

효과적인 Cu^{2+} 이온 제거를 위한 산화철(Fe_3O_4)/다공성 탄소 복합체 합성

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Synthesis of Fe_3O_4 /porous Carbon Composite for Efficient Cu^{2+} Ions Removal

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요약: 본 연구에서는 구리 이온(Cu^{2+} ion) 제거를 위한 산화철(Fe_3O_4)/다공성 탄소 복합체를 합성하였으며, 이를 바탕으로 구리 이온 제거에 대한 특성 평가를 실시하였다. SEM, XRD 분석을 진행하여 수열합성(hydrothermal) 반응을 이용한 산화철/다공성 탄소 복합체의 형태와 구조를 확인하였다. BET 분석을 통해 비표면적과 기공 크기를 확인하였으며, UV-vis 장비를 통해 성능 평가를 실시하여 자성이 있는 Fe_3O_4 와 다공성 탄소와의 시너지효과를 통해 액체 상태에서 존재하는 구리 이온을 제거할 수 있는 가능성을 제시하였다.

Abstract: In this study, the Fe_3O_4 /porous carbon composite was synthesized by hydrothermal method for removal of Cu^{2+} ions and the characteristic of Cu^{2+} ions removal was performed. The Fe_3O_4 /porous carbon composite was investigated via using SEM, XRD for its morphology and structure. BET analysis was conducted to conform a specific area and pore size distribution of the composite. For the investigation of the performance for removal of Cu^{2+} ions in the solution, UV-vis spectrometer was used. It suggests that a synergetic effect between magnetic Fe_3O_4 and porous carbon shows an improvement for removal of Cu^{2+} ions.

Keywords: Fe_3O_4 /porous carbon composite, copper ion removal, membrane, water treatment

1. Introduction

Heavy metal ions dissolved in water turn up a huge hazard by accumulating in a living organism[1]. When waste water which contains toxic heavy metal ions is discharged into an environment without any purification process, the toxicity will be accumulated in the inside of plants, marine organisms[2]. Thus, several purification systems have to be conducted before discharging of the waste water. In the purification systems, there are chemical precipitation, ion exchange, biosorption, reverse osmosis, membrane adsorption[3-7].

Cu^{2+} ions are known as one of the most existed heavy metals in the waste water[8]. Likewise other heavy metals such as mercury or lead, copper metals cause a big problem when they flow into the inside of a living organism. For example, when organism inhales spray containing copper metal, the possibility for having cancer increases[9].

Iron oxide nanoparticles such as Fe_3O_4 are used for arsenic adsorption in many years, it confirmed that they have a good affinity into heavy metals[10,11]. From their small sizes, they have a high specific surface area, relatively small resistance as well as their magnetic

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characteristic which enables fast separation using external magnetic field[12]. However, there are few drawbacks such as an aggregation during adsorption process, dissolved in acidic condition and lose their ability[13].

Porous carbon has a high specific surface area, a good chemical, mechanical property and high electrical conductivity[14]. If Fe₃O₄ nanoparticles uniformly embedded in porous carbon matrix, it efficiently prevent the aggregation of Fe₃O₄ nanoparticles during adsorption process. In addition, it improves the chemical, mechanical properties of composite. In this study, we synthesized porous carbon and Fe₃O₄ via their optimal composition and reaction conditions and identified the possibility for selective adsorption for Cu²⁺ ions as membrane.

2. Experimental

2.1. Materials

Dextrose and Fe(NO₃)₃ · 9H₂O were used as precursors for carbon and iron oxide each. Poly acrylic acid was used for synthesizing porous carbon.

2.2. Synthesis of Fe₃O₄/porous carbon composite

2 g PAA were mixed in 50 mL DI water and sonication process were carried out for 15 mins. Adding 2.49 g Fe(NO₃)₃ · 9H₂O, 2 mL HNO₃, additional sonication process were conducted. The solution was transferred into a beaker, 3.332 g dextrose were added and stirred for 1 h.

