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# Comparison of Arsenite Removal Mechanism Between Co-precipitation and Adsorption Processes in Several Co-existing ions

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Content

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Abstract

Arsenic (As) is well known as a useful compound in industrial applications such as smelting, agricultural pesticides and insecticides. It has also been considered as a strong poisonous chemical due to its effect on a sulfhydryl group of cells interfering with cells enzymes, cell respiration, and mitosis. Even small amounts of arsenic in drinking water can have adverse effects on human health. Therefore, the development of efficient technologies for arsenic removal is highly anticipated.There are some papers on the influence of common anions in wastewater such as nitrate, sulfate, phosphate, and on the removal of arsenic. There has been no study on the influence of coexisting anions on the removal of arsenic concerned with sedimentation rate and re-dissolution of arsenic in sludge which is one of the important factors for sludge disposal.The purpose of this study was to investigate the effect of coexisting anions such as nitrate, sulfate, phosphate on the removal of arsenic concerned with the removal property of As(III), sedimentation rate and re-dissolution of arsenic in sludge by ferrihydrite in co-precipitation and adsorption processes. The experiment was a batch test, and the experimental conditions were set as ionic strength 0.05 mol /$dm^3$, pH 7.The co-precipitation method is superior when Fe (III) is used as a removal agent in As removal. The nitrate and sufate ion were good effect on removal of As(III) while phosphate ion was adversely effected. The order of settling rate was $NO_3^-$ > $SO_4^{2-}$ > $PO_4^{3-}$ . The floc size of phosphate ion solution was the smallest particle and the settling speed was the lowest. The As re-dissolution amount of phosphate ion was the highest and that of nitrate ion was the lowest.

# Co-precipitation နှင့် Adsorption နည်းစဉ်များဖြင့် Arsenite ဖယ်ရှားရေးယန္တရားတွင် ပူးတွဲပါရှိသော အိုင်းယွန်းများ၏ သက်ရောက်မှုများအား နှိုင်းယှဉ်ခြင်း

ကျော်စွာဦး၊ ဒုတိယညွှန်ကြားရေးမှူး

သတ္တုတွင်းဦးစီးဌာန

## စာတမ်းအကျဉ်း

Arsenic(As)ကို သတ္တုအရည်ကျိုလုပ်ငန်းများ၊ စိုက်ပျိုးရေး ပိုးသတ်ဆေးများနှင့် ပိုးသတ်ဆေးများ ကဲ့သို့သော စက်မှုလုပ်ငန်းများတွင် အသုံးများသော ဒြပ်ပေါင်းအဖြစ် လူသိများပါသည်။ ၎င်းသည် ဆဲလ်အင်ဇိုင်းများ၊ ဆဲလ်အသက်ရှူခြင်းနှင့် mitosis နှင့် ဝင်ရောက်စွက်ဖက်သော ဆဲလ်များ၏ sulfhydryl အုပ်စုအပေါ် သက်ရောက်မှုကြောင့် အဆိပ်ရှိသော ဓာတုပစ္စည်းအဖြစ် သတ်မှတ်ထားပါသည်။ သောက်သုံးရေတွင် အာဆင်းနစ် အနည်းငယ်ပါဝင်ပါက လူ၏ကျန်းမာရေးကို ဆိုးကျိုးဖြစ်စေနိုင်ပါသည်။ ထို့ကြောင့် အာဆင်းနစ်ကို ဖယ်ရှားရန်အတွက် ထိရောက်သော နည်းပညာများကို တီထွင်ရန်လိုအပ်ပါသည်။ အာဆင်းနစ် ဖယ်ရှားခြင်းနှင့် စွန့်ပစ်ရေတွင် နိုက်ထရိတ်၊ ဆာလဖိတ်၊ ဖော့စဖိတ် ကဲ့သို့သော anion များ၏လွှမ်းမိုးမှုနှင့် ပတ်သက်သော စာရွက်စာတမ်းများ ရှိပါသည်။ အနည်ထိုင်နှုန်း နှင့် ဘေးထွက်ပစ္စည်း စွန့်ပစ်ရေးတွင် အရေးကြီးအချက်များအနက် တစ်ခုဖြစ်သည့် ပြန်လည်ပျော်ဝင်နှုန်းတွင် ပူးတွဲပါရှိသော anion များ၏လွှမ်းမိုးမှုအား လေ့လာသည့်သုတေသနအနည်းပါ ရှိပါသည်။ ယခု လေ့လာမှု၏ ရည်ရွယ်ချက်မှာ As(III)ဖယ်ရှားနှုန်း၊ အနည်ထိုင်နှုန်းနှင့် ဘေးထွက် ပစ္စည်းတွင် ပြန်လည်ပျော်ဝင်နှုန်းအပေါ် နိုက်ထရိတ်၊

ဆာလဖိတ်၊ ဖော့စဖိတ် ကဲ့သို့သော anion များ၏ အကျိုး သက်ရောက်မှုကို သိရှိရန်ဖြစ်ပါသည်။ စမ်းသပ်မှုသည် အတွဲလိုက် စစ်ဆေးခြင်းဖြစ်ပြီး အိုင်းယွန်းအင်အား (0.05 mol /$dm^3$, pH 7)အခြေအနေတွင် ဆောင်ရွက် ခြင်းဖြစ်ပါသည်။ As ဖယ်ရှားရေးတွင် Fe (III) ကို ဖယ်ရှားပေးသည့် ပစ္စည်းအဖြစ် အသုံးပြုသည့် အခါ Co-precipitation နည်းစဉ်က ပိုမိုသင့်လျော်ပါသည်။ As(III)ဖယ်ရှား နှုန်းတွင် ဖော့စဖိတ် အိုင်းယွန်းကဆိုးရွားစွာ ထိခိုက်သော်လည်း နိုက်ထရိတ်နှင့်ဆာလဖိတ် အိုင်းယွန်းများက ကောင်းသောအကျိုး သက်ရောက်မှု ရှိကြပါသည်။ အနည်ထိုင်နှုန်း အခြေအနေမှာ $NO_3^-$ > $SO_4^{2-}$ > $PO_4^{3-}$ ဖြစ်ပါသည်။ ဖော့စဖိတ်အိုင်းယွန်းပျော်ရည်၏ floc အရွယ်အစားမှာ အသေး ငယ်ဆုံးဖြစ်ပြီး အနည်ထိုင်နှုန်းမှာ အနိမ့်ဆုံးဖြစ်ပါသည်။ ဖော့စဖိတ် အိုင်းယွန်း၏ ပြန်လည် ပျော်ဝင်နှုန်းမှာ အမြင့်ဆုံးဖြစ်ပြီး နိုက်ထရိတ် အိုင်းယွန်းမှာ အနိမ့်ဆုံး ဖြစ်ပါသည်။

# Comparison of Arsenite Removal Mechanism Between Co-precipitation and Adsorption Processes in Several Co-existing ions

## 1. Introduction

Arsenic (As) is well known as a useful compound in industrial applications such as smelting, agricultural pesticides and insecticides. However, it has also been considered as a strong poisonous chemical due to its effect on a sulfhydryl group of cells interfering with cells enzymes, cell respiration, and mitosis. Even small amounts of arsenic in drinking water can have adverse effects on human health. Inorganic arsenic commonly exists in two valence states, As(III) and As(V), in groundwater or surface water [1]. Inorganic arsenic also has adverse effects on human health. As(III) effects on human health are more adverse than those of As(V). Therefore, the development of efficient technologies for arsenic removal is highly anticipated.

Metal oxides have been studied by many researchers as one of the most promising technologies for arsenic removal. Among them, ferrihydrite is a poorly ordered hydrous iron oxide commonly presents in low-temperature geochemical processes and in surface environments such as soils, lake and river sediments. Ferrihydrite is also a common product in hydrometallurgical operations involving the co-precipitation of iron and arsenate and in acid mine drainage [2].

Due to its high surface area, ferrihydrite shows strong affinity for arsenic at mineral–water interfaces. Therefore, the adsorption of arsenic toxic anions on ferrihydrite play a key-role in controlling the transport, fate and bioavailability of arsenate and arsenite in soils, groundwater and surface water systems. Accordingly, ferrihydrite can be used as adsorbent material for removal and immobilization of arsenic from wastewater [3]. The adsorption of arsenic on ferrihydrite involves an exchange of ligand between $AsO_4^{3-}$ /$AsO_3^{-}$ and $H_2O/OH^-$ on the substrate surface [4]. Thus, important factors influencing the adsorption of arsenic on ferrihydrite are the medium type, the concentration of coexisting ions, the initial As/Fe molar ratios and the pH.

Mineral processing effluents are usually sulfate-rich solutions due to the use of sulfuric acid as leaching agent or addition of ferric sulfate [5]. Application of phosphate fertilizers to lead arsenate contaminated soils increased soil arsenic solubility and downward mobility [6]. Therefore research on the adsorption of arsenic onto ferrihydrite from different coexisting ions is needed for a better understanding of removal and immobilization of arsenic. Y. Jia investigated that the influence of different media (nitrate vs sulfate) on the adsorption of arsenate onto ferrihydrite [7]. X. Meng also tried to know that the combined effects of anions on arsenic removal by iron hydoxides [8].

As(III) and As(V) removal mechanism by ferrihydrite in co-precipitation and adsorption processes was the previous study of our laboratory [9]. There are some papers on the influence of common anions in wastewater such as nitrate, sulfate, phosphate, and on the removal of arsenic. There has been no study on the influence of coexisting anions on the removal of arsenic concerned with sedimentation rate and re-dissolution of arsenic in sludge which is one of the important factors for sludge disposal.

The objectives of this study are to investigate the effect of coexisting anions such as nitrate, sulfate, phosphate on the removal of arsenic concerned with the removal property of As(III), sedimentation rate and re-dissolution of arsenic in sludge by ferrihydrite in co-precipitation and adsorption processes.

