

## Absorption of Phosphate Ion in Swine Urine Using CMC Gel

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Removal of phosphate ion in swine urine is a big concern for an environmental conservation. To solve the problem, phosphate ion absorbent in swine urine was developed using carboxymethyl cellulose (CMC) and iron compounds. Mixing CMC with iron salt aqueous solutions resulted in gels as known well. While the gel formation proceeded instantaneously when CMC and ferric salt [Fe(III)] aqueous solution were mixed, the gel was not formed immediately when ferrous salt [Fe(II)] aqueous solution was used. Oxidation of Fe (II) to Fe (III) occurs gradually in Fe(II) aqueous solution. However, addition of CMC to the Fe(II) solution promoted the oxidation to Fe (III). The rate of gel formation could be controlled by addition of acid to CMC-Fe(II) mixture. The absorbent made of CMC and Fe(II) seemed to be more effective than that made of CMC and Fe(III), in Fe content and phosphate ion removal. The resultant gels reduced the phosphorus content from 457 to 3 mg/l in artificial urine and from 78 to 2 mg/l in swine urine, respectively. The values fulfill the regulation of effluent from the pigsty.

Key words: CMC, Fe, Phosphate ion, Urine, Absorption

### 1. INTRODUCTION

Rivers in Gunma Prefecture are sources of water supply to metropolitan areas. There are many swine households near the rivers and treated waste water from the swine households comes into the rivers. According to an inquiry by the Agricultural Production Bureau, Ministry of Agriculture, Forestry and Fishery, the biggest problem in the swine breeding is water pollution [1]. Reducing amount of phosphate ion and nitrogen coming into the rivers is expected for environmental conservation and high quality water supply. Meanwhile, shortage of phosphorus becomes a big concern in the world. Animal waste is a potential phosphorus source. Aiming to solve both problems, Gunma Prefecture started a project, "Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence" sponsored by Science and Technology Agency of Japan (JST). Industries, universities and governments join the project to realize clean Gunma and utilization of animal waste as resources. Each institution is in charge of different objective. Gunma Industry Support Organization and Japan Atomic Energy Agency collaborate to develop a gel to reduce the amount of phosphate ion contained in the effluent from the swine breeders using carboxymethyl cellulose (CMC).

CMC itself does not absorb phosphate ion, however, combination of CMC and metal ion can provide absorbent. Known as a preparation of CMC gel, multivalent metal ion forms ionic crosslinks among CMC molecules. Aluminum and iron ions are the most commonly used metal ions in the CMC gel preparation.

A gel was formed instantaneously when CMC was mixed with ferric salt [hereafter expressed as Fe(III)] solution, however, it took time when ferrous salt

[hereafter expressed as Fe(II)] solution was used.

Eberhardt et al. [2] reported the use of refined aspen wood fiber treated with Fe(II) salt solutions to remove phosphate ion from stormwater runoff. They suggested pretreatment of the wood fiber with CMC to enhance phosphate ion removal.

Aqueous solutions of Fe(II) compounds are oxidized to those of Fe(III) compounds in the air. The oxidation proceeds gradually, however, we found CMC promoted the reaction. Immediately after the addition of CMC to aqueous solution of Fe (II) compound, the color of the solution changed from pale green to reddish brown.

We developed a novel method to prepare CMC gel using CMC and acid [3]. Mixing CMC with acid resulted in a gel replacing sodium in CMC with hydrogen.

Combination of both reactions, oxidation and gelation, is expected to result in CMC-Fe gel which can absorb phosphate ion in swine urine effectively.

### 2. EXPERIMENTAL

#### 2.1 Materials

CMC1380 (sodium salt, DS=1.36, Daicel Chemical Industries, Ltd., Japan) was used all through the experiment. Partially crosslinked polyacrylic acid (Sanfresh ST500MPS) produced by San-Dia Polymers, Ltd. was used for comparison. The chemicals used were reagent grade and used as received.

Artificial urine was prepared after analytical results of swine urine. It contained potassium, sodium, calcium, magnesium, ammonium, chloride, bromide, phosphate, sulfate, nitrate, and carbonate ions, organic acids and urea. The pH value of the artificial urine was adjusted to 8.2.

Swine urine after primary treatment at pigsty was also used. The pH value of the treated urine was 7.3.