Synthesis of Fe₃O₄/porous carbon composite is as follows: the solution was transferred into a teflon-lined autoclave and the hydrothermal reaction was carried out at 180°C for 18 h. The solution was cooled down at room temperature and washed several times with ethanol, DI water. The sample was obtained by centrifugation and dried in a convection oven at 50°C for 12 h. The Fe₃O₄/porous carbon composite were obtained by the carbonization and oxidation process. The sample were heated to 900°C for 2 h in a electrical

furnace at the heating rate of 5°C min⁻¹. Then, the sample were heated to 250°C for 2 h at the same heating rate.

2.3. Characterization

The obtained products were characterized by scanning electron microscope (SEM) using a SNE-3000M, X-ray diffractometer using a Rigaku RAD-3C for their morphology and structure. XRD analysis were carried in 2θ ranging from 10° to 70° with Cu Kα radiation at room temperature. For measuring a specific surface area and pore size distribution, Brunauer-Emmett-Teller measurement using Quantachrome NOVAtouchTM was used.

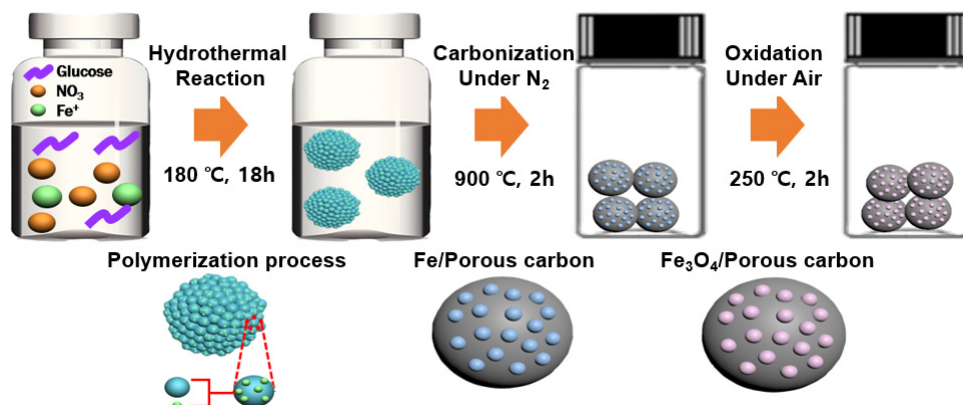
2.4. Adsorption experiments

Cu²⁺ ions adsorption experiment for were carried out using thermostat shaker at 30°C. 50 mg Fe₃O₄, Fe₃O₄/porous carbon composite were transferred in 50 mL, 150 ppm Cu²⁺ solution each. The adsorption was performed with 120 rpm rotating speed for 1 h. The pH value of the solution were fixed at 5.5 (± 0.1) using 0.1M NaOH. After the adsorption test, the residual concentration of Cu²⁺ ions were analyzed using the UV-vis spectra (Shimadzu, UV1800) with a maximum absorbance wavelength at 810 nm.

3. Results and Discussion

The synthetic process of Fe₃O₄/porous carbon composite is described in Scheme 1. For avoiding aggregation among Fe₃O₄ nanoparticles, porous structured carbon acts as matrix. Nitric acid was used for dissolving Fe(NO₃)₃ · 9H₂O, and dextrose was added additionally. The homogeneous solution was transferred into teflon-lined reactor for polymerization process. After that, following carbonization, oxidation were carried out to synthesize Fe₃O₄/porous carbon composite.

The Fe₃O₄/porous carbon composite was synthesized with 3 : 1 ratio of dextrose : Fe(NO₃)₃ · 9H₂O, 2.0 g PAA was used for its porous structure. XRD analysis were performed to identify structure of the composite.



Scheme 1. Synthesis of Fe_3O_4 /porous carbon composite.

