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# Removal of phosphite and sulfate from electroless nickel–phosphorus plating bath with hydrotalcite for the management of watershed

Yuki Kamimoto[a], Ryoichi Ichino[a], Yoshiaki Kiso[b], Takuya Hosotani[c], Koo-Ho Kwon[d], Kyung-Sok Min[d], Yong-Jun Jung[e,*]

[a]*EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*
[b]*Department of Environmental and Life Science, Toyohashi University of Technology, 1-1 Hibarigaoka Tenpaku-cho, Toyohashi, Aichi 441-8580, Japan*
[c]*TOHKEMY corporation, 19-2, Taitou1, Taitou-ku, Tokyo, Japan*
[d]*Department of Environmental Engineering, Kyungpook National University, Daegu 702-701, Korea*
[e]*Department of Environmental engineering, Catholic University of Pusan, 9 Bugok3-dong, Geumjeong-gu, Busan 609-757, Korea*
*Email: yjjung@cup.ac.kr*

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## ABSTRACT

This study was focused to remove both $HPO_3^{2-}$ and $SO_4^{2-}$ for the improvement of efficiency in electroless nickel–phosphorus plating process with hydrotalcite-like compound (HT). The adsorbed amount, $q_e$, of $H_2PO_2^-$ which was main component was low and $H_2PO_2^-$ had little influence on the adsorption of $HPO_3^{2-}$ and $SO_4^{2-}$. $HPO_3^{2-}$ and $SO_4^{2-}$ were similar in the adsorption behaviors of the adsorption isotherm and the influence of solution pH. The $q_e$ was increased with the increase of water temperature, because the $CO_3^{2-}$ was decreased with the increase of water temperature. On the coexisting adsorption, the $q_e$ of $HPO_3^{2-}$ was decreased with $SO_4^{2-}$. The ion selectivity of HT was in the order of $SO_4^{2-} > HPO_3^{2-} > PO_4^{3-} \gg H_2PO_2^-$ at pH 10. The results indicated that the HT-Cl is a useful adsorbent for $HPO_3^{2-}$ and $SO_4^{2-}$ removal in the exhausted electroless nickel-phosphorous plating bath.

*Keywords:* Hydrotalcite; Phosphorus recovery; Electroless Ni–P plating

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## 1. Introduction

As nutrients can cause the eutrophication into the water body, the control of nitrogen as well as phosphorus can play an important role on the management of water quality of watershed.

Phosphorus [1] is an important element in a wide range of industries such as agricultural, chemical, and medical industry. On the other hand, when phosphorus through domestic and industrial wastewaters is

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*Corresponding author.

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discharged to closed water body, it causes eutrophication by phosphorus. Several phosphorus removal technologies for domestic wastewater have been developed and employed in the world: chemical precipitation, crystallization, adsorption, and biological processes.

The most popular process is chemical precipitation method in which insoluble phosphate compound was formed and removed by settling, and calcium hydroxide, alum or poly-aluminum chloride and ferric salt have been used for this purpose. When wastewater contains ammonium ion at high concentration, magnesium ammonium phosphate can be formed by the addition of magnesium ion.

Many kinds of adsorbents have been used for the removal of phosphate: activated aluminum oxide [2], iron oxide [3], dolomite [4], calcite [5], $MnO_2$ [6], $TiO_2$ [7], $ZnO(OH)_2$ [8], schwertmannite [9–10], etc. [11]. Hydrotalcite-like compound (HT) is an effective phosphate adsorbent for wastewater [12–15], and the formula is expressed as follows: ${M_{1-X}}^{2+}{M_X}^{3+}(OH)_2(A^{n-})_{x/n}\cdot yH_2O$. In the case of HT used for phosphate removal, $M^{2+}$, $M^{3+}$, and $A^{n-}$ are commonly $Mg^{2+}$, $Al^{3+}$, and $Cl^-$, respectively. Another type of HT was also developed, where $Mg^{2+}$ was replaced with $Ni^{2+}$ or $Al^{3+}$ with $Fe^{3+}$ [16,17]. HT is a type of an intercalated compound, and anion and water molecules are trapped between positive charged brucite-like octahedral layers formed of divalent and trivalent metals. Kuzawa et al. [18] indicated that phosphate can be recovered from the HT which was adsorbed phosphate.