## 2. Materials and Method

Experimental methods and conditions conducted in each section are shown. All solution experiments were carried out using distilled water from ion exchanged water produced from a pure water production machine (ADVANTEC, aquarius RFD 240 NA). Measurement sample was prepared on the same day of the measurement to avoid adsorbing to the storage container. In addition, when measuring the concentration with an ICP emission spectrophotometer, measurements were made after adding an acidic solution by adding one drop of concentrated nitric acid (69%) to avoid introducing a neutral solution.

2.1.1. Preparation of As solution

The As (III) solution was prepared by dissolving $As_2O_3$ in distilled water. Since $As_2O_3$ was sparingly soluble in the vicinity of neutral, once 8 M KOH was added to distilled water to make it basic, then $As_2O_3$ powder was dissolved. After dissolving all, acidic solution was made with 1 M $HNO_3$ and used in the experiment[24]. In order to avoid oxidation of As (III), As (III) solution was prepared on the same day of experiment.

2.1.2. Removal experiment of As (III) with Nitrate, Sulphate and Phosphate ion by Co-precipitation method

Removal experiments by co-precipitation method were conducted to adjust insoluble ions and adsorbed ions to the appropriate pH in the coexistence state to generate insoluble precipitates. The method is shown below. 1 M $HNO_3$ and 1 M KOH, As solution having a predetermined concentration and $Fe(NO_3)_3 \cdot 9\ H_2O$ were dissolved in distilled water so as to have a predetermined ionic strength (0.05 mol / $dm^3$) in a 100 mL measuring flask. The Fe solution thus obtained was added so as to have a predetermined concentration, and the volume was adjusted with pure water. The predetermined concentration here is a value corresponding to the As (mol) / Fe (mol) ratio, and the amount of Fe relative to the As amount was varied from 0.125 to 10, and the experimental conditions were adopted.

Each of these solutions was transferred to a beaker and stirred at 200 rpm using a magnetic stirrer. When the pH fluctuated, 1 M $HNO_3$ and 1 M KOH were used so that pH 7

was appropriately adjusted. At the time of pH adjustment, the solution was carefully dropped one by one so as not to change the amount of the solution as much as possible. After pH stabilization, the removal experiment was terminated by stirring for 1 hour. The targeted pH was 7 because most of the countries guided the environmental standards of pH as 6.5 to 8.6.

After 1 hour of reaction, the solution was sampled and filtrated with a simple filter having a pore size of 0.1 μm, and then a solution sample was obtained. The filtrated solution was made acidic and then As concentration was measured using an Inductively Couple Plasma Atomic Emission Spectroscopy analyzer.

$Fe_2(SO_4)_3 \cdot 5\ H_2O$ was used for the sulphate ion experiment as same procedure.

2.1.3. Removal experiment of As (III) with Nitrate, Sulphate and Phosphate ion by Adsorption method

In order to compare removal by co-precipitation method with removal by general adsorption method, amorphous ferric hydroxide was generated in advance and removal experiment by adsorption method used for As removal was carried out. 1 M $HNO_3$ and 1 M KOH and an As solution so as to have a predetermined concentration were placed in a 50 mL measuring flask so as to obtain a predetermined ionic strength (0.05 mol / $dm^3$ after introduction of the iron solution), and constantly mixed with pure water to obtain As a solution. Meanwhile, an Fe solution was added to a 50 mL measuring flask to a predetermined concentration, and an Fe solution constantly filled with pure water was prepared.

Initially the Fe solution was transferred to a beaker and stirred at 200 rpm using a magnetic stirrer to adjust the pH to 7. When the pH fluctuated, 1 M $HNO_3$ and 1 M KOH were used so that pH 7 was appropriately adjusted. After pH stabilization, stirring for 1 hour stabilized the formation reaction of ferric hydroxide. The As solution was transferred to a beaker until Fe precipitate formation stabilized, and the pH was adjusted to 7 by stirring at 200 rpm using a magnetic stirrer. It was adjusted using 1 M $HNO_3$ and 1 M KOH so that pH 7 was appropriately obtained.

$Fe_2(SO_4)_3 \cdot 5\ H_2O$ was used for the sulphate ion experiment as same procedure.

**2.2. XRD analysis of precipitates**

The measurement sample of XRD was prepared in the same flow as the solution experiment (co-precipitation method: Fig. 4.1, Fig.4.2, Fig. 4.3, adsorption method. Fig. 4.4, Fig. 4.5, Fig. 4.6), but not the As amount but the Fe amount was unified to 20 ppm and the As/Fe ratio was changed to prepare a precipitate. In addition, in order to ensure a sufficient amount of precipitation for XRD measurement, an experiment was conducted with the amount of liquid set at 2 L at the time of making the precipitate. The precipitate was placed in a freeze dryer together with the filter paper, dried for 24 hours, and then used as a measurement sample. Amorphous ferric hydroxide was used as reference sample.

### 2.3. Sedimentation rate

The amount of Fe to be added was fixed at 20 mg/dm$^3$ and the amount of As was changed to molar ratio of As/Fe 0.125. After agitation 1hour, sedimentation rate measuring was started in time interval of 0.5, 1, 3, 6, 12, 24 hour by using turbidity meter.

2.4. Re-dissolution of sludge

The initial As concentration was 10 mg/dm$^3$ and Fe was changed to molar ratio of As/Fe 0.125 at pH 7. After agitation 1hour, solid liquid separation was conducted by using 0.1 μm filter. The precipitate was placed in a freeze dryer together with the filter paper, dried for 24 hours. 10 mg of sludge was used for re-dissolution experiment and pH was not controlled at that time but pH condition was recorded.

## 3. Results and Discussion

### 3.1.1. Removal property

In order to elucidate the adsorption mechanism of As to ferrihydrite, removal experiments were carried out using the co-precipitation method and the adsorption method to prepare a removal property graph. The amount of Fe(III) charged and the residual As concentration in the ordinate were taken to examine the influence on the As removal with respect to the iron addition concentration. The results are shown in Fig.1 and Fig. 2. The initial As concentration was set at 10 mg/dm$^3$, and all experiments were carried out at pH 7, ionic strength 0.05 mol /dm$^3$.

From Fig. 1, it can be confirmed that the residual As concentration in the solution decreases as the iron added concentration increases in nitrate and sulfate ions experiments under both conditions. As(III) residual amount was 1.14 mg/dm$^3$ in co-precipitation and 2.25 mg /dm$^3$ in adsorption while using nitrate ion at As/Fe molar ratio 0.125. As(III) residual amount was 0.25 mg/dm$^3$ in co-precipitation and 0.57 mg/dm$^3$ in adsorption while using sulfate ion at As/Fe molar ratio 0.125. Sulfate ion was more effect in the removal of As(III) by using ferrihydrite than that of nitrate ion. The adsorbed sulfate anions are later displaced by the stronger complexing arsenate anions when the ferrihydrite is brought into contact with arsenate solution [25]. Therefore, the increased density of sulfate active sites and optimized steric effect are probable factors explaining the higher arsenite adsorption capacity on sulfate-media.

In addition, D.A Dzombak and F.M.M Morel reported that in the colloidal solution containing ferric hydroxide, the sulfate ion previously adsorbed on ferric hydroxide was replaced with a complex of As(V). According to Jia, sulfate ion was bonded to the exposed reactive group, and it may be considered that As(V) may be replaced later as in the reaction of the following formula [7].

$$\equiv FeSO4 + H_2AsO_4^- \rightarrow \equiv FeAsO_4 + HSO_4^- + H^+$$

At the same time, Jia reported that there was a difference in the influence of this effect depending on the As/Fe ratio, and that there was a large influence in the order of As /Fe = 0.5, As/Fe = 0.25, As/Fe = 0.125. Although these papers have described As(V) removal, consider the fact that the adsorption form of As(III) changes according to the As /Fe ratio. It was susceptible to the influence of the surrounding solution state and the rise in removal performance with sulfate ion.

As a bivalent anion, $SO_4^{2-}$ possesses more charges per ion than a monovalent anion. This feature may be partially explained the excellent performance of $SO_4^{2-}$ in improving As(III) removal.

From the above results, it was confirmed that the co-precipitation method is superior when Fe (III) is used as a removal agent in As removal. The adsorption method is inferior to the co-precipitation method is thought to be that crystal growth of Fe precipitation suppressed As removal. In the adsorption method, ferric hydroxide as a removing agent is generated in another beaker for 1 hour beforehand and used for As removal. As a result, since there is time enough for crystal growth, it is considered that the specific surface area contributing to the reaction narrowed, the adsorption site decreased, and the amount of removed As decreased. In addition, the superiority of the co-precipitation method can be considered as many factors such as surface precipitation formation and various electrical characteristics.

From Fig. 2, the removal property of As(III) by using ferrihydrite can be shown the adverse effect of phosphate ion. In this case, As/Fe molar ratio was fixed at 0.125 and $PO_4$/Fe molar ratio was changed from 0.02 to 1. As(III) residual amount was 0.58 mg/dm$^3$ in co-precipitation and 2.18 mg/dm$^3$ in adsorption while using phosphate ion at PO4/Fe molar ratio 0.02. When phosphate concentration increased, residual amount of arsenic increased in both processes. $FePO_4$ precipitated and amount of ferrihydrite decreased and then phosphate ion disturbed formation of arsenic surface complexation onto ferrihydrite. Phosphate caused the greatest percentage decrease in arsenic removal rate among the three anions and the nitrate and sulfate had less effect on the arsenic removal. Phosphate element and arsenic element are located in the same main group, and the molecular structure of phosphate ion is very similar to that of arsenic ion. Phosphate decreased both As(III) and As(V) sorption by ferrihydrite depending strongly on pH and phosphate concentration [26]. The inner-sphere complex-forming phosphate competes strongly with As(III) for sorption site.

