

## Radiation graft copolymerization of phosphorous containing monomer on CMC-based hydrogel for metal adsorption

Kyushu Univ.: Tran Thu Hong, Hirotaka Okabe, Yoshiki Hidaka, Kazuhiro Hara

E-mail: hong@athena.ap.kyushu-u.ac.jp

### Introduction

Over 120 years, more and more reports have been devoted to phosphorus-containing polymers, mainly due to their fire resistance, metal-adhesion properties and anti-corrosion<sup>1</sup>. Moreover, phosphate groups are known to show excellent chelating properties. Thus, phosphorylated polymers were used as metal-chelating products, as cation exchange materials and for the treatment of pollution<sup>2</sup>. Nevertheless, trying to lessen these phosphorus-containing polymers impact on the environment and toward “green chemistry” by replacing phosphorylated additives and petro based chemicals is currently challenging both research and industry. The use of bio-based polymeric backbones might allow the reduction of toxic bio-accumulation by using renewable materials and by achieving more easily biodegradable. In addition, reuse and recycling become possible.

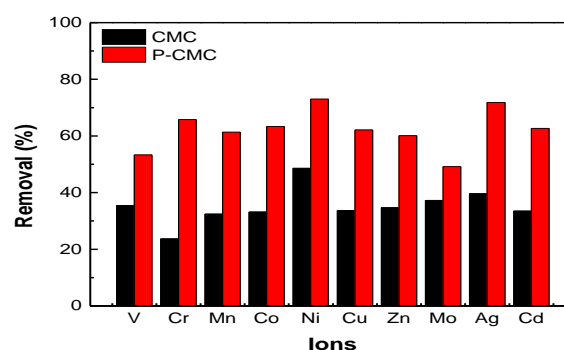
The aim of this study is radiation introduction of phosphoric groups on a type of polysaccharide, namely carboxymethyl cellulose (CMC) which is abundantly found in nature. CMC is renewable, biodegradable, bio-compatible, CO<sub>2</sub> neutral and therefore very promising in terms of “green chemistry”. Bis[2-(Methacryloyloxy)Ethyl] Phosphate (BMEP) and its derivatives are capable of hydrogen bonding and has a strong affinity for a broad variety of inorganic surfaces and metal ions<sup>2</sup>. BMEP was used as a graft copolymerization agent to functionalize CMC-based hydrogel and improve its metal adsorption capacity. Free radical polymerization has been applied to attach BMEP to CMC polysaccharide by gamma rays. The modified CMC-based hydrogels were characterized by thermal analysis, microscopy, water uptake and evaluated their use as metal adsorption materials.

### Experimental

Phosphated CMC-based hydrogels (P-CMC) were prepared by the following procedure. The sets of aqueous solution of 20 wt% CMC and Styrene sodium sulfonate in paste-like state with different added concentration of BMEP were into polypropylene tubes. Each mixture was centrifuged at 10<sup>4</sup> rpm for at least 5 hours to remove tiny bubbles and then were synthesised in 60-kGy- $\gamma$ -radiation at atmosphere condition. After washing with distilled water to remove all un-reactants, the structure, thermal stability, and morphology of P-CMC hydrogels were

characterized by Fourier transform infrared (FTIR) and Energy-dispersive X-ray spectroscopy (EDS), Differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) to confirm the presence of phosphorous groups. Batch adsorption experiments were performed in a wide variety of conditions including different pH, temperature and weight of hydrogels. Effects of each factor were determined keeping other variables constant. All tests were carried out at least three times and the averages was used in the analysis.

### Results and Discussion



**Fig. 1.** The metal removal efficiency of CMC vs. P-CMC hydrogel.

In preparation of hydrogel, the presence of BMEP showed the clear effect on the metal removal (%), as shown in Fig. 1. For CMC hydrogel, metal ions in aqueous solution were uptake low, < 50%. However, when introducing of BMEP to CMC backbone, most of metal removed significantly by phosphated CMC hydrogel (> 50%). The better removal efficiency of the gel could be attributed to the fact that strong ionic groups such as  $-\text{PO}_4^-$ ,  $-\text{SO}_3^-$  and  $-\text{COO}^-$  groups present on hydrogel network and lead to higher binding affinity with metal ions.

Other results will be presented at the meeting.

### Acknowledgment

This work was supported by JSPS KAKENHI Grant Numbers JP21656239, JP24360398.

### References

1. Illy N, et al. *Polym Chem.* 2015; 6; 6257. doi:10.1039/c5py00812c.
2. Sannigrahi A et al. *R Soc Chem.* 2013; 4207-4218. doi:10.1039/C3PY00513E.