A large amount of phosphorous has been used in plating industry: especially electroless nickel–phosphorus (Ni–P) plating has been employed for a wide variety of industrial parts. Hypophosphite ($H_2PO_2^-$) is used as a reducing agent in electroless nickel–phosphorus plating. Phosphite ($HPO_3^{2-}$) is generated by the oxidation of $H_2PO_2^-$ and inhibits the nickel-plating reaction. Therefore, it is an important subject to remove $HPO_3^-$ for effective plating. Ni can be recovered from the exhausted Ni–P plating bath [19–21], but phosphorus recovery technologies have not been found. Electroless Ni–P plating is conducted in both alkaline and acidic conditions. We have developed the method to separate phosphorous selectively with schwertmannite under acidic condition [22]. It is also important to recover phosphorous from alkaline Ni–P plating bath. Because $NiSO_4$ is used for the source of Ni plating, $SO_4^{2-}$ ion is contained in Ni–P plating bath and works as a competitive component for $HPO_3^{2-}$.

It is an important subject to remove both $HPO_3^{2-}$ and $SO_4^{2-}$ for the improvement of efficiency in electroless Ni–P plating process. When only both $HPO_3^{3-}$ and $SO_4^{2-}$ are removed from the exhausted plating bath, the recycled use of the bath can be available. HT containing $Cl^-$ as an intercalating anion is an effective ion-exchanger for multivalence anions such as phosphate, sulfate and arsenite [15,18,23–25].

In this study, we have focused on HT as an adsorbent in order to remove both $HPO_3^{2-}$ and $SO_4^{2-}$ preferentially from the exhausted alkaline electroless Ni–P plating bath containing $H_2PO_2^-$. The separation among these compounds was estimated by the adsorption capacity. In addition, phosphate ($PO_4^{3-}$) was examined for comparison.

## 2. Materials and methods

### 2.1. Hydrotalcite

The synthetic HT (HT-Cl) contained chloride as an interaction anion was used in this study. The powdered HT-Cl was purchased from Tomita Pharmaceutical Co. Ltd. (Japan). The rational formula of the HT-Cl is expressed as follows: $Mg_{0.683}$-$Al_{0.317}(OH)_{1.995}(CO_3)_{0.028}Cl_{0.226}\cdot 054H_2O$. The ion-exchange capacity of the HT was reported as follows: $CO_3^{2-} > HPO_4^{2-} \gg SO_4^{2-} \gg Cl^- \gg NO_2^- > NO_3^-$ [14], and $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ [26] under neutral pH condition.

### 2.2. Adsorption experiment

The HT-Cl is an inorganic ion-exchanger, and anion such as phosphate is removed by ion-exchange. However, since the experimental method and data analysis are similar to those of adsorption processes, the term of adsorption was used for the phosphorous removal.

The adsorption properties were examined by batch-type adsorption experiments. The solutions containing phosphorous and/or sulfate were prepared with the following reagents: $NaH_2PO_2\cdot H_2O$, $Na_2HPO_3\cdot 5H_2O$, $Na_2HPO_4$, and $Na_2SO_4$. The reagents were obtained from NACALAI TESQUE, INC. (Kyoto, Japan). The concentrations of phosphorous were adjusted at 3.23 mmol/L (100 mg-P/L) and that of sulfate was done at 3.13 mmol/L (100 mg-S/L). The pH of the solutions was adjusted with 1 N-HCl and 1 N-NaOH. In this study, pure water was used without removal of carbonic ion.

The HT-Cl of 0.05 g was added into the phosphate solution (50 mL), and the adsorption reaction was conducted for 24 h at 20˚C under the mixing condition by a rotary shaker or magnetic stirrer.

