Development of Comprehensive Hybrid Hydrogel Adsorbents for Decontamination of Heavy Metals and Organic Pollutants from Concentrated Solutions

オモンヂ, ブライアン, アダラ

（様式２）

氏　　名　：OMONDI BRIAN ADALA (オモンヂ ブライアン アダラ)

論 文 名　：**Development of Comprehensive Hybrid Hydrogel Adsorbents for Decontamination of Heavy Metals and Organic Pollutants from Concentrated Solutions（濃厚溶液より重金属及び有機汚染物質の包括除去を行う複合ハイドロゲル吸着剤の開発）**

区　　分　：

論 文 内 容 の 要 旨

In typical contaminated solutions, only a few contaminants are very toxic (or are more valuable as resource). Therefore, applied extraction techniques need to ensure a combination of high selectivity, expediency and high efficiency. This dissertation proposed new type of hybrid hydrogel adsorbents for simultaneous and selective adsorption of both organic and inorganic pollutants from aqueous solutions.

Previously, the removal of BTEX organic pollutants had relied on surfactant modified diatomite and zeolites, despite much lower adsorption capacities of $5x10^{-4}$ and 0.08 mg/g, respectively. So far only polyethylene glycol modified clay (PEG-Mt) has been able to achieve considerable adsorption capacities of 3.47 mg/g after 24 hrs. Our current research using hybrid hydrogel demonstrated significant BTEX adsorption of 2.81 mg/g from concentrated aqueous solution within a much shorter time of only 6 hrs. Further, unlike PEG-Mt whose BTEX adsorption is based on general properties of organic compounds, hybrid hydrogel adsorption mechanism via electrophilic aromatic alkylation was more selective towards BTEX by targeting a unique reaction chemistry of BTEX compounds. This ensured overall improved efficiency of BTEX removal.

For application on heavy metal adsorption, hybrid hydrogel network was infused with three types of specialized macrocyclic ring groups to produce three functionalized hybrid adsorbents. This research outcome was the first type of ringed functional hydrogels for selective metal adsorption within the ring cavities, which had not been previously attempted. Actual metal selectivity performance of hybrid hydrogels was tested by analyzing adsorption from a concentrated solution comprising 14-metal ions (Li, Cr, Mn, Fe, Co, Ni, Cu, Bi, Zn, Mo, Ag, Cd, Cs and Pb). The first type of hybrid hydrogel was able to adsorb only Bi, demonstrating high selectivity and efficiency (9.5 mg/g) attained within 16 hours. The second type of hybrid hydrogel was able to adsorb five types of metal ions from the 14-metal ion solution, with special preference towards Fe (16.29 mg/g) Cr (15.88 mg/g) and Cu (15.39 mg/g) compared to Ni (3.16 mg/g) and Co (2.59 mg/g). The final hybrid hydrogel was tested against actual hard chrome electroplating wastewater samples where there was remarkable selective extraction of only the main Cr(VI) pollutant ions with nearly 98 % of this metal ion extracted from the original waste solution to record adsorption capacity of 15.55 mg/g. This was achieved despite very low pH (pH = 0.5) and extremely high concentrations of multiple metal ions (Sn, Ti, Cr, Fe, Zn, Sn, Sb) within the wastewater solution. High selectivity Cr(VI) adsorption enables potential recovery of this metal ion for subsequent re-use.

By using macrocyclic ring groups, hybrid hydrogels were able to achieve high efficiency and highly selective adsorption of target metal ions compared to conventional treatment of heavy metal wastewater which uses chemical precipitation of all metals in solution. Conventional method does not use any special

functional groups such as cyclic rings, hence there is no selectivity property, and thus is unsuitable for recovery and re-usability of waste components as valuable resources. Finally, conventional treatment of organic/inorganic pollutants applies different techniques in the decontamination of BTEX and heavy metal ions. But the hybrid hydrogel is a comprehensive type, that enables simultaneous adsorption of both classes of pollutants through customized functional groups within its network for both BTEX and heavy metal ions.

The dissertation has been divided into 6 main chapters.

Chapter 1 introduced the various types of pollutants and their waste solution environments such as radionuclides, organic pollutants and heavy metal wastes. It also discusses the concept of shielding effect, and finally the main objectives for this research.

In Chapter 2 the research methodology was elaborately explained. Synthesis and characterization methods of hybrid and macrocyclic functional hydrogels are presented including modes of performance testing.

Chapter 3 presented the initial results on poly (butadiene-co-acrylic acid) hybrid hydrogel for simultaneous adsorption of BTEX compounds and heavy metal ion pollutants from aqueous solutions. This was a unique concept on the nature of adsorbents design by integrating two separate functional groups to formulate a hybrid hydrogel adsorbent for extractive capture of two classes of pollutants (organic and inorganic). BTEX adsorption recorded high adsorption capacities (q = 2.81 mg/g) and total extraction of 96.2 wt% of from original concentrated solution. However, metal ion via ion exchange was non-selective and inefficient at low pH environment, which then required modification of the hybrid hydrogel functional groups for metal adsorption.

Chapter 4 was the main novelty of this research regarding successful development of new macrocylized-hydrogel adsorbents. Three new macrocyclic rings were fabricated into fully functionalized hydrogel adsorbents named according to the type of macrocyclic rings, i.e. poly (1,4-diazocane-5,8-dione) hydrogel; poly (1,4-dioxa-7,12-diazacyclotetradecane-8,11-dione) hydrogel and poly (1,4,7-trioxacycloundecane-8,11-dione) hydrogel, respectively. Selectivity of adsorbed metal ions by the macrocycles was a size-match selectivity whereby the most stable complex would be formed if the match in cavity of the macrocycle and ionic radius of the metal ion was closest. The first two hydrogels were found selective towards **Fe** and **Cr**, respectively, whereas third hydrogel was selective towards **Bi** adsorption.

Chapter 5 reported the actual application of poly (1,4-dioxa-7,12-diazacyclotetradecane-8,11-dione) hydrogel against industrial sourced wastewater solutions from hard-chrome plating factory. Adsorption results showed this material selectively and totally extracted Cr(VI) with high precision and efficiency (q=15.55 mg/g) from the original multi-metal ion contaminated electroplating wastewater.

Chapter 6 concluded this research by highlighting the feasibility of the functionalized hydrogels. This research proposes macrocyclic groups and butadiene as co-monomers towards development of a new hybrid hydrogel for selective and simultaneous adsorption of both BTEX and heavy metal ions/radioactive metals from contaminated waters. Further suggestions in regards to improvements of the macrocyclic functional groups and hydrogels are discussed.