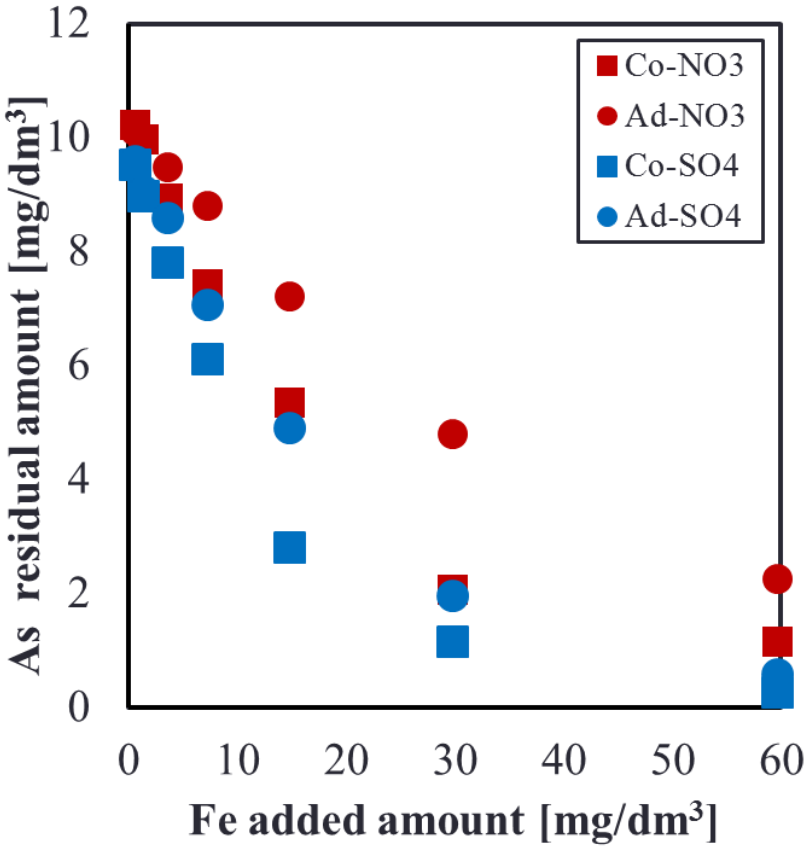


**Fig. 1 Relationship between Fe(III) conc. and residual As(III) conc. pH7 Ionic strength 0.05 mol/dm$^3$ Co=co-precipitation, Ad=adsorption**

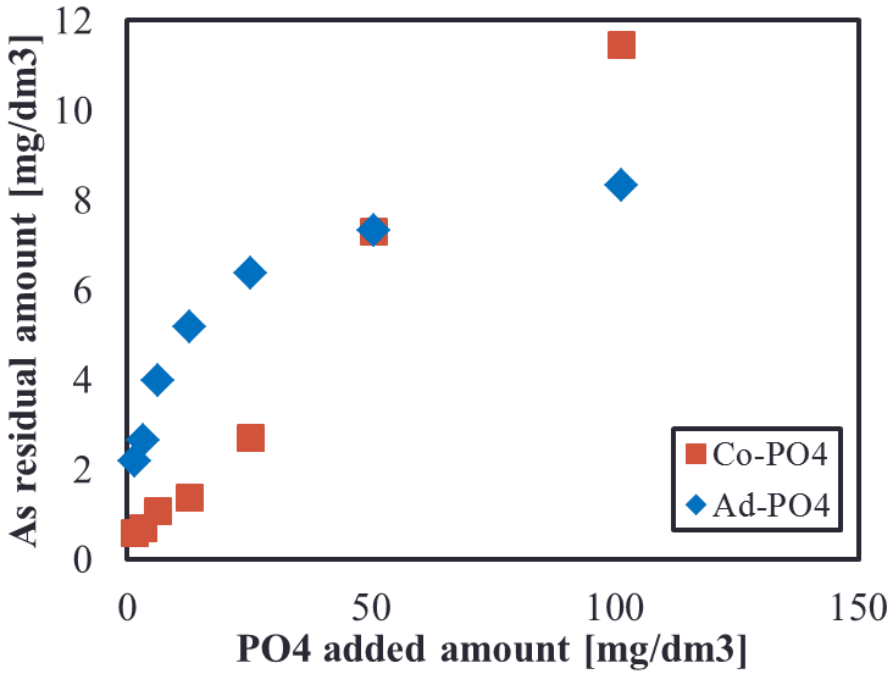


**Fig. 2 Relationship between $PO_4$ conc. and residual As(III) conc. pH7 Ionic strength 0.05 mol/dm$^3$ Co=co-precipitation, Ad=adsorption**

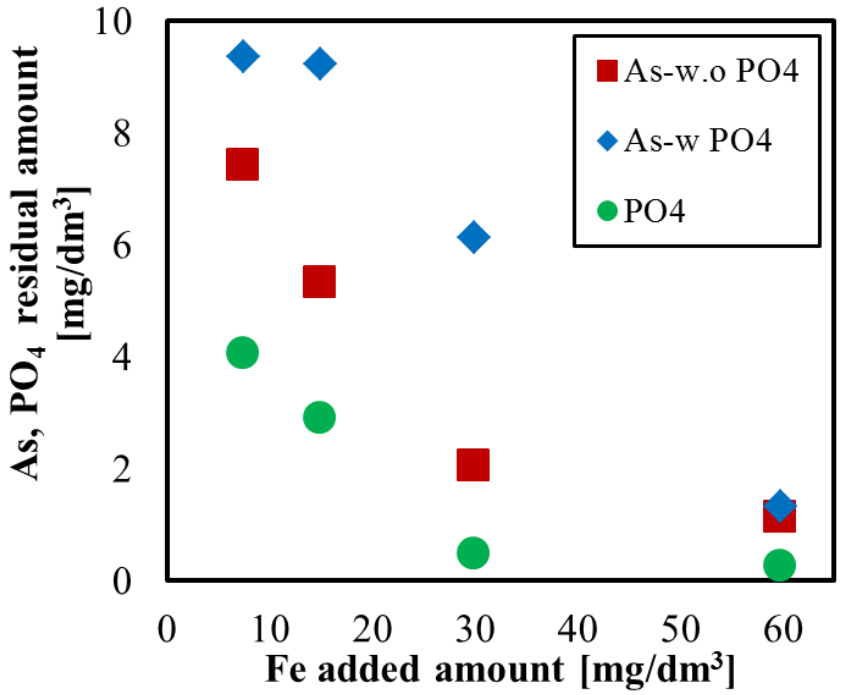


**Fig. 3 Relationship between Fe(III) conc. and residual As(III) conc. , residual $PO_4$ conc. in co-precipitation (initial As(III)=10 mg/dm$^3$ , initial $PO_4$ =10 mg/dm$^3$ , pH7, Ionic strength 0.05 mol/dm$^3$ )**

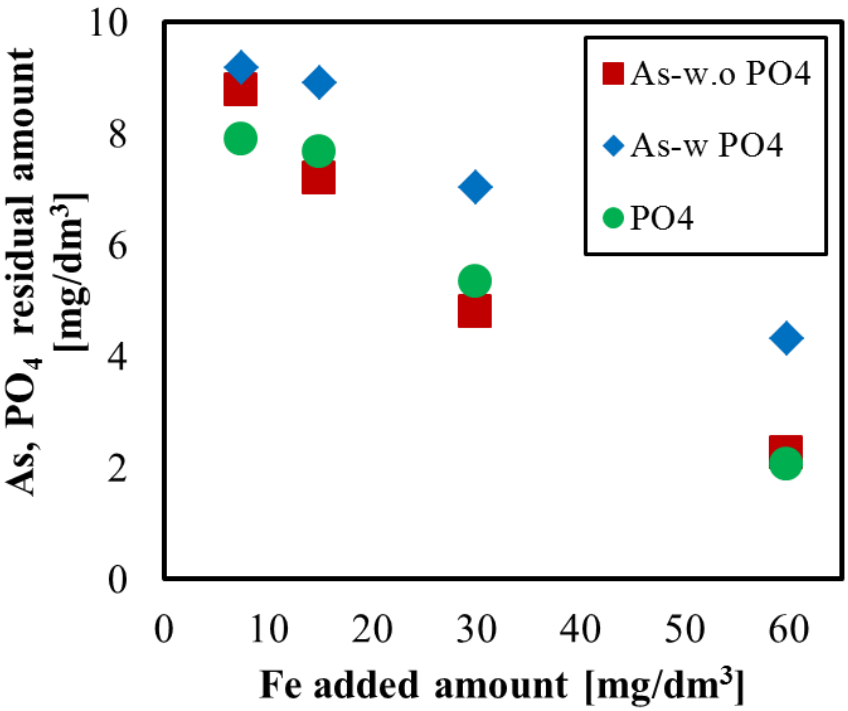


**Fig. 4 Relationship between Fe(III) conc. and residual As(III) conc. , residual $PO_4$ conc. in adsorption (initial As(III)=10 mg/dm$^3$ , initial $PO_4$ =10 mg/dm$^3$ , pH7, Ionic strength 0.05 mol/dm$^3$ )**

### 3.1.2. XRD patterns of sludge

The XRD results of precipitation after removal of As(III) by each removal method. As a reference sample, ferric hydroxide is added in the graph.