### 2.3. Analytical methods

Anion was detected by ion chromatography (IC850, Metrohm, Swiss) equipped with nonsuppressor column. TSK-gel IC-Anion SW (Tosho, Japan) was employed for the phosphorus and chloride ion analysis. Sulfate ion was analyzed with TSK-gel Anion PW$_{XL}$ (Tosho, Japan). HT in the reaction mixture was removed by filtration with membrane filter (0.45 μm, Advantec Toyo, Japan).

## 3. Results and discussion

### 3.1. Effect of pH on adsorption capacity of HT

HT-Cl is dissolved under strong acidic condition, and the purpose of this study is to remove phosphate from alkaline solution. Therefore, the effect of pH was examined in alkaline region (pH 7–12). The amounts ($q_e$: mmol/g) of the adsorbed phosphorous and sulfate under equilibrium condition were influenced by chemical species and pH condition as shown in Fig. 1. The experiments were conducted for 24 h at 20˚C under mixing condition by a rotary shaker.

Hypophosphite ($H_2PO_2^-$) was not removed effectively with HT-Cl under the entire pH conditions: the maximum $q_e$ was 0.09 mmol/g-HT at pH 11. Hypophosphite exists to be mono-valence ion ($H_2PO_2^-$), and it was indicated that the affinity as intercalating anion of $H_2PO_2^-$ is quite lower than Cl$^-$. The result is similar to those for the removal of $NO_2^-$ and $NO_3^-$ [22]. The results for hypophosphite shown in Fig. 1 indicated very important performance of HT-Cl because of the following points: hypophosphite play an important role in a reducing reagent in the plating process, and the residual hypophosphite in the exhausted plating solution may be recovered even by the treatment with HT-Cl.

$HPO_3^{2-}$, $PO_4^{3-}$, and $SO_4^{2-}$ were removed with the HT-Cl, but the values of $q_e$ were decreased with increase in pH. The $q_e$ value of phosphate decreased linearly with increase in pH. On the other hand, those of phosphite and sulfate decreased rapidly at around pH 11. In addition, phosphite was removed more effectively in the entire pH range than sulfate. The pH of alkaline electroless Ni–P plating bath was about 10, and $q_e$ was 1.21 mmol/L for $HPO_3^{2-}$ and 1.27 mmol/L for $SO_4^{2-}$. Considering the pH condition of plating bath, the HT-Cl may be a useful adsorbent for the removal of both $HPO_3^{2-}$ and $SO_4^{2-}$ in the exhausted plating bath, and another merit is that the HT-Cl does not remove $H_2PO_2^-$ which is an essential chemical in the plating bath.

### 3.2. Adsorption rate

The adsorption rate for each component was examined at 20˚C with using the solution containing 5 g/L of HT-Cl, where the mixed solution was adjusted at pH 10 and agitated by a magnetic stirrer. The initial concentrations of phosphorous species and sulfate were 3.23 and 3.13 mmol/L, respectively. The sampling was conducted 10 times for 3 h, but the total volume of the samples was less than 10% of the initial volume. The concentration profiles for the components are shown in Fig. 2.

The concentrations of all components in the exception of $H_2PO_2^-$ decreased rapidly to 0.01 mmol/L, and the results indicated that the reaction finished until about 15 min. The concentration of $H_2PO_2^-$ decreased

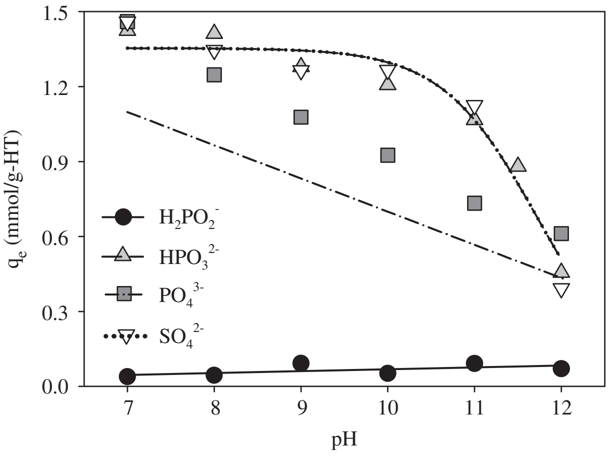

Fig. 1. Influence of pH on adsorption amount ($q_e$) HT-Cl: 1.0 g/L; initial concentration of phosphorous and sulfate: 3.23 mmol/L; reaction time: 24 h; reaction temperature: 20˚C.

