18PB-084

Immobilization of Prussian Blue onto Graphite-encapsulated Magnetic Nanoparticles by Making Use of Plasma Surface Modification

プラズマ表面修飾を用いたグラファイト被覆磁気ナノ微粒子への プルシアンブルー固定化

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So far, we have carried out the experiments of removal of cesium ion from liquid by magnetic nanoparticles(MNPs) encapsulated with graphite layers. To improve the adsorption efficiency, we are trying to immobillize Prussian Blue(PB), which is one of the most effective sorption for cesium ion. In this study, to develop a method how to immobilize PB onto MNPs, we treated plasma surface modification of MNPs and PB. The carboxy groups or amino groups were introduced onto the surfaces of MNPs by plasma. The preliminary results of the immobilization and adsorption characteristics of new type of MNPs-PB nanocomposites are presented.

1. Introduction

Nowadays in Japan, the radioactive cesium outflow issue due to the nuclear action at Fukushima is an urgent and important problem to be solved. Furthermore, heavy metal ions outflow problem is causing pollution of soil and water in any other Asian countries. In general, there are a few methods to remove metal ions from liquid, e.g., one is a chemical deposition method by using chemical reaction and another is an adsorption method by using adsorbent. In our previous study, we have carried out to adsorb cesium ion from liquid by using graphite-encapsulated nanoparticles (MNPs) (Fig. 1) and we could improve adsorption efficiency by plasma surface modification and plasma treatment of MNPs surface to activate the surface.

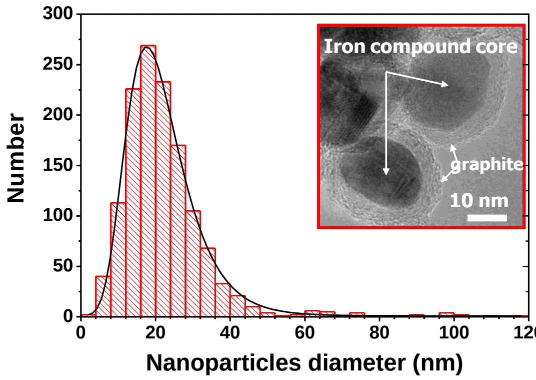

Fig. 1 TEM image and size distribution of MNPs.

In this study, we tried to immobilize Prruisan Blue onto MNPs to improve adsorption efficiency.

2. Experimental setup

Figure 2 shows the schematic view of the inductively-coupled radio frequency plasma device we used. The MNPs were treated by Ar/H_2O plasma to introduce carboxy groups and modify the PB by Ar/NH_3 RF plasma to modify amine groups by the RF device, respectively. Here, we consider a simple immobilization process between amino group modified PB and carboxy group modified MNPs, as shown in Fig. 3.

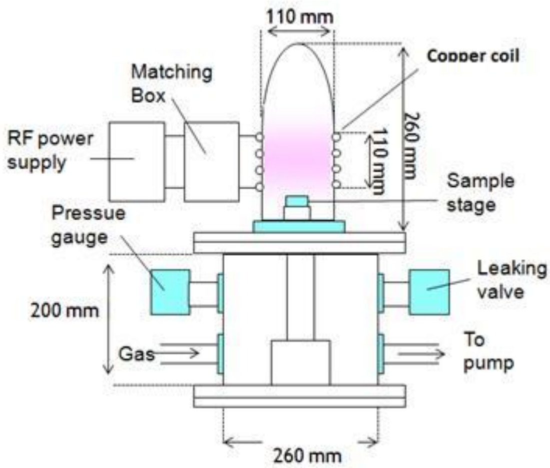

Fig. 2 Experimental setup of inductively coupled RF plasma.

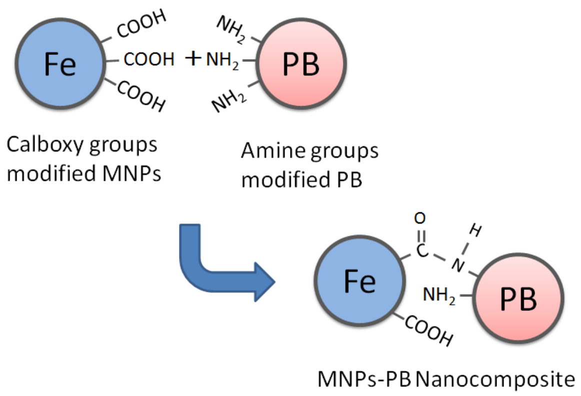

Fig. 3 Illustration for immobilization process.