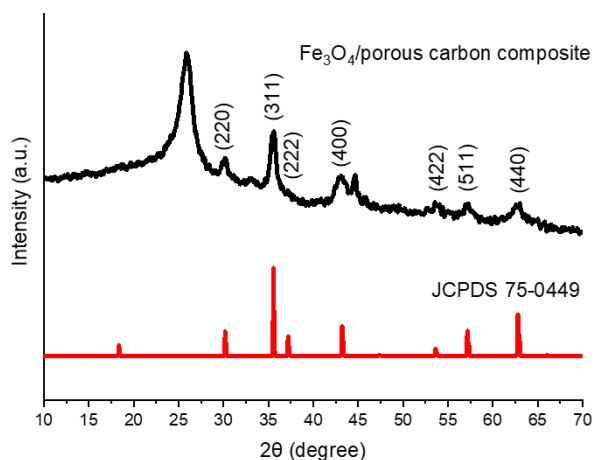


Fig. 1. XRD pattern of Fe_3O_4 /porous carbon composite.

Fig. 1 shows that the composite included Fe_3O_4 was successfully synthesized from the XRD peaks. The peaks of Fe_3O_4 /porous carbon composite at 26° , which shows broad carbon peak and Fe_3O_4 peaks at the same time. In comparing the Fe_3O_4 peaks (JCPDS 75-0449), the composite confirms that it is constructed with carbon and Fe_3O_4 .

As shown in Fig. 2(a), (b), the composite has about 3~5 μm size with spherical shape. They show the composite consists of porous carbon matrix. From these porous structures, we can expect that the increased surface area will allow to facilitate the adsorption for Cu^{2+} ions. In Fig. 2(c), the SEM image of reference Fe_3O_4 particles shows that about 500 nm size of Fe_3O_4 nanoparticles compose nano-micro particles.

BET measurement were performed to analyze the

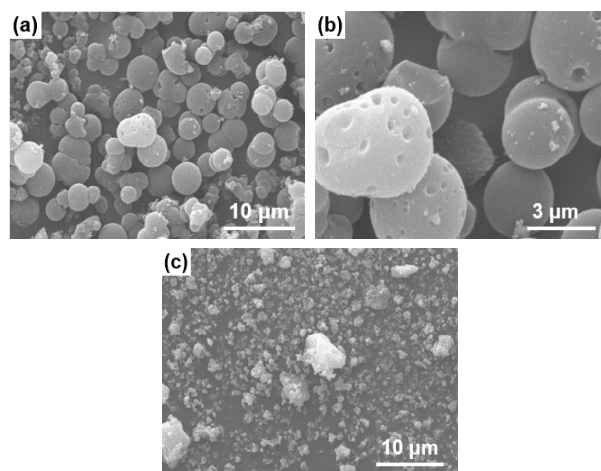
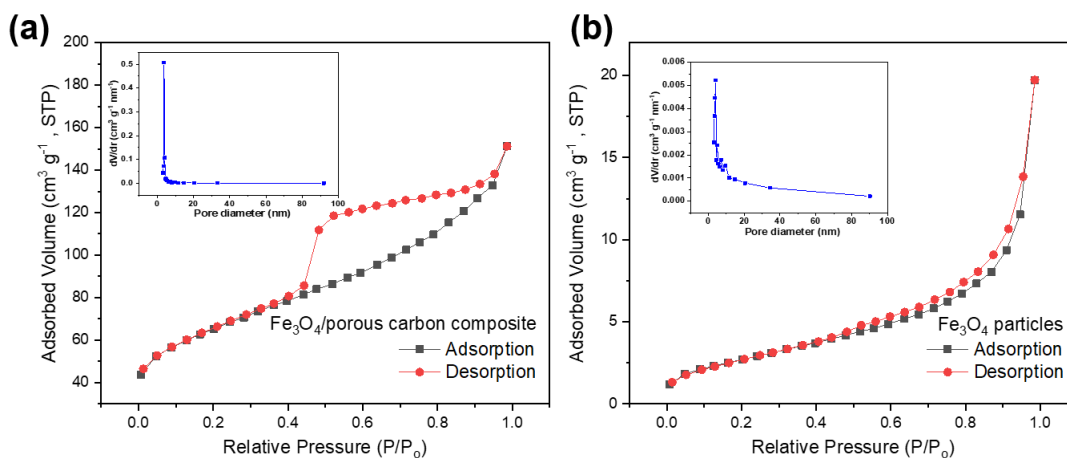
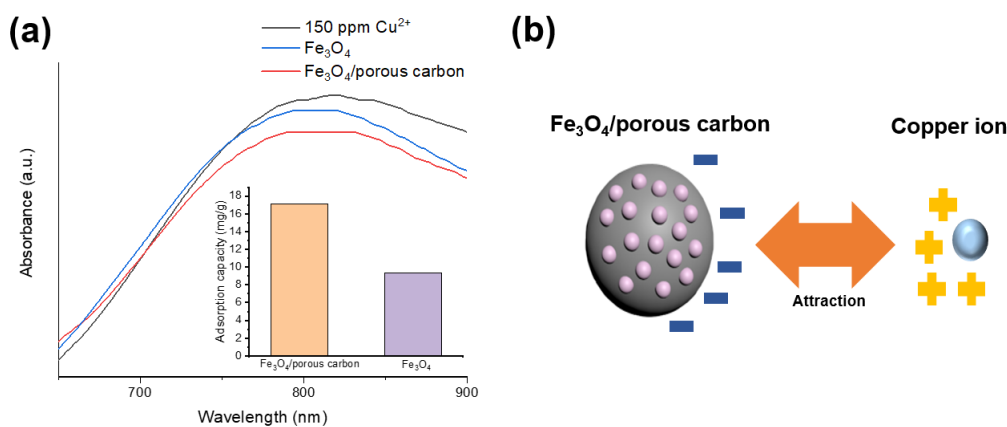