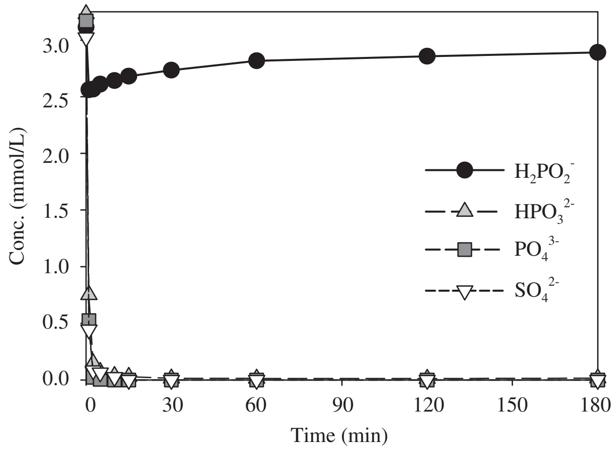

Fig. 2. Adsorption rate pH 10; HT-Cl: 5 g/L; initial concentration of phosphorous and sulfate: 3.23 mmol/L.

slightly in a moment but increased gradually after 1 min. The increase in $H_2PO_2^-$ concentration may be caused by the exchange of $H_2PO_2^-$ with other ionic components: considering the pH condition in the experiments, $CO_3^{2-}$ ion generated from atmosphere may be a potential species.

### 3.3. Adsorption isotherm

The adsorption isotherm was examined at 20℃, where the reaction was conducted for 24 h. The adsorption isotherms for $HPO_3^{2-}$, $PO_4^{3-}$ and $SO_4^{2-}$ are shown in Fig. 3, where the results for $H_2PO_2^-$ are not plotted, because $H_2PO_2^-$ was not adsorbed effectively.

Fig. 3 shows that the adsorption approached to the saturated state at high equilibrium concentration: the maximum adsorption capacity of $HPO_3^{2-}$, $PO_4$, and $SO_4$ was 1.37, 0.94, and 1.33 mol/g-HT-Cl, respectively. The adsorption isotherms for $HPO_3^{2-}$, $PO_4^{3-}$ and $SO_4^{2-}$ were approximated by Langmuir equation as follows;

$$q_e = \frac{177.2Ce}{1 + 245.0Ce} \text{ for } HPO_3^{2-}$$

$$q_e = \frac{130.2Ce}{1 + 127.6Ce} \text{ for } PO_4^{3-}$$

$$q_e = \frac{106.7Ce}{1 + 138.4Ce} \text{ for } SO_4^{2-}$$

The relationship between adsorbed anions and $Cl^-$ was shown in Fig. 4. At pH 10, the exchanging ratio of Cl for $PO_3$ and $SO_4$ was 2.3 mol-Cl/mol, and $PO_4^{3-}$ was 3.3 mol-Cl/mol. Theoretical exchange ratio between Cl and $PO_3$ and $SO_4$ was 2, the gaps were about 0.3 mol-Cl/mol. It was shown that the differences were influenced by $CO_3$ adsorption.