As shown in Fig. 5 (co-precipitation experiment with nitrate ion), the peak of the precipitate prepared under As/Fe condition higher than As(III)/Fe = 1 increased from 34 ° as As/Fe ratio increased it was confirmed that it gradually transited to 31 °. Therefore, it was suggested that the precipitate prepared under these conditions is different from the structure of ferric hydroxide. From the above results, the precipitate prepared under the As/Fe condition higher than As/Fe = 1 shows that As(III) has been removed by surface precipitation. The interatomic distance has been extended while keeping ferric hydroxide can be considered.

On the other hand, since the peak of the precipitate prepared under the condition of As/Fe = 0.5 or less is consistent with that of ferric hydroxide, and it was confirmed that As(III) was removed by formation of surface complex under low As/Fe condition even with co-precipitation method.

From the Fig. 6 (adsorption method experiment with nitrate ion), the peak of the precipitate prepared under all As / Fe conditions can be confirmed was identified as ferrihydrite.

In Fig. 7 and 8 (co-precipitation and adsorption method experiment with sulfate ion), the peak of the precipitate prepared under all As/Fe conditions can be confirmed was identified as ferrihydrite. The sulfate ions compete with arsenite for similar adsorption sites thereby reducing the adsorption capacity of arsenite. The reduction on adsorption follows the following order by anions sulfate > chloride > carbonate > bicarbonate > nitrate [27]. These ions may be competing for the active sorption sites along with the arsenic during adsorption process which resulted in decrease in adsorption capacity. Apart from this, the effect of these anions towards adsorption may be due to their affinity towards the adsorbent material.

As shown in Fig. 9 (co-precipitation experiment with phosphate ion), the peak of the precipitate was shifted like $FePO_4$ at higher molar ratio of $PO_4$/Fe. The phosphate ion may be disturbed the formation of ferrihydrite and favored to ferric phosphate. The affinity of As(III) for iron hydroxide was much weaker than phosphate and the removal of As(III) was reduced significantly by phosphate. The affinity of the anions for the iron hydroxide sites decreased in the order arsenate > phosphate > arsenite > silicate > bicarbonate. Even at relatively low concentrations and low surface site coverage of phosphate, silicate and bicarbonate decreased the removal of As (III) [8].

From the Fig. 10 (adsorption method experiment with phosphate ion), the peak of the precipitate prepared under all $PO_4$/Fe conditions can be confirmed was identified as ferrihydrite. Ferrihydrite was partially formed before disturbing of phosphate ion in adsorption process.

From the above result, the inner-sphere complex-forming phosphate was competed strongly with As(III) for sorption sites, whereas sulfate and nitrate do not compete effectively.

