学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Development of magnetic separation using modified magnetic chitosan for removal of pollutants in solution

(溶液中の汚染物質除去のための修飾マグネティックキトサンを用いた磁性分離法の開発)

Water is one the most important compounds on the earth and essential for all living creatures in the world. Although water is considered as a precious resource, pollution of water sources such as river, lake and sea has continuously occured. Water pollution alters the property of water to hazardous toward environments and makes it undrinkable. Water pollution with heavy metal ions has become the most serious problem on environment due to their mobility in nature and toxicity. The exposure to heavy metal ion even at trace level often leads to serious problem towards human health. Therefore, the removal of heavy metal ion from water becomes a great of interest. Among many methods to treat polluted water, adsorption is the most popular method due to its effective performance of removal. However, the conventional adsorbents are difficult to be recollected and reused after removing water pollutants. If they were not recollected, there is a possibility of the secondary pollution with the adsorbent itself. The aim of this study is to develop newly modified magnetic chitosan based adsorbents which can remove pollutants and easy to be recollected in water using a magnet. The first part of this study focused on magnetic separation of Cr(VI) by the pyridinium diethylenetriamine functionalized magnetic chitosan (PDFMC). The second part of this study focused on magnetic separation of Cu(II) by a dendrimerized magnetic chitosan. The magnetic separation of humic acid from solution was demonstarted in the third part of this study.

The wastewater containing Cr(VI) with various pH was discharged from industry to environments. However, most of developed chitosan based adsorbents for removal of Cr(VI) work well only in acidic water due to protonation of amino function groups. In the other hand, the protonation of amino groups was decreased by increasing of pH. In this study, the PDFMC was synthesized by reacting magnetic chitosan with diethylenetriamine and pyridine in the presence of 1,2-dibromoethane as a bridging agent. In comparison with unfunctionalized magnetic chitosan, the PDFMC could remove Cr(VI) in a wider range of pH. The interaction of the PDFMC with Cr(VI) was dominated by the electrostatic interaction. In order to study the regeneration of the PDFMC, adsorption-desorption cycles using the PDFMC were repeated. As the result, the PDFMC could be used for magnetic separation of Cr(VI) in acidic, near-neutral and basic solution for five cycles without any significant loss.

Chitosan is the excellent adsorbents for removal of Cu(II) ion in the water because of the presence of amino group on the surface. The performance of chitosan as an adsorbent depends on the number of amino group on its structure. In order to obtain an adsorbent with a higher number of amino group and the easiness to be recollected after adsorption, the dendrimerized magnetic chitosan was synthesized by using ethylenediamine or diethylenetriamine in the presence of methyl acrylate as a bridging agent. The reaction of magnetic chitosan with methyl acrylate and ethylenediamine was repeated to obtain the first and second generation of dendrimerized magnetic chitosan. The second generation of dendrimerized magnetic chitosan (MCE-G2) showed a higher amount of amine group in comparison with the magnetic chitosan. The MCE-G2 could remove Cu(II) in the solution effectively at pH 6. In order to simulate magnetic separation of Cu(II) in real water, the effect

of the presence of humic acid in the solution on magnetic separation of Cu(II) was investigated. In the presence of humic acid, the amount of Cu(II) removed by the PDFMC was slightly increased. It indicated that humic acid did not interfere the magnetic separation of Cu(II). The magnetic separation performance of the MCE-G2 toward Cu(II) did not change significantly even after 10 cycles.

Humic acid is a natural compound, which is ubiquitous in water. However, the presence of humic acid in water also leads to the odor, taste and color problem of water. Moreover, humic acid forms carcinogenic products by reacting with chlorine during wastewater treatment. Magnetic separation of humic acid in water was conducted by using quaternary ammonium-dendrimerized magnetic chitosan (QAMCE-G2). The QAMCE-G2 was prepared by contacting the MCE-G2 with an excess of glycidyltrimethylammonium chloride. Humic acid in solution could be removed in a wider range of pH with the QAMCE-G2 in comparison with MC. This behaviour is due to the presence of positively charged ammonium group on the surface of the QAMCE-G2. The interaction of QAMCE-G2 with humic acid was dominated with the electrostatic interaction. The regeneration study showed that the QAMCE-G2 could be used for the removal of humic acid without any significant loss even after 10 cycles.

Modification of magnetic chitosan by introducing pyridinium-diethylenetriamine, dendrimer and quaternary ammonium groups enhanced the performance on magnetic separation of pollutants in solution. The modified magnetic chitosan was effective for the removal of pollutant in comparison with unmodified magnetic chitosan. The modified magnetic chitosan could be recollected easily by a magnet and be used for several cycles. Consequently, the modified magnetic chitosan could be considered as a prospective magnetic material for magnetic separation of pollutants in solution.