## 2.2 Preparation of Phosphate Ion Absorbent

CMC and Fe (II, III) chloride aqueous solution (1.26 M) were mixed and stored at 30°C. The mixture was washed with water repeatedly to remove water-soluble part, and then dried at 50°C. The fraction, which did not pass the stainless steel mesh (80  $\mu$ m) was defined as gel.

In some experiments, acid was added to the Fe (II) solution.

Gel fraction was determined according to the following equation.

$$\text{Gel fraction (\%)} = 100 \times \frac{\text{Weight of insoluble part}}{\text{Initial weight of CMC and Fe}}$$

For the following experiments, only the insoluble gel was used.

## 2.3 Phosphate Ion Absorption by CMC-Fe Mixture

Phosphate ion contained in the artificial urine and the swine urine after primary treatment was absorbed by CMC-Fe gel shaking at 100rpm and at room temperature. The liquor ratio was 100.

Iron, sodium and phosphate ion contents in the absorbent were analyzed by ICP Atomic Emission Spectroscopy (ICP-AES). Phosphate ion contents in the artificial urine and the swine urine were measured by Ion Chromatography and ICP-AES, respectively.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Preparation of CMC-Fe Gel

CMC and Fe (II, III) chloride aqueous solution (1.26 M) were mixed changing the ratio of carboxyl groups to Fe. For comparison, partially crosslinked polyacrylic acid (PAA) was used. As described in introduction, Fe (II) solution is oxidized to Fe (III) solution in the air. Fe (II) solutions immediately after preparation and Fe (II) solution prepared 6h before use were used to compare the effectiveness.

CMC precipitated when mixed with Fe (III) and did not form gel as long as the COOH/Fe ratio did not exceed 2. CMC mixed with Fe (II) formed gel as shown in Fig. 1. The gel fraction increased with increase of COOH/Fe ratio. The gel fraction was higher in freshly prepared Fe (II) than in previously prepared Fe (II). PAA also formed gel when mixed with Fe (III), and the gel fraction was rather higher than CMC-Fe (III) gel.

Most commercial CMC is sold as sodium salt due to the production process. While the sodium content analyzed by ICP was less than 0.3% in all gels prepared, that in original CMC is 7.5%. It means that most of sodium existed as a counter ion of carboxyl group is replaced with others after gelation.

The Fe content in the CMC-Fe gel before and after absorbing phosphate ion is shown in Fig. 2. Fe content was more in gels prepared using Fe (II) than in gels prepared with Fe (III). While Fe content did not change in CMC-Fe (II) gel, that decreased a lot in CMC-Fe (III) and PAA-Fe (III) gels after absorbing phosphate ion.

Assuming that one carboxyl group in the CMC has one Fe as counter ion, to say COOH/Fe = 1/1, the

maximum amount of Fe contained in the gel becomes 24.1% [ $100 \times 1.36 \times 56 / ((162 - 1.36) + 1.36 \times (58 + 56))$ ], where Fe=56, CH<sub>2</sub>COO=58, repeating unit of glucose = 162, and 1.36 is degree of substitution

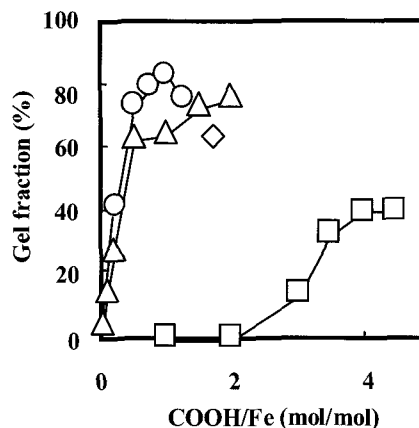


Fig. 1 Gel fraction of CMC-Fe gel. CMC was mixed with the followings and kept for 3 days at 30°C.

- : Fe (II) solution immediately after preparation.
- △ : Fe (II) solution prepared 6h before use.
- : Fe (III) solution.
- ◇ : PAA mixed with Fe (III) solution.

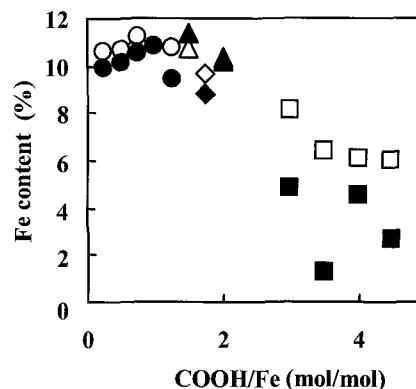


Fig. 2 Fe content in CMC-Fe gel. Closed symbols shown below are for the gels after absorption of phosphate ion in the artificial urine. Open symbols are the same with those shown in Fig. 1.