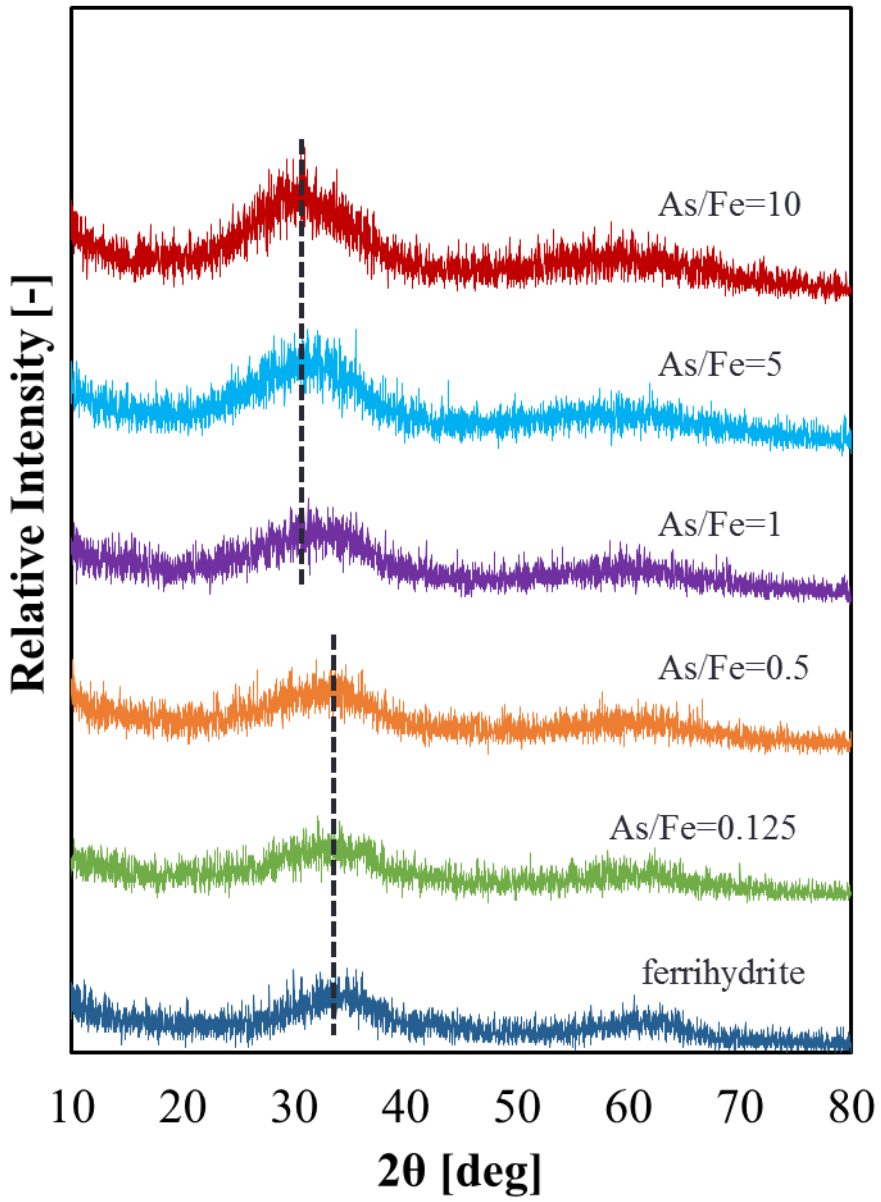


**Fig. 3. XRD spectrums of precipitates in variant As(III)/Fe with nitrate ion in Co-precipitation process**

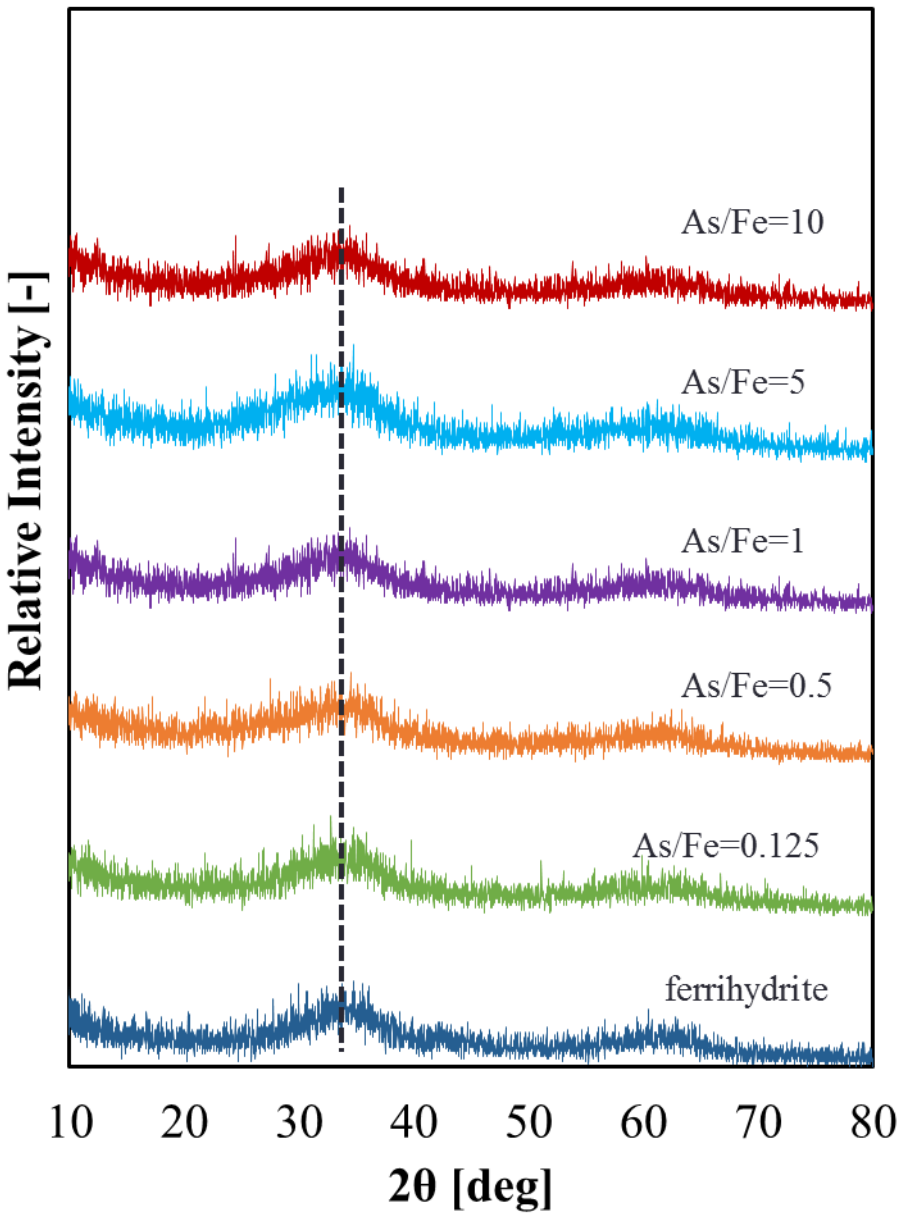


**Fig. 6. XRD spectrums of precipitates in variant As(III)/Fe with nitrate ion in Adsorption process**

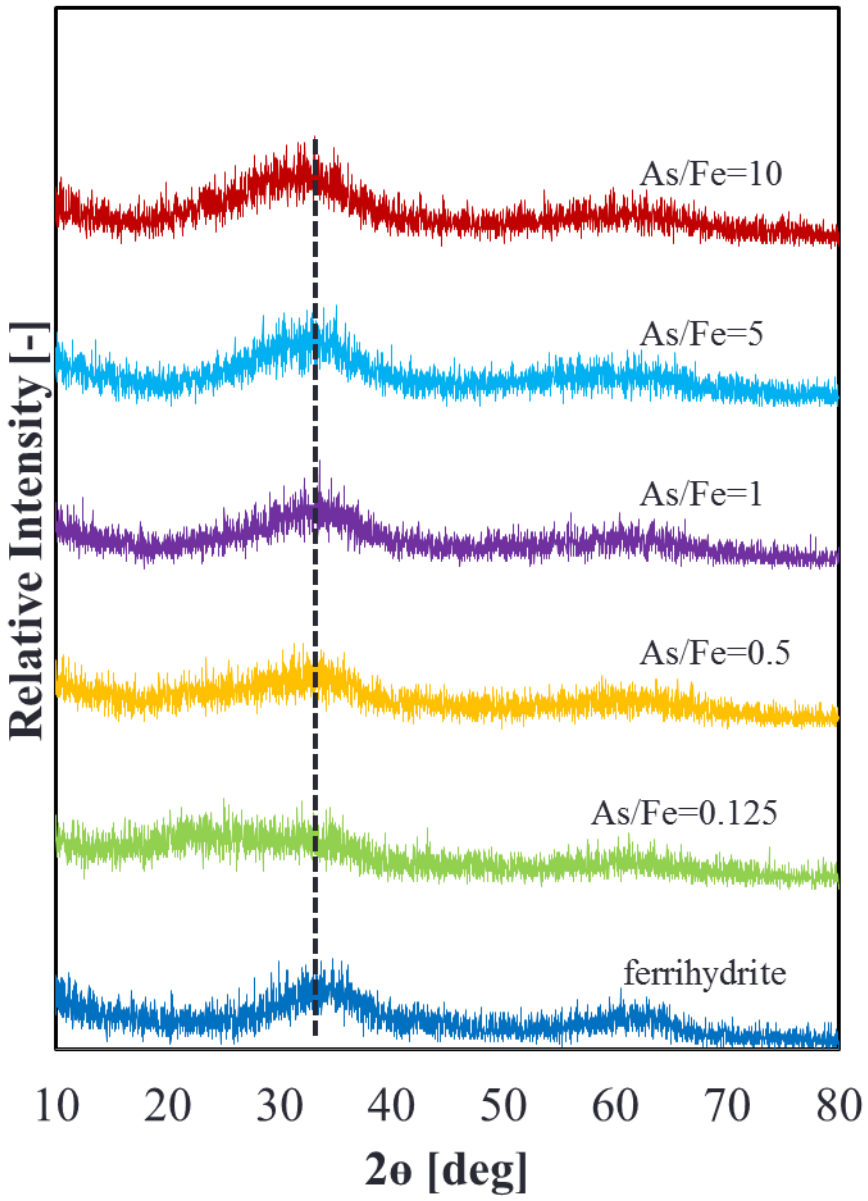


**Fig. 7. XRD spectrums of precipitates in variant As(III)/Fe with sulfate ion in Co-precipitation process**

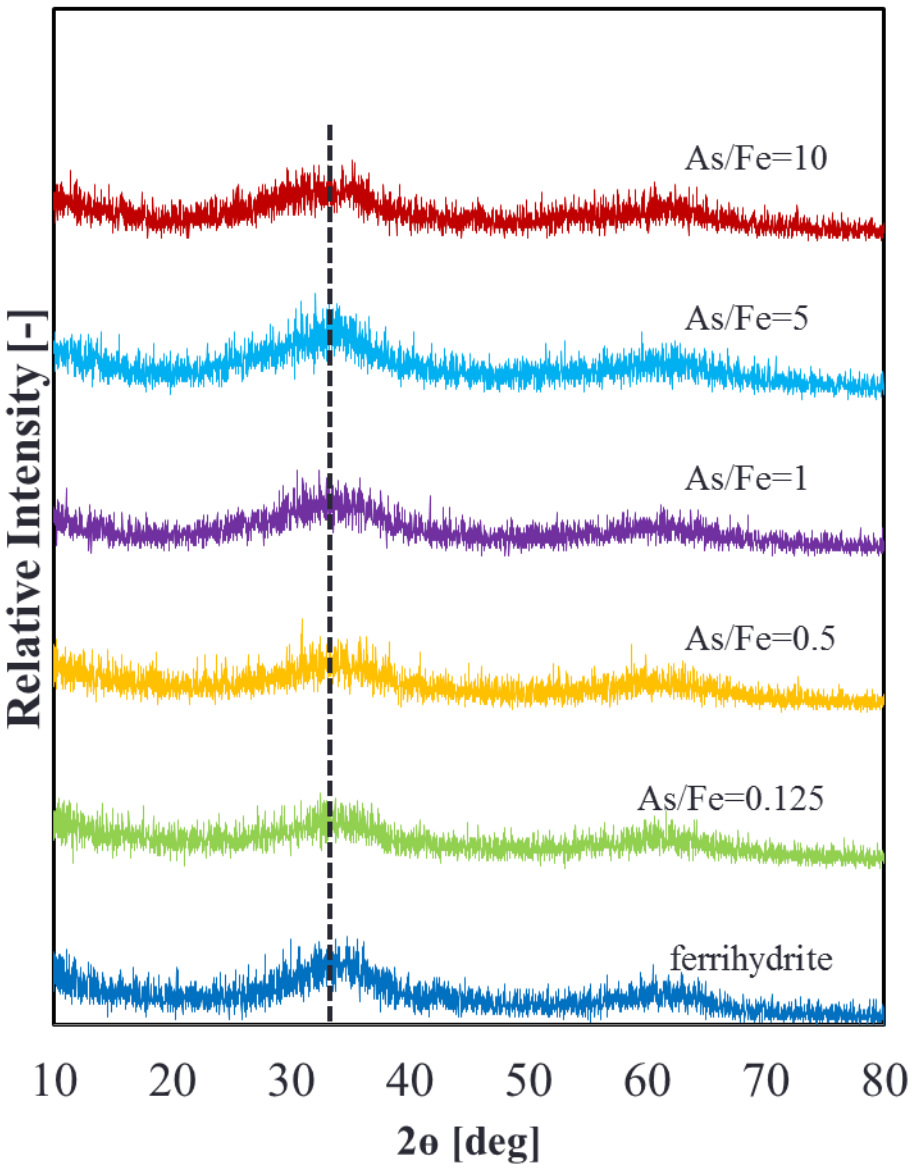


**Fig. 8. XRD spectrums of precipitates in variant As(III)/Fe with sulfate ion in Adsorption process**

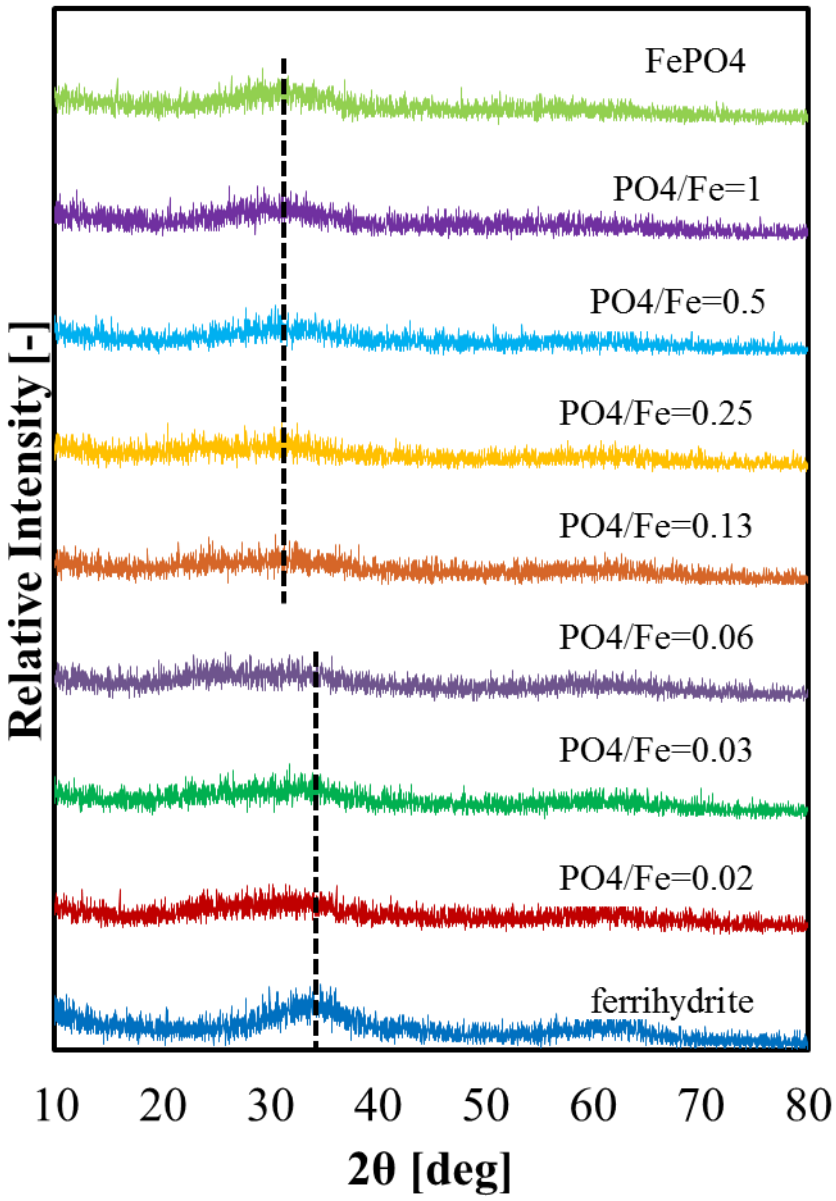