These two plasma functionalized materials were put in water and stirred about 2 days at 60°C. Then they were washed several times with urtlasonic cleaning, and then, dried at 70°C in the oven. Then we could get MNPs-PB nanocomposites.

3. Result and discussion

First, we measured adsorption rate of PB of cesium ion. Figure 4 shows the cesium adsorption effect, where PB(3mg) were thrown into CsCl solution (4ml, 0-50ppm). After 2days shaking, residual cesium ion concentration was measured by Atomic Absorption Spectroscopy. In 0-10 ppm range, we confirmed 100% adsorption removal and it means that PB is a good adsorbent.

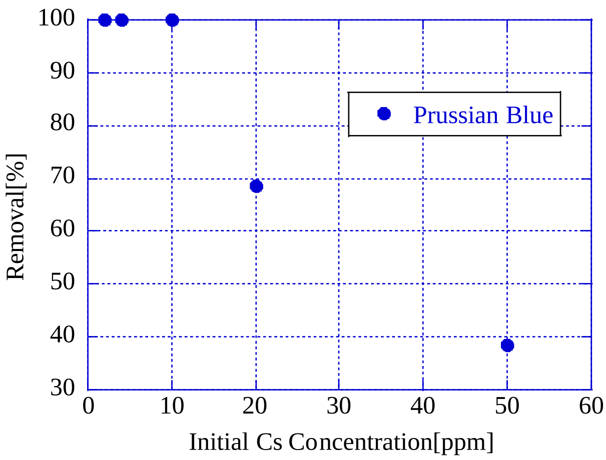

Fig. 4 Removal rate of Cs ion from CsCl solution using Prussian blue as adsorbents.

The results of the RF plasma modification were checked by fluorescence microscope or derivatization method. Figure 5 shows the result of the derivatization to check amino group modification of PB. Ar plasma pretreatment 1 min, and then Ar/NH_3(Ar:47Pa/NH_3:3Pa) plasma post-treatment were done, where an input RF power was 200 W. With absorbance instrument, we can see absorbance peak at around 343 nm, if there are amine groups.

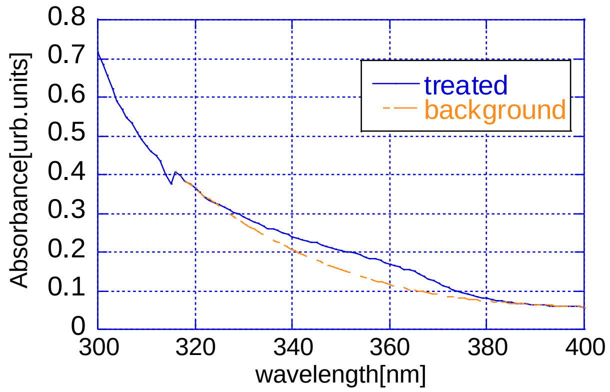

Fig. 5 Result of derivatization of amino group of PB.

Figure 6 shows the appearance that nanocomposites we got were controlled by a magnet in pure water. It is a most valuable characteristic that we can collect nanocomposite after adsorption by magnetic field.

Fig. 6 Magnetic nanocomposites were collected by magnet.

4. Conclusion

Introduction of carboxy group onto MNPs and amine group onto PB were carried out. The each modification results were confirmed by using fluorescence microscope or derivatization method. PB immobillization onto MNPs were carried out, and new adsorbent for Cs ion was developed.

In this conference, we will investigate more detail of immobilization process, and report the adsorption ability of magnetic nanocoposites as Cs ion removal materials.

Acknowledgments

This work has been supported in part by a Grant-in-Aid for Challenging Exploratory Research (No. 25600120) from the JSPS.

References

[1] S. Yang, H. Cho, X. Wang and M. Nagatsu, J. Hazard. Mater.,274 (2014) pp. 46–52.