- : Fe (II) solution immediately after preparation.
- ▲ : Fe (II) solution prepared 6h before use.
- : Fe (III) solution.
- ◆ : PAA mixed with Fe (III) solution.

of CMC)]. Fe (II) is divalent, however, the maximum amount of Fe which can be bound to carboxyl group becomes 13.7% [ $100 \times 0.68 \times 56 / ((162 - 1.36) + 1.36 \times 58 + 0.68 \times 56)$ ]. In the same way, maximum amount of Fe (III) becomes 9.5%. Therefore, most of Fe might be bound to carboxyl groups in the prepared gels.

Judging from the results mentioned above, Fe binds to carboxymethyl group. The difference between Fe(II) solutions immediately after preparation and that prepared 6 h before use shows that a part of Fe(II) is

oxidized to Fe (III). However, details are not elucidated yet.

### 3.2 Phosphate Ion Absorption by CMC-Fe Gel

1 g CMC-Fe gels were put in 100ml of the artificial urine, in which phosphate ion content is 1400 mg/l (457 mg/l as for phosphorus). The Fe contents of the gels were 10.4 and 8.1% in CMC-Fe (II) and CMC-Fe(III) gel, respectively. The phosphate ion concentration was measured by ion chromatography and decreased with absorption time as shown in Fig. 3. If one Fe molecule absorbs one phosphate ion, 1 g CMC-Fe (II) and (III) gels absorb 130 and 100 mg phosphate ion, respectively. Actually 140 and 120 mg of phosphate ion were absorbed on CMC-Fe (II) and (III) gels. In CMC-Fe (III) gel, desorption occurred after long time absorption.

Although many researchers have used Fe (III) compounds for absorption of phosphate ion, Fe (II) seems to be better for phosphate ion binding.

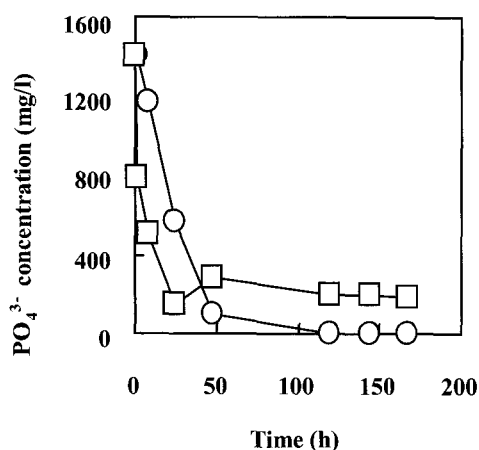


Fig. 3 Phosphate ion binding on CMC-Fe gels. Captions are the same with those shown in Fig. 1.

### 3.3 CMC-Fe (II)-Acid Gel

As described above, CMC-Fe (II) gel seems to give better results than CMC-Fe (III) gel. Sodium as a counter ion of carboxyl group was easily replaced by Fe. The results are explained by the ionization tendency of cations. In the existence of acid, replacement of sodium by Fe might be competitive with that by hydrogen. Fe thus replaced might bind more phosphate ion.

Fig. 4 shows Fe content in gels. The amount of Fe in CMC-Fe gel decreased with the increase of acid concentration. It infers the competitive reactions in the replacement of sodium with Fe and hydrogen. However, the phosphate ion absorption by CMC-Fe (II)-acid gels was very little as seen in Fig. 5.

Amount of phosphate ion absorbed by 1g Fe is almost the same regardless of hydrochloric acid concentration used for the preparation of gels (Table I).

Gel made of CMC-Fe (II)-0.1M HCl was high in Fe content and absorb much amount of phosphate ion. Besides, the supernatant of the CMC-Fe (II)-0.1M HCl was clear after absorption of phosphate ion, however, it took some time to be clear in CMC-Fe (II)-water gel.

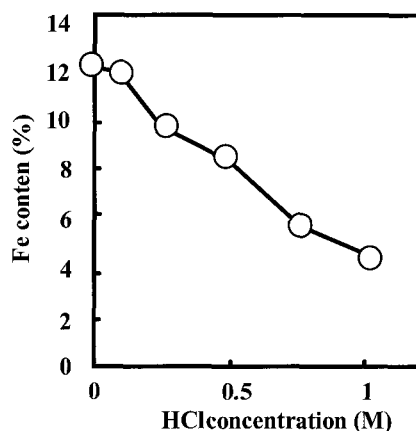


Fig. 4 Fe content in CMC-Fe (II)- acid gel.