### 3.4. Effect of temperature

Electroless Ni–P plating bath was commonly hearted in the range of 70–95℃. When the HT-Cl adsorption process is employed for exhausted electroless Ni–P plating bath, it is preferable to be worked without cooling the bath. Therefore, the effect of water temperature was examined in the range of 20–80℃. The adsorption experiments were conducted under the following conditions: HT-Cl concentration was 1.0 g/L, the initial concentration of ionic species was 3.23 mmol/L, and the mixed solution was agitated for 30 min by a magnetic stirrer. The obtained adsorption amount corresponded to the saturated adsorption amount for each species. Wajima et al. [23] examined

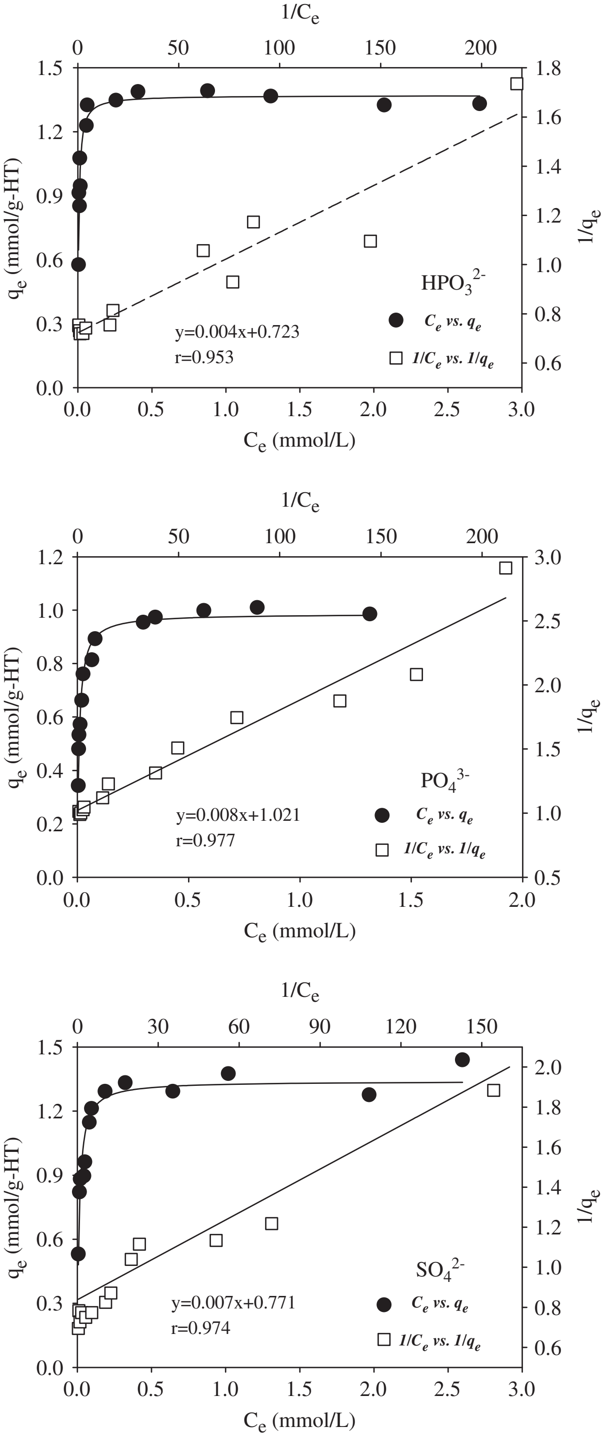

Fig. 3. Adsorption isotherm at pH 10 and 20℃.

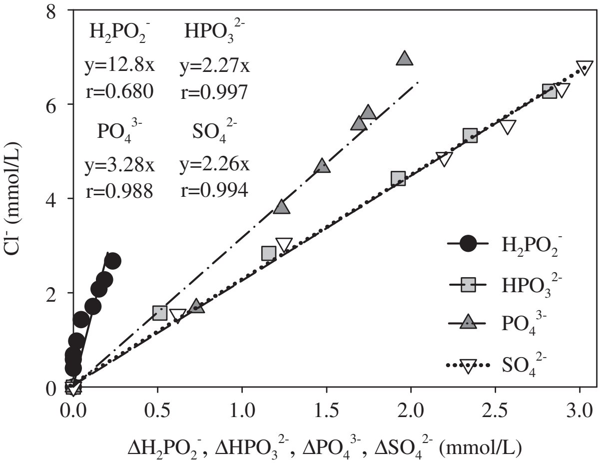

Fig. 4. Relationship between adsorbed $H_2PO_2^-$, $HPO_3^{2-}$, $PO_4^{3-}$ and $SO_4^{2-}$ and discharged $Cl^-$.

