

A MAGNETIC HUMUS CORE-SHELL COMPOSITE SYNTHESIZED BY ABIOTIC HUMIFICATION METHOD FOR Cr(VI) REMOVAL

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ABSTRACT

Synthesized humus displays a high adsorption capacity for heavy metals in water due to an abundance of active functional groups and to a flexibility of modification resulting from the readily controllable synthesis process. Herein, a new method is proposed to prepare magnetic humus with high performance in the removal of Cr(VI) in water. The synthesized humus is produced through the abiotic humification technology with small molecular precursors including phenols, amino acids, and glucose. Nanoferriferic oxide (Fe_3O_4) plays an important role in the enhancement of the humus synthesis process. The high affinity of humus towards Fe_3O_4 nanoparticles, enables growing of humus on the surface of Fe_3O_4 nanoparticles. The surface morphology of the manufactured magnetic humus suggests that this material has a core-shell structure. The magnetite nanoparticles in magnetic humus show the largest amount of humus (~33.37 w/w%) at pH 8. The high loading ability of humus results in a high removal efficiency of 99.95% in a 7.30 mg/L Cr(VI) solution involving 4 mg/mL magnetic humus. Therefore, the present method is feasible to construct a core-shell magnetic humus composite to achieve high removal of Cr(VI) in water.

1. INTRODUCTION

Humus is a type of naturally transformed organic macromolecular material obtained from fresh organic residues, mainly animal and plant remnants. This compound is suitable for use as a sorbent material due to the presence of a variety of active functional groups, including carboxyl, phenolic hydroxy, carbonyl, methoxy, and amino groups, which feature a high capacity of adsorption for heavy metals in water resources (Liu et al., 2016; Singhal et al., 2017; Yang et al., 2012). However, the high solubility of humus limits its practical applications.

To compensate for the disadvantage of high solubility of humus, immobilization of this material on different solid materials such as biochar and TiO_2 particles is recommended. Magnetic nanoparticles (Fe_3O_4) resemble remarkable merits in separation of materials due to magnetic properties and efficient immobilization because of high surface area and rich hydroxyl groups on their surface (Peng et al., 2012; Singhal et al., 2019, 2020a, 2020b). As reported, the high affinity of humus to Fe_3O_4 nanoparticles strongly improves stability of magnetic humus and promotes the nanodispersion of Fe_3O_4 nanoparticles (Koesnarpadi et al., 2017; Rashid et al., 2018; Tang et al., 2016). But the weight of natural humus loaded on Fe_3O_4 is limited because of the distinct steric hindrances in the humus loading process. These limitations have a negative effect on the perfor-

mance of magnetic humus in water treatment.

The artificial humus obtained from a polyphenol-maleic anhydride polymerization reaction has the advantages of controllable synthesis process and is considered as an acceptable alternative (Zhang et al., 2017, 2019). The humification process can easily attain synthesized humus with different molecular sizes via regulation of temperature, time and air supply. This kind of mouldability in molecular size is an effective approach to reduce steric hindrances in the humus loading process. The structure of humus highly relies on the variety of humus precursors and humification conditions (Zhang et al., 2017). According to Yang's study, the amount of acidic functions on the synthesized humus is much higher than that of the natural one, allowing the former to possess a better complexation ability towards heavy-metal contaminated soil remediation (Yang & Hodson, 2018). This means that the structure of synthesized humus could be designed as required. Therefore, these advantages enabled humus to be applied in the environmental remediation.

In this work, a new method is disclosed to prepare magnetic humus (Figure 1) with a high efficacy in the removal of heavy metals. Fe_3O_4 nanoparticles were used to enhance humification, integrating small molecular precursors including catechol, glycine, and glucose into humus. To improve loading of the synthesized humus on Fe_3O_4 nanopar-

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ticles, pH was regulated in the synthesis process. The surface morphology of magnetic humus was confirmed by TEM. Eventually, the performance of the generated humus was evaluated in the removal of Cr(VI) from a solution contaminated by 7.30 mg/L hexavalent chromium.