Fig. 2. SEM images of (a) Fe_3O_4 /porous carbon composite, (b) an enlarged view of the Fe_3O_4 /porous carbon composite, (c) Fe_3O_4 particles.

specific surface area and pore size distributions of Fe_3O_4 , Fe_3O_4 /porous carbon composite. As shown in Fig. 3(a), the Fe_3O_4 /porous carbon composite represents IV types isotherm which demonstrates a capillary condensation at mesoporous region[15]. In other words, hysteresis loop occurs between 0.4~0.95 relative pressure and the composite is mainly composed of mesoporous. In addition, the adsorption of Cu^{2+} ions can be expected to be more effective based on the specific surface area and the total pore volume of the Fe_3O_4 /porous carbon composite than the Fe_3O_4 particles (Table 1). On the other hand, in the case of Fe_3O_4 particles, the hysteresis loop is formed relatively small, which indicates that mesoporous are significantly less than the Fe_3O_4 particles/

Table 1. Porosity Parameters of Fe₃O₄, Fe₃O₄/porous Carbon

Samples	BET specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore size (nm)
Fe ₃ O ₄	10.21	0.0292	4.07
Fe ₃ O ₄ /porous carbon	230.08	0.1864	3.72

**Fig. 3.** N₂ adsorption-desorption isotherms and pore size distributions of (a) Fe₃O₄/porous carbon composite, (b) Fe₃O₄ particles.**Fig. 4.** (a) The UV-visible spectra for adsorption of Cu²⁺ ions of Fe₃O₄ particles and Fe₃O₄/porous carbon composite. The inset in (a) presents adsorption capacity of Fe₃O₄/porous carbon composite and Fe₃O₄ particles. (b) Schematic image of the adsorption affinity between Fe₃O₄/porous carbon composite and copper ion.

porous composite.