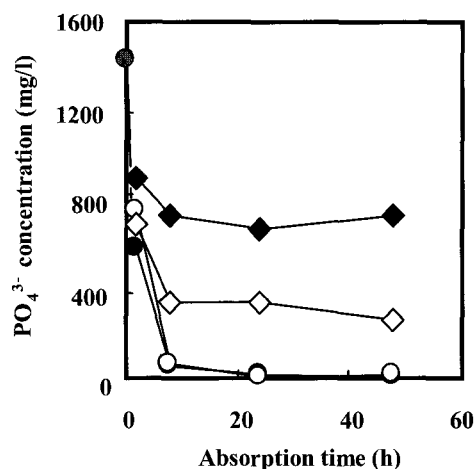


Fig. 5 Phosphate ion binding on CMC-Fe(II)-acid gels. The concentration of hydrochloric acid used for the preparation of gel was:

● : 0 M, ○ : 0.1 M, ◇ : 0.25M, ◆ : 0.75M.

Table I Phosphate ion absorption on CMC-Fe (II) gel

HCl concentration (M)	PO <sub>4</sub> <sup>3-</sup> /Fe (mg/g)
0	120
0.1	120
0.25	115
0.75	125

Acid promoted gelation of CMC resulting hydrogen bonds among CMC molecules [3].

CMC-Fe (II)-acid gels were prepared using various acids with the concentration of 0.1M. Some of the gels were prepared at 30°C and 50°C, kept 3 days, 8 days and 14 days. Regardless of the species of acids, preparation temperature, keeping time, they all effectively absorbed phosphate ion in the artificial urine as shown in Fig. 6. They absorbed phosphate ion in shorter time and did not release phosphate ion after long time absorption.

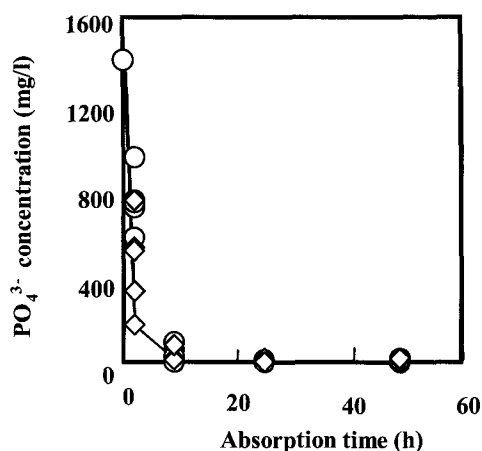


Fig. 6 Absorption of phosphate ion by CMC-Fe (II)-acid gel. Gel was prepared at: ○ : 30°C and ◇ : 50°C.

#### 3.4 Phosphate Ion Absorption in Swine Urine

Phosphate ion contained in swine urine primarily treated in a swine breeder was absorbed by CMC-Fe (II) acid gels in the same way with that in the artificial urine. As the phosphate ion content could not be measured by ion chromatography, phosphorus content was measured by ICP-AES. Initial phosphorus concentration of the swine urine was 78 mg/l. It decreased to less than 2 mg/l after treatment with gels. The value was less than 8 mg/l; which is the regulation average value in a day eluted from swine breeders.

As shown in Fig. 7 more than 97% of phosphate ion was removed by the gels regardless of the species of acids.

Not only phosphate ion in the artificial urine but also phosphorus in the swine urine could be removed by the gels.

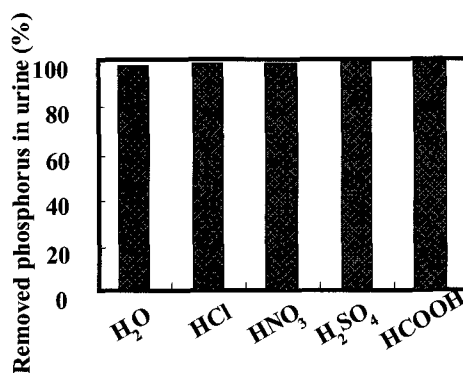


Fig. 7 Removal of phosphorus in swine urine by CMC-Fe (II)-acid gels.

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