**Fig. 9. XRD spectrums of precipitates in variant As(III)/Fe with phosphate ion in Co-precipitation process**

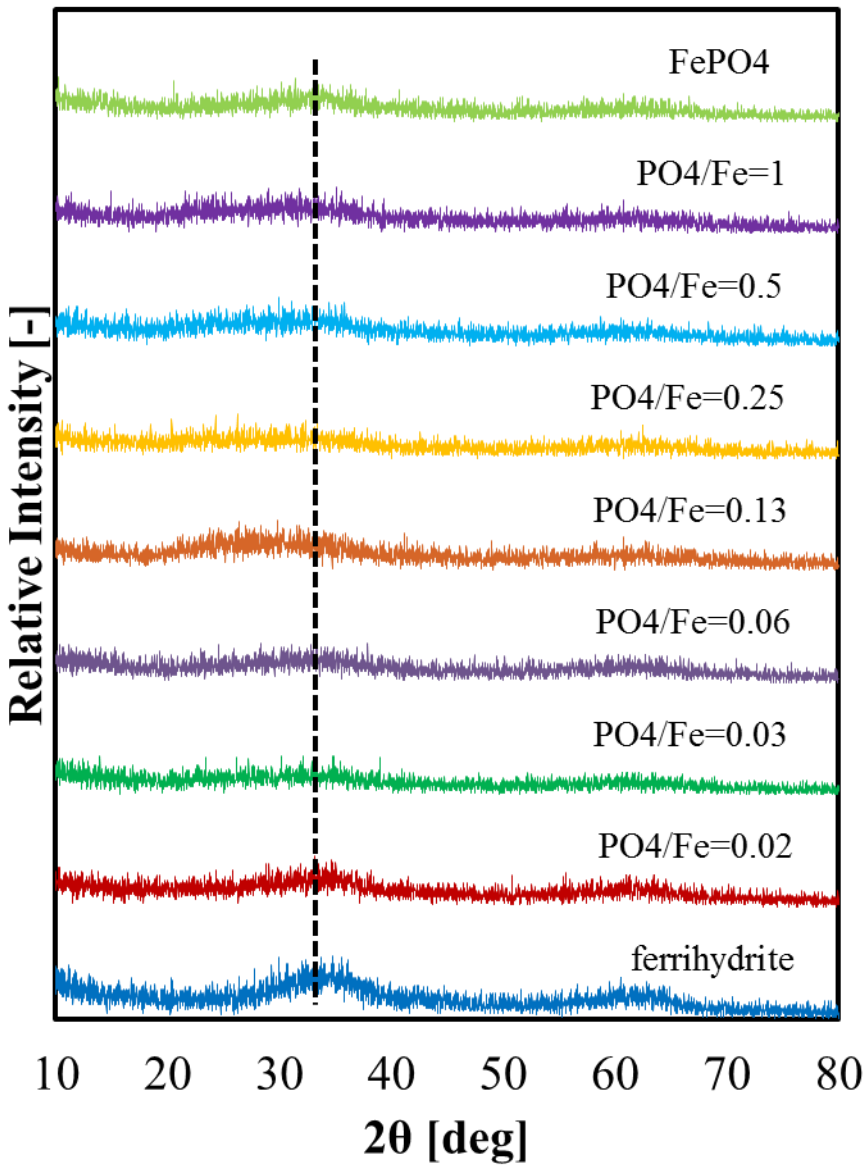


**Fig. 10. XRD spectrums of precipitates in variant As(III)/Fe with phosphate ion in Adsorption process**

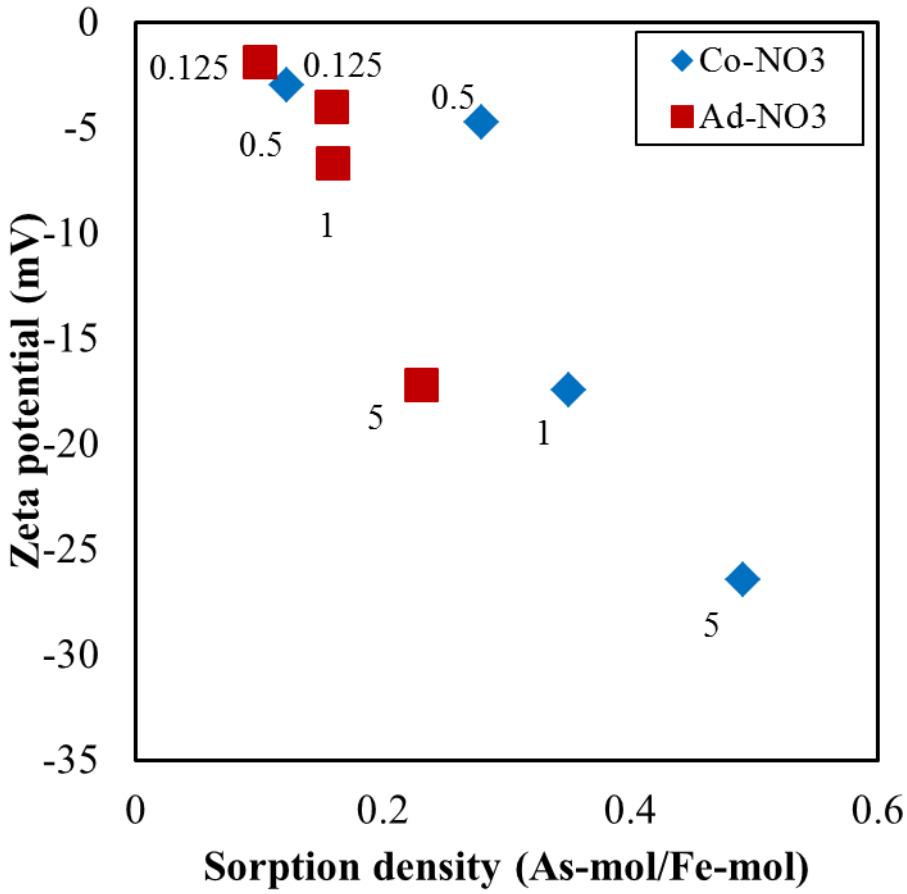


**Fig. 11. Relationship between Zeta potential and Sorption density (As/Fe) with nitrate ion, Co=co-precipitation, Ad=adsorption**

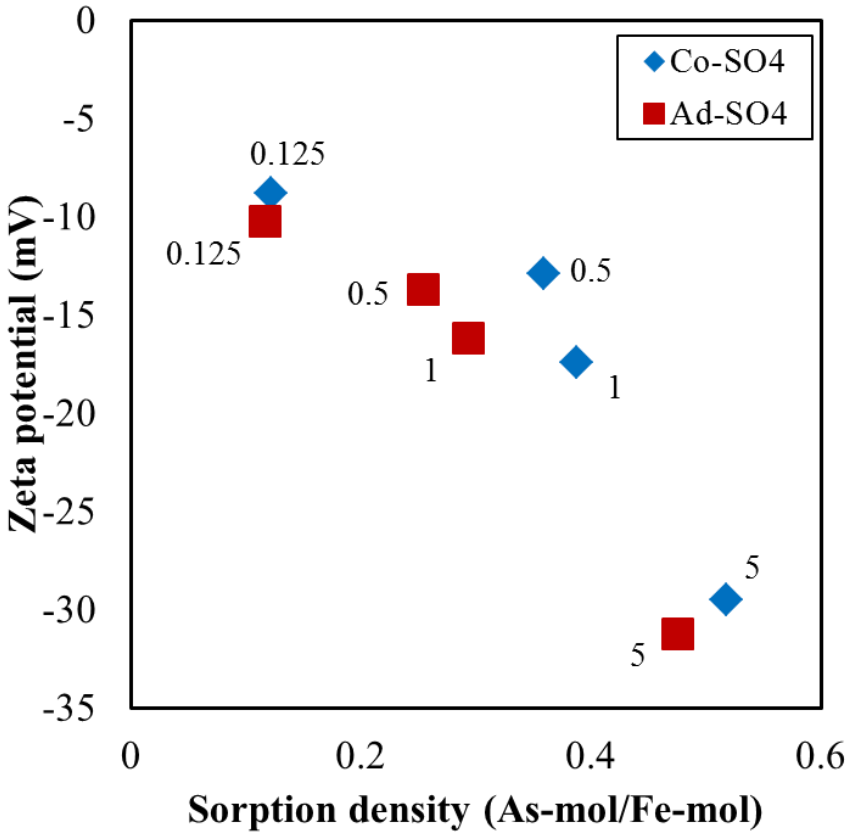


**Fig. 12. Relationship between Zeta potential and Sorption density (As/Fe) with sulfate ion, Co=co-precipitation, Ad=adsorption**