2. MATERIALS AND METHOD

2.1 Chemicals and apparatus

Catechol (> 99% purity) was purchased from Tokyo Chemical Industry. Glycine (> 99% purity) and glucose (> 99% purity) were obtained from Nacalai Tesque. Potassium dichromate was purchased from Beijing Chemical Works. Fe_3O_4 nanoparticles were obtained under oxygen-free conditions. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (24.35 g) was dissolved in 250 mL ultrapure water (70°C) and added to a 250 mL solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Then, $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (90 mL) was added to the above mixture and incubated at 300 rpm for 90 min. After that, the mixture was set in an external magnetic field, the precipitate was separated and washed for five times using deionized water. Finally, the synthesized magnetic humus was resuspended in ultrapure water for further usage.

The transmission electron microscope (TEM) images were obtained using a Tecnai G2 F20 S-Twin electron microscope (FEI, USA). The TOC-V CSN type analyzer (Shimadzu, Japan) was used to analyze the DOC of humus. A PE-Optima 8000 Inductively Coupled Plasma Emission Spectrometer was used to analyze the total amount of Cr, while the amount of Cr(VI) was determined by UV-1601 (Shimadzu, Japan).

2.2 Experiments

Magnetic humus was synthesized in a conical flask (1000 mL) at 35°C with shaking at 200 rpm. Fe_3O_4 nanoparticles (2000 mg/L) were added into the solution involving the precursors of catechol (3500 mg C/L), glycine (1750 mg C/L) and glucose (1750 mg C/L). To investigate the effect of pH on the weight of loaded humus on the surface of Fe_3O_4 nanoparticles, the initial pH of $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ solution (0.2 M, 500 mL) was set to 4, 6, 8, and 10.

1.0 mL samples were withdrawn from the flask at 0, 4, 9, 20, 32, 45, 80, 120, 160, 260, 360 and 500 h intervals and set in an external magnetic field for solid-liquid separation. A 0.1 mL aliquot withdrawn from the above supernatant was diluted to 10 mL and subjected to UV-Vis absorption spectroscopy at 400 nm. Another 0.5 mL sample was diluted to 20 mL and used to dissolve the organic carbon content before analysis, while, the magnetic humus was used to humus loading analysis. Briefly, the magnetic humus was separated from a 10 mL solution with an external magnet and extracted for three times by 3×10 mL NaOH solution (0.1M). After that, the obtained NaOH solutions were analyzed by a TOC analyzer with the extraction efficiency of 84.86%. The magnetic humus separated from the incubated samples for 500 h was applied for the TEM surface morphology study.

3. RESULTS AND DISCUSSION

3.1 Reinforcement effect in the darkening experiment

The formation of organic chromophoric groups due to the darkening effect of humification and generation of the browning substances, as a key process of humification, can be justified through studying absorbance at 400 nm. Fe_3O_4 nanoparticles were used to enhance the humification in four systems with the pH of 4, 6, 8 and 10. The absorbance of supernatant solutions at 400 nm was varied with incubation time, as shown in Figure 2A. When pH was set to 4, the slow increase of supernatant absorbance indicated slow humification reaction throughout the entire experimental process. While, absorbance of the extracted humus from the magnetic counterpart was sharply increased in the first 45 h and, then, remained constant (Figure 2B). This observation could be explained by the fact that humus has been formed fast in the first 45 h, followed by adsorption on Fe_3O_4 nanoparticles to form a core-shell composite through electrostatic forces. However, the shell-like humus directly covered the active sites of Fe_3O_4 nanoparticles and weakened its ability to enhance humification. This behavior can also be found in the humification process at pH 6, but

