



## Original Research Paper

Thermodynamic and kinetic studies for the adsorption of Hg(II) by nano-TiO<sub>2</sub> from aqueous solutionZinab Ghasemi<sup>a,\*</sup>, Ahmad Seif<sup>b</sup>, Temer S. Ahmadi<sup>c</sup>, Behroze Zargar<sup>a</sup>, Fatemeh Rashidi<sup>b</sup>, Goodarz M. Rouzbahani<sup>b</sup><sup>a</sup> Department of Chemistry, Science and Research Branch, Islamic Azad University, Khozestan, Iran<sup>b</sup> Department of Chemistry, Islamic Azad University, Boroujerd Branch, Boroujerd, Iran<sup>c</sup> Department of Chemistry, Villanova University, Villanova, PA 19085, USA

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## ABSTRACT

Titanium dioxide nanocrystals were employed, for the first time, for the sorption of Hg(II) ions from aqueous solutions. The effects of varying parameters such as pH, temperature, initial metal concentration, and contact time on the adsorption process were examined. Adsorption equilibrium was established in 420 min and the maximum adsorption of Hg(II) on the TiO<sub>2</sub> was observed to occur at pH 8.0. The adsorption data correlated with Freundlich, Langmuir, Dubinin–Radushkevich (D–R), and Temkin isotherms. The Freundlich isotherm showed the best fit to the equilibrium data. The Pseudo-first order and pseudo-second-order kinetic models were studied to analyze the kinetic data. A second-order kinetic model fit the data with the ( $k_2 = 2.8126 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ , 303 K). The intraparticle diffusion models were applied to ascertain the rate-controlling step. The thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) were calculated which showed an endothermic adsorption process. The equilibrium parameter ( $R_L$ ) indicated that TiO<sub>2</sub> nanocrystals are useful for Hg(II) removal from aqueous solutions.

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## 1. Introduction

Mercury is a very toxic and hazardous element to the human body and to the environment. Volcanic action, burning of fossil fuels, waste discharge from chlorine, paper and pulp, plastic and battery manufacturing industries as well as improperly disposed barometers, thermometers, pumps, and lamps make up the major sources of Hg in the environment [1]. The toxicity of Hg depends strongly on its oxidation state; the most toxic form of Hg is the Hg<sup>2+</sup>, which is highly reactive and binds to the amino acid cysteine in cases of mercury poisoning [2]. Low dose mercury exposure can affect various organs of human adults and children. Humans absorb mercury and its compounds through the gastrointestinal tract, the skin, and lungs. Mercury is then stored in the liver, kidneys, brain, spleen and bones, leading to carcinogenic, mutagenic, and teratogenic developments as well as tyrosinemia, paralysis, serious intestinal and urinary complications, dysfunction of the central nervous system and in more severe cases, intoxication and death [3]. Mercury enters our food chain through bacterial formation of

methyl mercury in lower level sediments which are taken in by fish.

The upper safe limit for mercury is 0.001 ppm before metal toxicity occurs, which is the lowest among all heavy metal ions [4]. Therefore, in order to minimize the harmful effects of Hg(II), it is important to find ways to remove it from the environment before it poses a treat. There are several techniques already available for the removal of mercury from solutions which includes chemical precipitation, conventional coagulation, line softening, reverse osmosis, ion-exchange, and solid phase extraction. These methods are costly and have disadvantages such as incomplete metal removal, high energy requirements, and generation of toxic sludge. Adsorption of pollutants on solid adsorbents is an effective method used for removal of heavy metals from aqueous solutions [5,6]. Still, there is a need for efficient and environmentally friendly systems for reducing heavy metal contamination. With such objectives in mind, developing an adsorbent with large surface area and small diffusion resistance is important.

Nano-sorbents have emerged as a new area of research with potential application, due to their large surface areas, in removal of heavy metal ions from liquid solutions. In addition, synthesis of nano-sorbents is simple, their adsorption process is rapid, they provide a high number of surface active sites, and they are non-toxic; these attributes lead to high adsorption efficiency. Among

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