICS STUDIES

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Abstract—The removal of Co\textsuperscript{2+}, Ni\textsuperscript{2+}, and Pb\textsuperscript{2+} from aqueous solutions using a modified zeolite was investigated because of the need to eliminate toxic contaminants from wastewaters. In the present study the ways in which equilibrium, thermodynamics, and kinetics parameters affected the removal of heavy metals were evaluated and compared. An Iranian clinoptilolite with a Si/Al ratio of 6.5 was used as an adsorbent. In order to increase the adsorption capacity of the adsorbent, it was converted to a manganese oxide-coated zeolite (MOCZeo) using various Mn solutions. The initial concentration of metals, pH, contact time, and temperature were the variables studied and optimal conditions were established. The maximum amount of Co\textsuperscript{2+}, Ni\textsuperscript{2+}, and Pb\textsuperscript{2+} adsorption on MOCZeo was ascertained. A thermodynamics study, using ΔG, ΔH, and ΔS state functions showed that adsorption of Pb\textsuperscript{2+} was more spontaneous than that of Co\textsuperscript{2+} and Ni\textsuperscript{2+} ions. The adsorption of these ions on MOCZeo was an endothermic reaction. Investigation of the adsorption models revealed that the adsorption of Pb\textsuperscript{2+}, Co\textsuperscript{2+}, and Ni\textsuperscript{2+} on MOCZeo followed both the Langmuir and Freundlich models. Kinetics studies showed that the adsorption of Pb\textsuperscript{2+}, Co\textsuperscript{2+}, and Ni\textsuperscript{2+} on MOCZeo followed the pseudo-second order kinetics model with a high correlation coefficient.

Key Words—Ion-exchange Adsorption, Manganese Oxide, Wastewater, Zeolite Kinetics and Thermodynamics.

INTRODUCTION

Heavy-metal contamination arises through the disposal of industrial materials from a variety of industrial processes, including the paper industry and iron and steel manufacturing plants (Inglezakis et al., 2002, 2007). Dealing with the wastewater discarded from industrial processes is a critical environmental issue. Some metals included in the discarded material are toxic (Moattar and Hayeripour, 2004; Rahmani et al., 2004), and nickel can have serious effects on human and animal health (Turtureanu et al., 2008). The small amounts of Pb present may have adverse effects on the human brain and central nervous system (Inglezakis et al., 2007). Finding ways to improve the quality of industrial wastewaters was, therefore, the main motivation for the present study. Cobalt, Ni, and Pb ions were selected here because of their wide use in various industries and adverse effects on the aqueous environment.

The elimination of heavy metals from industrial effluents has been studied extensively. Several processes such as liquid-liquid extraction, membrane extraction, filtration, ion exchange, and adsorption have been developed to remove dangerous species from wastewater. Of these methods, adsorption processes are acknowledged as being the simplest and most economical. Activated carbon, activated carbon composites, silicates (Erto et al., 2013; Karnib et al., 2014; Azari et al., 2015), kaolins and ball clays (Chantawong et al., 2004), leaf powders (Li et al., 2013), mixed Fe-Al oxides (Violante et al.), activated carbon fibers (Park et al.), silica gels (Tzvetkova et al., 2009), Na-purified natural clays (Fröhlich et al., 2015; Ghorbel-Abid and Trabelsi-Ayadi, 2015), bentonites (Wu et al., 2015), attapulgites (Guo et al., 2014), fruit peels (Mallampati et al., 2015), zeolite X/chitosans (Lu et al., 2015), montmorillonites (Kalantari et al., 2015), clinoptilolite (Miličević et al., 2013; Irannajad et al., 2015), agricultural soils (Zhang and Zheng, 2007), and coal bottom ash (Asokhunyarat et al., 2015) are some of the adsorbents that have been or are applied in remediation of contaminated water. Of these adsorbents, natural zeolites are considered to be the cheapest, having large adsorption capacities and appropriate selectivities (Al-Degs et al., 2000; Irannajad et al., 2016c). Zeolites are also more readily available than some of the other adsorbents such as montmorillonite. Several studies have been performed on the removal of various species using a natural zeolite (Doula, 2006; Ören and Kaya, 2006; Taffarel and Rubio, 2010; Mehdizadeh et al., 2014a; Irannajad et al., 2016c). The activation of natural zeolites, using various chemical reagents, is done to increase the adsorption capacities of natural minerals. The literature shows that modification of a zeolite with manganese oxide increases the adsorption capacity significantly to levels which are greater than that of minerals such as montmorillonite, for example.

The chemical modification of natural zeolites has also been investigated (Doula, 2006; Taffarel and Rubio, 2010; Gonzalez et al., 2015; Irannajad et al., 2016c). One of the chemical reagents used to modify zeolites is