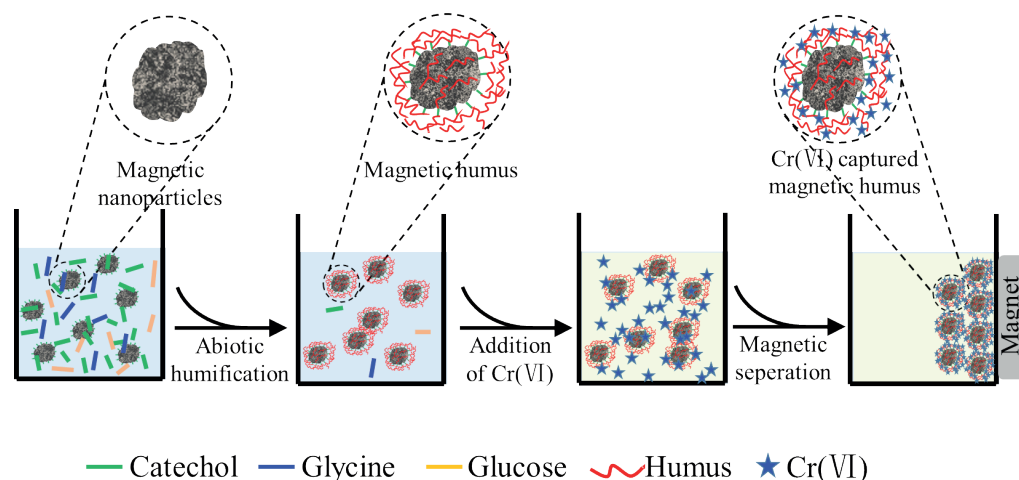


FIGURE 1: Representations of the procedures for magnetic humus preparation and Cr(VI) removal.

the supernatant samples were gradually darkened as the extension of incubation time and, finally, the absorbance reached to 0.60 after 500 h incubation. This finding suggested that the colored humus has been continuously generated. By contrast, the absorbance of supernatant solution at pHs of 8 and 10 was sharply increased over time within the first 45 h, and then set at a nearly constant value of 1.15, suggesting that the humus has been significantly generated and reached to a maximum weight after 45 h. On the other hand, absorbance of the extracted humus showed a similar trend with that of supernatant samples. The slight increase of absorbance after 45 h could be due to the connection of free small amount of humus to magnetic humus under the action of metal oxides. Therefore, the alkaline condition is suitable to enhance humification on Fe₃O₄ nanoparticles in the presence of catechol, glycine, and glucose as precursors.

3.2 Generation of magnetic humus

The TEM image of Fe₃O₄ nanoparticles confirmed that Fe₃O₄ nanoparticles have a regular spherical shape with the

uniform size of about 11.59 ± 0.23 nm (n = 17), as shown in Figure 3A. The inset of this figure shows a lattice with the width of 0.26 nm for Fe₃O₄ nanoparticles. The magnetite nanoparticles were surrounded by a layer of an organic material after coating with humus (Figure 3B). This organic material can be extracted by 0.1 M NaOH for total organic carbon analysis.

The weight of humus loaded on Fe₃O₄ nanoparticles was analyzed, as depicted in Figure 4. The total organic carbon of humus on the surface of Fe₃O₄ nanoparticles was detectable, confirming the successful synthesis of magnetic humus. It is clearly demonstrated that humus can gradually grow on the surface of Fe₃O₄ nanoparticles, as the carbon content was varied with the incubation time throughout the entire experiments. Due to the faster generation of humus in an alkaline condition, the humus loading on Fe₃O₄ nanoparticles was higher under this condition compared to that in the acidic environment. The Fe₃O₄ nanoparticles separated at pH 8 and under the incubation time of 500 h revealed the largest amount of humus with the total carbon content of 243.13 mg per gram of