Adsorption experiments were conducted to identify that the Fe₃O₄/porous carbon selectively adsorb Cu²⁺ ions, one of the heavy metal ions. The adsorption experiments were performed in the condition that the Cu²⁺ ions are dissolved in the liquid phase. After 1 hour adsorption, the residual solution was analyzed by UV-visible spectra. As shown in Fig. 4(a), Cu²⁺ ions

shows the maximum peak near the wavelength at 810 nm. Since Cu²⁺ ions tend to precipitate in the form of Cu(OH)₂ in a solution having a pH value of about 6.5 or higher[16], the adsorption experiment was conducted after adjusting the pH of the initial solution about 5.5. In comparison to the adsorption capacity of Cu²⁺ ions at the wavelength of 810 nm, the adsorption capacity of the Fe₃O₄ particles shows 9.38 mg/g after 50 mins,

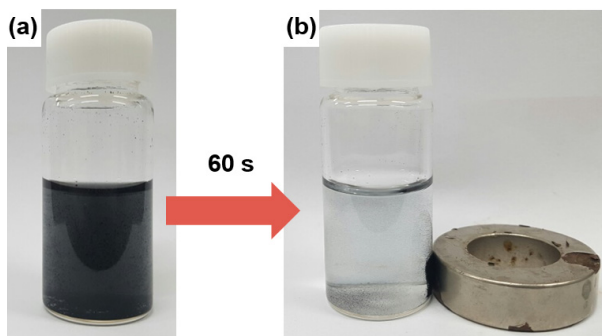


Fig. 5. Photographs of the separation process of Fe_3O_4 /porous carbon composite: (a) without external magnetic field and (b) with external magnetic field.

whereas the adsorption capacity of the Fe_3O_4 /porous carbon composite shows 17.14 mg/g [Fig. 4(a) inset]. In this reason, the Fe_3O_4 /porous carbon composite has greater adsorption capacity, about 1.8 times higher than Fe_3O_4 particles. On the basis of the experimental results, the adsorption capacity is increased from less aggregated during adsorption process and its higher specific surface area of Fe_3O_4 /porous carbon composite. That is, the interaction between positively charged Cu^{2+} ions and negatively charged Fe_3O_4 particles, the synergistic effect of preventing the aggregation of the Fe_3O_4 nanoparticles and increasing the contacting area enable its higher adsorption capacity [Fig. 4(b)][14].

In order to confirm the magnetic characteristic of the Fe_3O_4 /porous carbon composite, it was dispersed in a solution in which Cu^{2+} ions contained, and the external magnetic force was applied. The Fe_3O_4 /porous carbon composite is easily dispersed in DI water containing Cu^{2+} ions [Fig. 5(a)], and the solution becomes black due to the Fe_3O_4 /porous carbon composite. As soon as the neodymium magnet was placed near the vial, the Fe_3O_4 /porous carbon composite interacted rapidly and gathered near the magnet. After 60 seconds, most of the Fe_3O_4 /porous carbon composite was collected [Fig. 5(b)]. On the basis of this, when the Fe_3O_4 /porous carbon composite is used as a membrane, handy separation using external magnetic force will be possible in the solution where the heavy metals are dissolved.

4. Conclusions

Hydrothermal synthesis was used to synthesize the Fe_3O_4 /porous carbon composite for the effective adsorption of Cu^{2+} ions. The composite consists of a porous carbon matrix in which Fe_3O_4 nanoparticles are embedded in. It shows an improved adsorption capacity of Cu^{2+} ions by increasing the contacting area based on the relatively high specific surface area. Aggregation during the adsorption process, which is a drawback of the Fe_3O_4 nanoparticles for Cu^{2+} ions adsorption, can be alleviated through the porous carbon matrix of the composite. In addition, the composite can be easily separated from a heavy metal ions containing solution by using an external magnetic force, suggesting the possibility of using it as a membrane for selective adsorption of Cu^{2+} ions.

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