別紙様式第１５号（論文内容の要旨及び論文審査の結果の要旨）

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学 位 論 文 題 目	Development of magnetic mesoporous silica composites as adsorbents for aqueous pollutants （水質汚染物質の吸着剤としての磁性メソポーラスシリカ複合材料の開発）
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論 文 内 容 の 要 旨

The rapid growth of global population and industrialization may lead to many issues including the decreasing of environmental water quality. Since water is one of the most essential resources for life and human, the issues on clean water resources and water pollution are among the global concerns today. Among many types of water pollutants, synthetic dyes from textille industry are one of the top pollutants. The extensive use of synthetic dyes in textille industry has resulted in the discharge of dye-containing effluents in a large volume into the water bodies. Dye residues in water may cause aesthetic problems due to the unwanted change of water color, prevent the sunlight penetration through water which further may reduce the rateof photosynthesis of the aquatic plants. The synthetic dyes are also known for their toxicity, carcinogenic and mutagenic properties and persistency in environmental compartments. Various physical, biological and chemical methods have been applied to remove synthetic dyes from water. Adsorption is one of the most widely used methods due to its efficiency, low-cost process, technical feasibility, reusability and easy operation.

In this study, magnetic mesoporous silica-based composite adsorbents were developed and tested for their ability in removing synthetic dyes from water. Mesoporous silica and metal-organic frameworks (MOFs) are among the most studied porous materials for the application as adsorbents. Mesoporous silica is amorphous silica material with the pore size between 2 and 50 nm. Mesoporous silica exhibits some excellent properties such as generally stable, tunable structures, controlled pore size, chemically inert, and high functionalizable surface area. MOFs are crystalline, porous frameworks which self-assemble to form coordination bonding between transition metal cations and organic ligands. Porous MOFs also exhibit superior characteristics which are preferable fo application in adsorption process, such as high specific surface area, surface functionality, and uniform porosity which can be tuned by tuning the synthesis' parameters. The presence of organic ligands on MOFs structure provides more functionalities for the adsorption of synthetic dye molecules through one or more interaction mechanism such as van der Waals interaction, π-π interaction, dipole-dipole, chelation, hydrophobic interaction, hydrogen bonding, *etc*.

The use of porous materials in the conventional adsorption process, however, requires a tedious adsorbent separation process from the treated water (usually using filtration or centrifugation method). This limitation can be overcome by the addition of magnetic properties into the porous materials. The presence of magnetic properties on the adsorbent will allow an easy separation of the used adsorbents using an external magnetic force. Two types of composites were prepared in this study using environmentally friendly methods. Magnetic mesoporous silica (MMS) was synthesized in a one-pot system and the composite of magnetic Fe_3O_4@SiO_2 (*i.e.* Fe_3O_4 coated SiO_2 core shells) and a type of metal organic frameworks (MOF), MIL-100(Fe) was prepared by microwave-assisted hydrothermal method. The latter composite is referred as Fe_3O_4@SiO_2-MIL-100(Fe).

MMS composites have been synthesized in one-pot system using various alkanolamines (triethanolamine, diethanolamine, tris (hydroxymethyl)aminomethane) as a basic catalyst. The produced MMS were studied using SEM-EDX, TEM, XRD, BET, and XPS instruments. The results revealed that the use of different alkanolamine affected the properties of MMS, including specific surface area, pore volume, and average pore diameter. Adsorption kinetic study suggested that the adsorption of brilliant green dye (BG) onto the prepared MMS composites was mainly chemisorption process, which most likely involves electrochemical interaction and hydrogen bonding between BG molecule and the surface of the composites. On the other hand, in preparing Fe_3O_4@SiO_2-MIL-100(Fe) composite, Fe_3O_4 nanoparticles were firstly prepared under microwave irradiation. After that, tetraethyl orthosilicate and amino propyl trimethoxy silane were added to produce the Fe_3O_4@SiO_2-NH_2 nanoparticles, followed by mixing the as-synthesized Fe_3O_4@SiO_2-NH_2, $FeCl_3$.6H_2O, trimesic acid, and H_2O in a microwave reactor to produce the final product *i.e.* Fe3O4@SiO2-MIL-100(Fe). After a sequential washing and drying processes, the produced powder was thoroughly characterized by SEM, TEM, XRD, FTIR, BET, and TGA instruments and applied in the adsorption process of synthetic dyes in water. When tested for the adsorption of synthetic dyes, the produced composite showed high selectivity for Congo red (CR) dye. The adsorption process of CR dye onto Fe_3O_4@SiO_2-MIL-100(Fe) composite was better explained by pseudo-second order kinetic model and the Freundlich isotherm model.

Although the magnetic mesoporous silica-based composites synthesized in this study showed superior performance in synthetic dyes adsorption process, the application of the composites in a scale-up process is still a challenging task. Many aspects related to the optimization of the synthesis and adsorption processes are necessary.

論文審査結果の要旨

本論文は，水質汚染物質の吸着剤としての磁性メソポーラスシリカ複合材料の調製および性能評価について検討している。具体的に，メソポーラスシリカおよび金属有機構造体(MOF)を合成し，合成染料の保持挙動や吸着メカニズム，さらに吸着剤の再利用等について評価・考察している。メソポーラスシリカの合成には，塩基性触媒としてさまざまなアルカノールアミンを使用しワンポット反応にて調製されている。MOF の合成について，マイクロ波照射を使用することにより，迅速かつ均一性のあるナノ粒子の調製に成功している。これらの吸着剤のキャラクタリゼーションについて，官能基の同定に FT-IR 分析，粒子の形状とサイズの分析に走査型・透過型電子顕微鏡，表面積とポアサイズの測定に BET・BJH 装置，さらに結晶とアモルファス特性分析に X 線回折を使用して評価している。

最終試験結果の要旨

３名で構成する学位審査委員会は，本論文および論文の基礎となる発表論文（査読付論文 2 編）の内容を確認し，2 月 10 日（木）に開催された最終試験（公聴会）における申請者との質疑応答・口頭試問等に基づき慎重に審査した結果，合格と判定した。

発表論文（論文名、著者、掲載誌名、巻号、ページ）

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