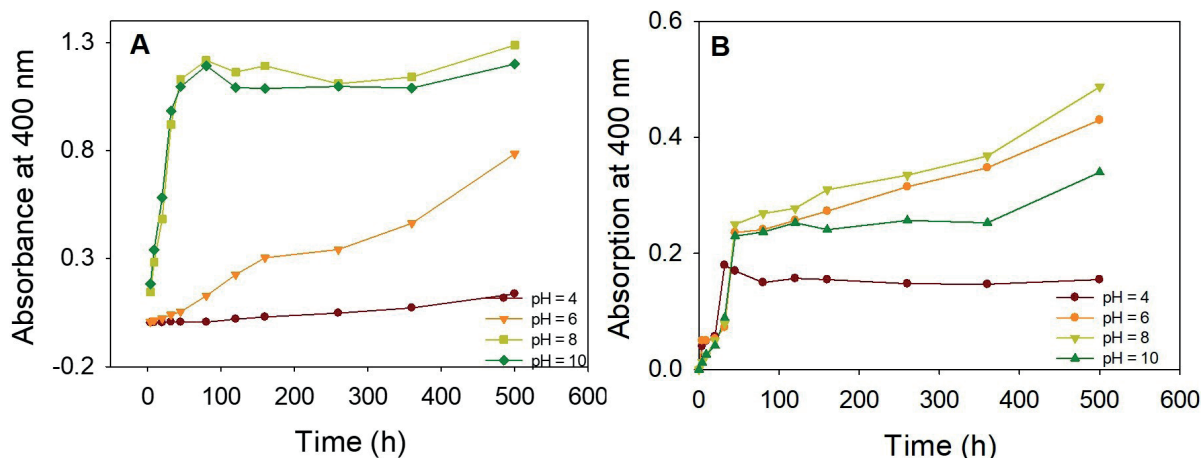


FIGURE 2: Absorbance at 400 nm of (A) the supernatant solutions after 100 times dilution (B) the extracted humus from the magnetic humus after 50 times dilution.

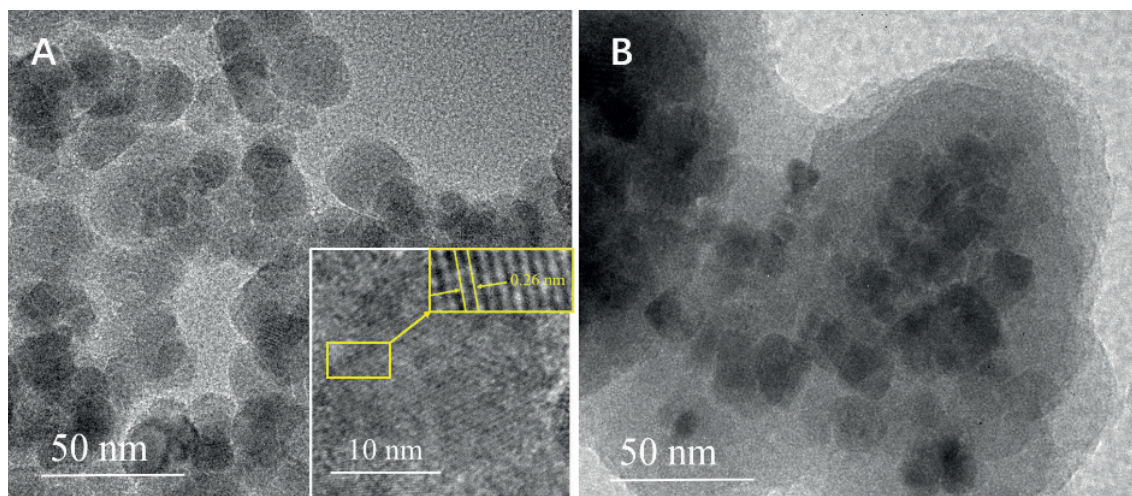


FIGURE 3: TEM images of (A) Fe₃O₄ and (B) magnetic humus.

nanoparticles, which was about 0.5 mg humus/mg Fe₃O₄ based on the humus carbon percentage of 48.54% (Zhang et al., 2015). Therefore, the magnetic humus should be contained 33.37% humus, which is much higher than 11% attained in the previous report (Liu, et al., 2008). This observation can be explained by consideration of the further exposure of Fe₃O₄ active sites involved in the humification process under alkaline condition. These active sites contribute to the formation of humus with a higher aromaticity, so more active sites mean a higher generation rate of humus (Zou et al., 2020). Instead of the spherical structure at a low pH, humus was existed in a rather linear or stretched structure at high pH values, as alkaline conditions contribute to the formation of further amounts of humus. This is because the dissolution process of humus avoids occupying further spaces and provides more free spaces for the humus formation near the metal oxide surface. However, too high pH is not conducive to the binding of humus with nanoparticles, therefore, the pH of 8 was adjusted for the generation of magnetic humus.

3.3 Availability of the synthesized magnetic humus

To investigate the ease of separation, performance of the magnetic humus was evaluated in an external magnetic field. As shown in Figure 5, the magnetic humus was scattered in the solution, even after 1 h incubation, in the absence of an external magnetic field. This finding proved good dispersion of the magnetic humus. However, the suspended magnetic humus can be quickly attracted towards a permanent magnet in 2 min, confirming the utility of magnetic humus separation in the presence of an external magnetic field.