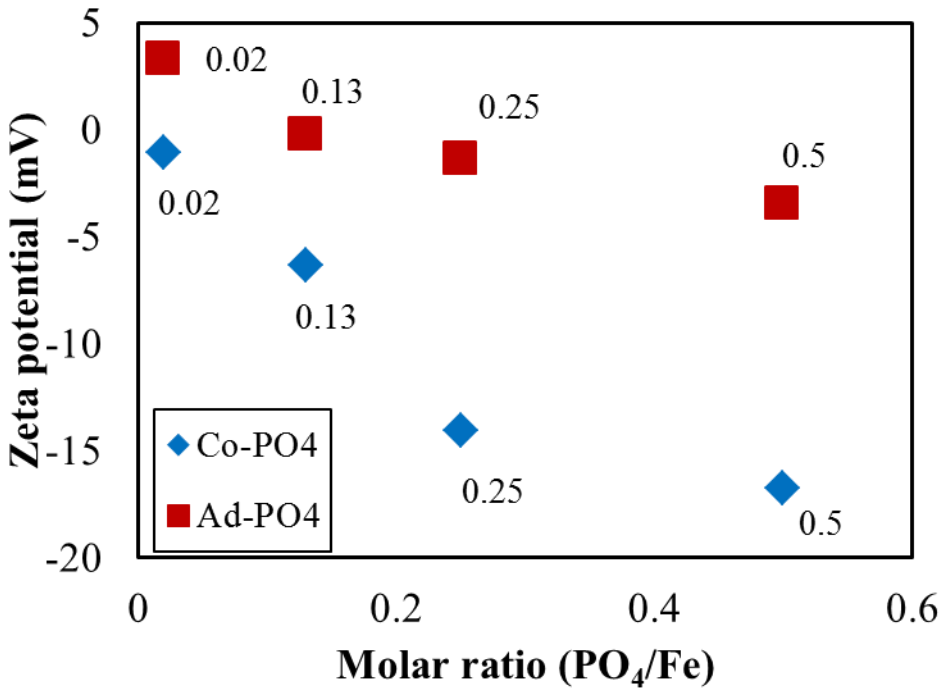


**Fig. 13. Relationship between Zeta potential and Molar ratio ($PO_4$/Fe) with phosphate ion, Co=co-precipitation, Ad=adsorption**

From Fig. 11 and Fig. 13, it was confirmed that the zeta potential linearly decreases as the sorption density increases regardless of co-precipitation method/ adsorption method. From this result, it was suggested that As(III) removal using ferric hydroxide predominates the surface complexation mechanism. Regarding the zeta potential when the sorption density is small, a large difference cannot be confirmed between the co-precipitation method and the adsorption method. But as the sorption density increases, there is a difference in value between the co-precipitation method and the adsorption method. The zeta potential of sulfate ion was lower than that of nitrate ion. The adsorption of As(III) decreased the zeta potential of ferrrihydrite and suggesting the formation of negatively charge inner-sphere surface complex.

In Fig. 13, the zeta potential of co-precipitation process was lower than that of adsorption process.

### 3.2. Sedimentation rate

From Fig. 14 and Fig. 15, the settling rate of nitrate, sulfate and phosphate ions solution was different before 12 hour and just little different at 24 hour. The order of settling rate was $NO_3^-$ > $SO_4^{2-}$ > $PO_4^{3-}$ . The initial turbidity numbers were 15.3 NTU for nitrate ion solution, 21.5 NTU for sulfate ion solution and 12.67 NTU for phosphate ion solution in co-precipitation process. In the adsorption process, the initial turbidity numbers were 14.93 NTU for nitrate ion solution, 21.73 NTU for sulfate ion solution and 14.87 NTU for phosphate ion solution. The floc size of phosphate ion solution was the smallest particle and the settling speed is the lowest. According to Stokes equation of sedimentation, the terminal settling velocity of a particle in a liquid is proportional to the square of the diameter of the particle. NTU is nephelometric turbidity units and it is the unit of turbidity. Sedimentation rate is the speed of the particles suspended in water to settle down to bottom.

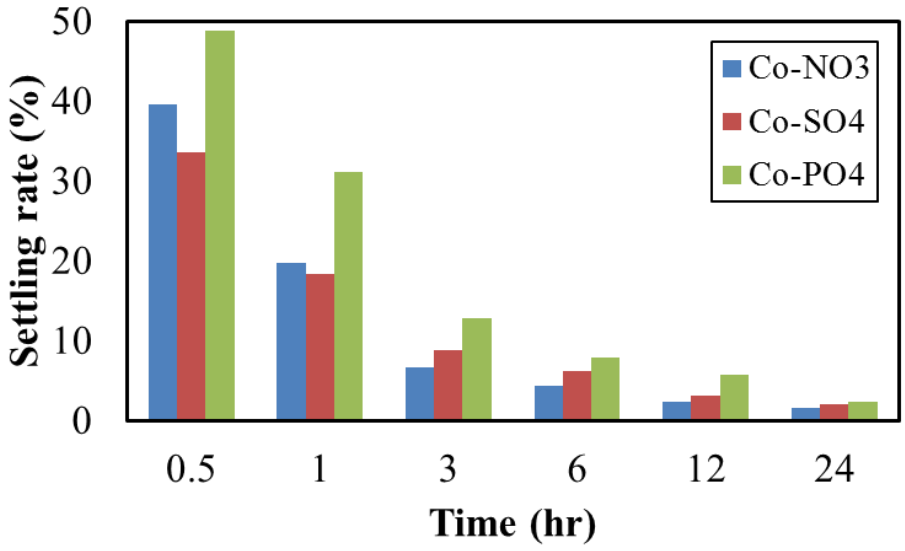


**Fig. 14. Sedimentation rate in nitrate, sulfate and phosphate ion, Co=co-precipitation**

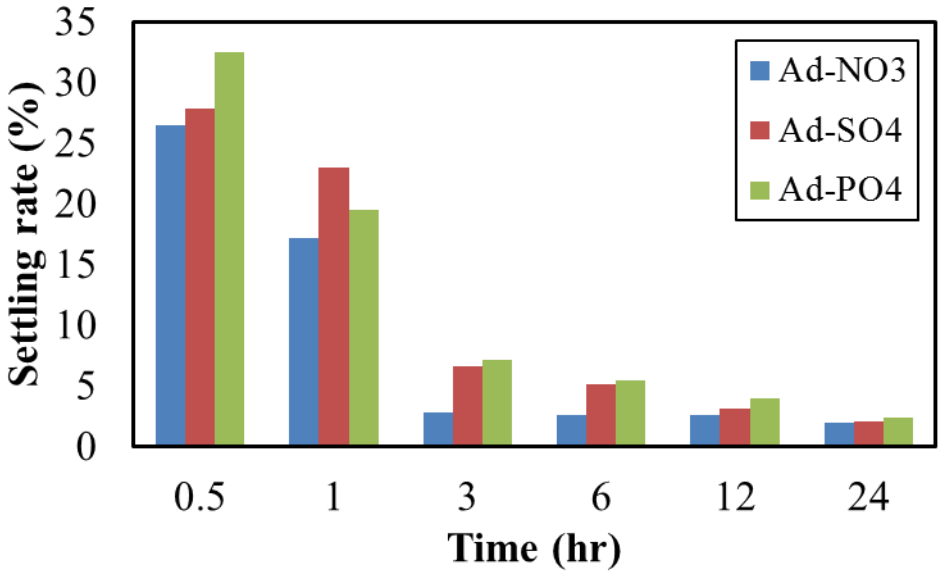


**Fig. 15. Sedimentation rate in nitrate, sulfate and phosphate ion, Ad=Adsorption**

### 3.3. Re-dissolution of As in sludge

In Fig. 14, As re-dissolution amount was higher in adsorption process than co-precipitation process of all of the three ions case. As was removed deeply into ferrihydrite structure and extended the atomic distances of Fe. Therefore As was difficult to dissolve again from the sludge of co-precipitation process.

The As re-dissolution amount of phosphate ion was the highest and that of nitrate ion was the lowest. Sulfate ion was better effect on As removal property but easy to re-dissolve again, whereas phosphate ion was adverse effect on the removal property and re-dissolution of As.

From Fig. 15, pH increased by the time and pH value was higher in adsorption process than co-precipitation process of all of the three ions case. As the pH increases, the surface becomes more negatively charged, so desorption of arsenic becomes more suitable. This result was indicated that electrostatic bonding plays a significant role in arsenic adsorption/desorption on most metal oxide surfaces. The multivalent anions (e.g. $PO_4^{3-}$) would be expected to be particularly significant.

It was also observed that the presence of phosphate into the suspension of the sludge raised the pH value of the solution leading to desorption of As(III) oxyanion from the iron surfaces. Therefore, the associated pH rise as a result of phosphate might enhance As extraction. Jain et al. have also opined that high pH values could cause desorption of As(V) and sometimes As(III) from Fe oxyhydroxides [4].