The stability of magnetic humus was evaluated in distilled water. After shaking at 200 rpm for 12 h, the supernatant was collected and analyzed with a TOC analyzer to detect the leached humus. The concentration of free carbon was less than 15 mg/L (as TOC), indicating only 6.17% of humus has been leached. The main reason to explain this phenomenon is that the surface of Fe₃O₄ nanoparticles bear a negative charge (PZC = 7.9) at pH 8, which

avoids the electrostatic attraction of Fe₃O₄ nanoparticles to the negatively charged humus and achieves growing of humus on the surface of Fe₃O₄ by covalent binding. Thus, the humus loading would be further enhanced apart from pH variation, upon addition of a non-magnetic metal oxide with enhanced humification function. Therefore, the outer humus molecules can be connected to form a bigger humus molecule through covalent bonding, which result in a big network, enclose the inner humus and avoid the inner humus molecular diffusion. In this way, the humus loading, as well as its stability would be enhanced.

In order to evaluate application of the synthesized humus in water treatment, the magnetic humus was added to a water sample solution containing 7.30 mg/L of Cr(VI). After 6 h, the synthesized magnetic humus (4 mg/mL) showed a high adsorption efficiency of 99.17% to Cr(VI) with the final concentration of 60 µg/L, which was lower than the maximum contaminant limits for the total chromium in drinking water (100 µg/L), as announced by the United States Environmental Protection Agency.

4. CONCLUSIONS

A new abiotic humification method is presented to synthesize magnetic humus with a high performance for Cr(VI) adsorption. The change of TEM image after humus loading indicated the successful synthesis of magnetic humus. pH greatly affects formation of humus and weight of the humus loaded on Fe₃O₄ nanoparticles. When pH is set to 8, the largest loading weight would be obtained, which accounts for 33.37% of the synthesized magnetic humus. The prepared magnetic humus exhibits good separation ability in aqueous solution and a high adsorption efficiency of 99.17% can be attained for Cr(VI). Therefore, the synthesized magnetic humus can be recommended as a potential candidate to remove Cr(VI) from water resources.

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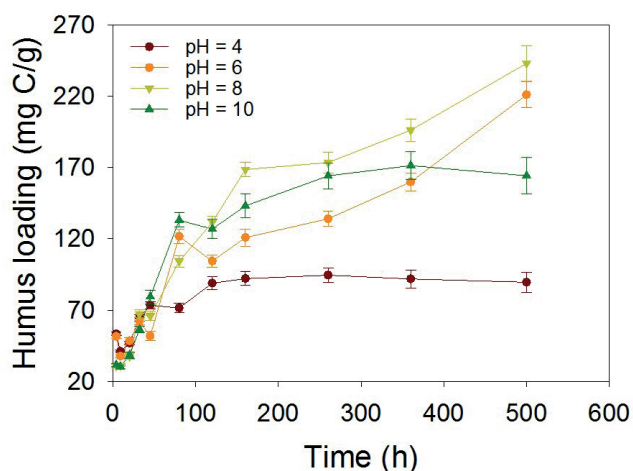


FIGURE 4: Effect of pH on humus loading in different incubation times.

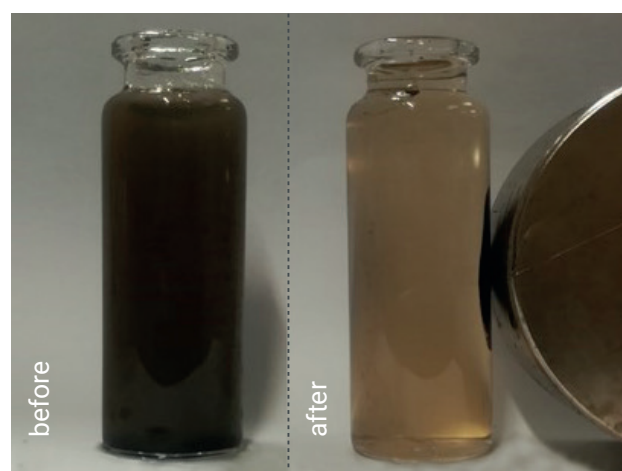


FIGURE 5: Digital images of magnetic humus without or with an external magnetic field added.

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