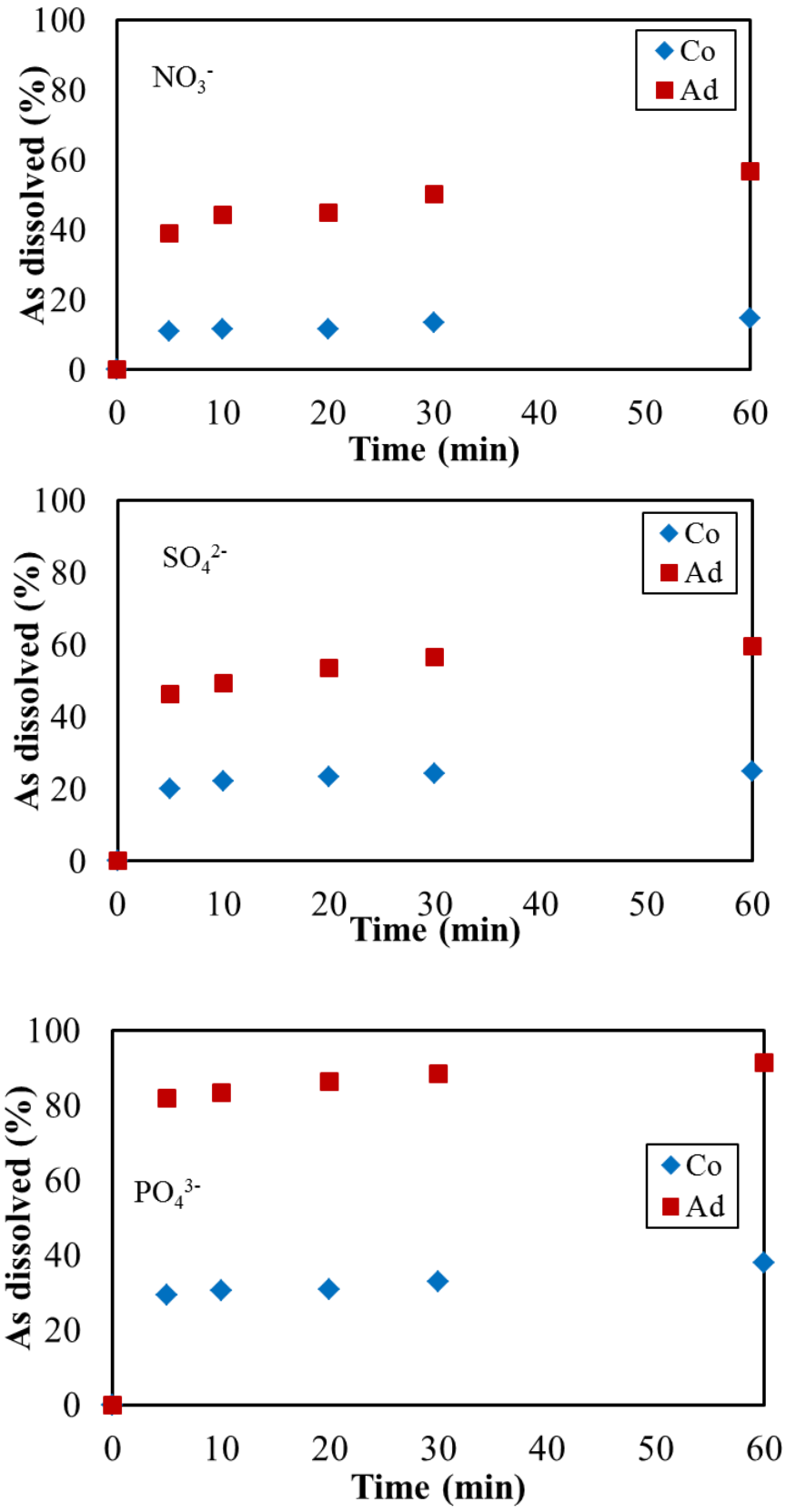


**Fig. 16. As dissolved in sludge in nitrate, sulfate and phosphate ion, Co=co-precipitation, Ad=adsorption**

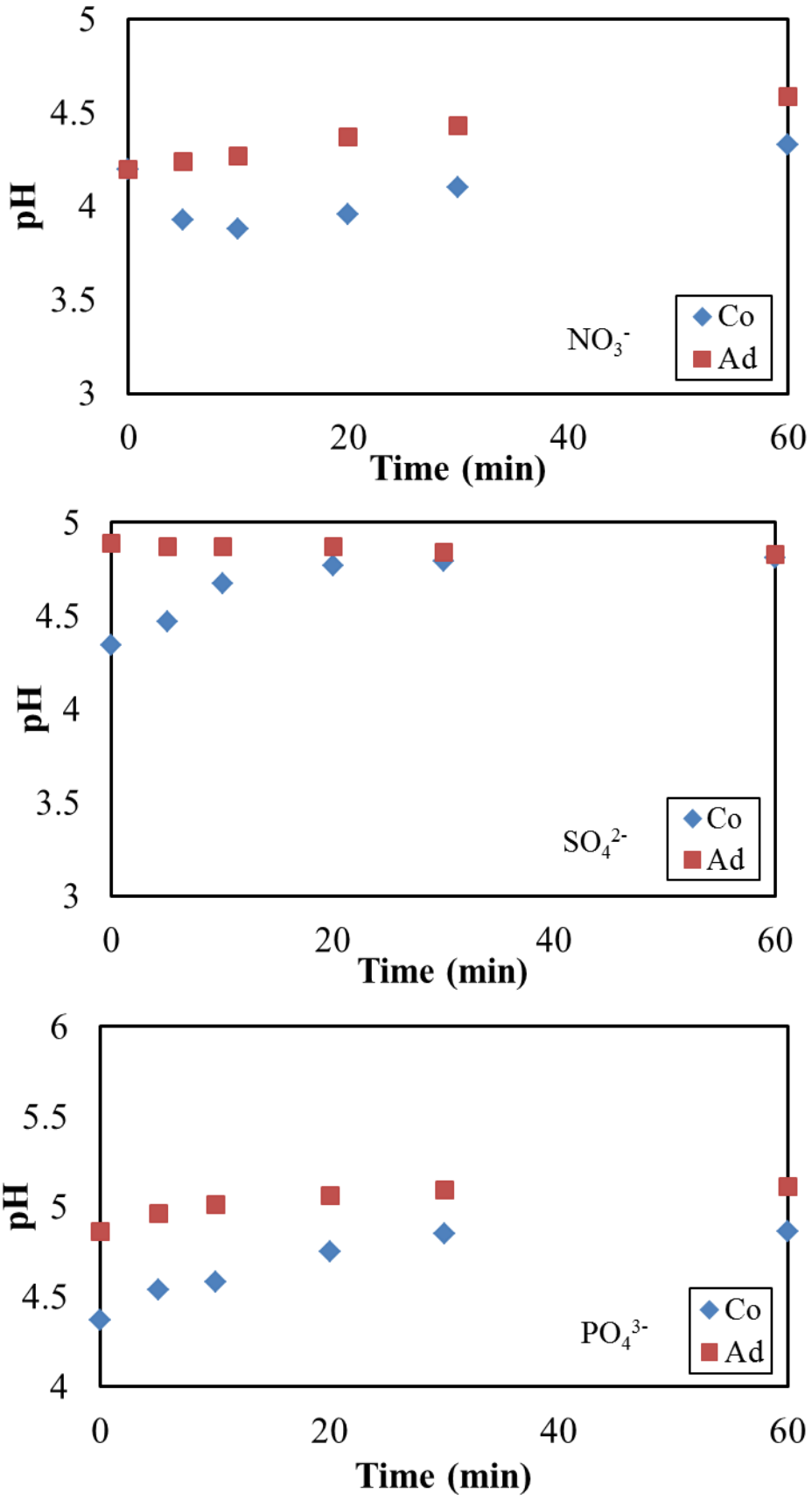


**Fig. 17. pH in sludge in nitrate, sulfate and phosphate ion, Co=co-precipitation, Ad=adsorption**

## 4. Conclusion

The purpose of this study was to investigate the effect of coexisting anions such as nitrate, sulfate, phosphate on the removal of arsenic concerned with the removal property of As(III), sedimentation rate and re-dissolution of arsenic in sludge by ferrihydrite in co-precipitation and adsorption processes. The experiment was a batch test, and the experimental conditions were set as ionic strength 0.05 mol /$dm^3$, pH 7.

As the result of the removal experiment, As(III) residual amount was 1.14 mg/$dm^3$ in co-precipitation and 2.25 mg/$dm^3$ in adsorption while using nitrate ion at As/Fe molar ratio 0.125. As(III) residual amount was 0.25 mg/$dm^3$ in co-precipitation and 0.57 mg/$dm^3$ in adsorption while using sulfate ion at As/Fe molar ratio 0.125. Sulfate ion was more effect in the removal of As(III) by using ferrihydrite than that of nitrate ion. The adsorbed sulfate anions are later displaced by the stronger complexing arsenite anions when the ferrihydrite is brought into contact with arsenite solution. The increased density of sulfate active sites and optimized steric effect are probable factors explaining the higher arsenite adsorption capacity on sulfate-media. As a bivalent anion, $SO_4^{2-}$ possesses more charges per ion than a monovalent anion. This feature may be partially explained the excellent performance of $SO_4^{2-}$ in improving As(III) removal.

As(III) residual amount was 0.58 mg/$dm^3$ in co-precipitation and 2.18 mg/$dm^3$ in adsorption while using phosphate ion at $PO_4$/Fe molar ratio 0.02. When phosphate concentration increased, residual amount of arsenic increased in both processes. $FePO_4$ precipitated and amount of ferrihydrite decreased and then phosphate ion disturbed formation of arsenic surface complexation onto ferrihydrite. The inner-sphere complex-forming phosphate competes strongly with As(III) for sorption site.

The co-precipitation method is superior when Fe (III) is used as a removal agent in As removal. The adsorption method is inferior to the co-precipitation method is thought to be that crystal growth of Fe precipitation suppressed As removal. Since there is time enough for crystal growth, it is considered that the specific surface area contributing to the reaction narrowed, the adsorption site decreased, and the amount of removed As decreased. In addition, the superiority of the co-precipitation method can be considered as many factors such as surface precipitation formation and various electrical characteristics.

The order of settling rate was $NO_3^- > SO_4^{2-} > PO_4^{3-}$ . The floc size of phosphate ion solution was the smallest particle and the settling speed is the lowest. According to Stokes equation of sedimentation, the terminal settling velocity of a particle in a liquid is proportional to the square of the diameter of the particle.

The As re-dissolution amount of phosphate ion was the highest and that of nitrate ion was the lowest. Sulfate ion was better effect on As removal property but easy to re-dissolve again, whereas phosphate ion was adverse effect on the removal property and re-dissolution of As. The presence of phosphate into the suspension of the sludge raised the pH value of the

solution leading to desorption of As(III) oxyanion from the iron surfaces. The associated pH rise as a result of phosphate might enhance As extraction.

The phosphate ion was adversely effected on the removal of As(III) by using ferrihydrite in the case of As removal property, sedimentation rate and re-dissolution of As in sludge in the co-precipitation and adsorption processes while nitrate and sulfate ions were slightly effected.

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