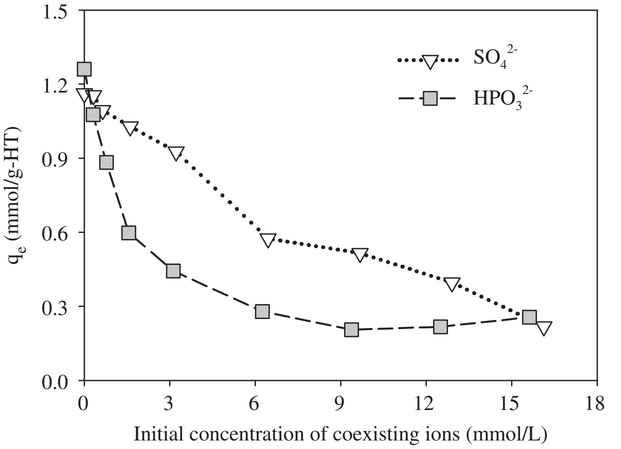

Fig. 6. Influence of competitive adsorption between $HPO_3^{2-}$ and $SO_4^{2-}$.

the property of HT-Cl for arsenate removal from geothermal water and indicated that the adsorption capacity of HT-Cl for arsenate was not influenced by water temperature. The results suggested the effect of water temperature on $HPO_3^{2-}$, and $SO_4^{2-}$ removal may be little influenced.

The relationship between adsorption capacity ($q_e$) and water temperature is shown in Fig. 5. For all species, the adsorption capacity increased slightly with the increase in water temperature, and $HPO_3^{2-}$ indicated the highest capacity at more than 80℃. Detailed experimental data were not obtained presently, but the results may be caused by the fact that most chemical reactions including sorption were influenced by the thermal condition, which was also the same case in this study. The $HPO_3^{2-}$ and $SO_4^{2-}$ removal performance of the HT-Cl is effective rather at high water temperature, and this is preferable to the treatment of exhausted electroless Ni–P plating bath.

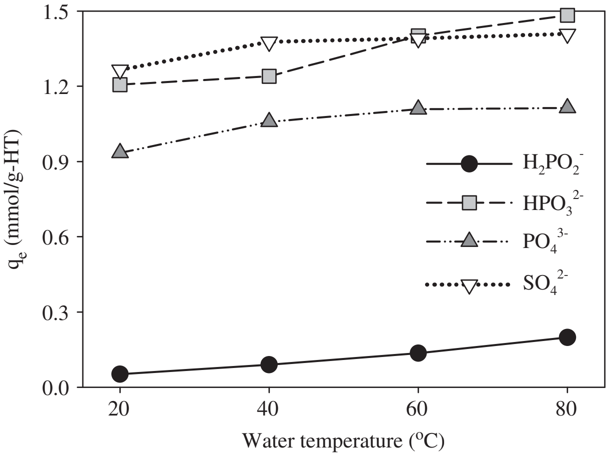

Fig. 5. Influence of water temperature on adsorption amount ($q_e$).

### 3.5. Effect of coexisting species

The low ion-adsorption selectivity of $H_2PO_2^-$ for HT-Cl was revealed, and it was the similar adsorption isotherm between $HPO_3^{2-}$ and $SO_4^{2-}$. The $q_e$ of $HPO_3^{2-}$ and $SO_4^{2-}$ was examined by the coexisting conditions under the following conditions: the HT-Cl concentration was 1.0 g/L, the initial concentration of ionic species was 3.23 mmol/L and that of coexisting ionic species was 0.32–16.1 mol/L, the reaction temperature was 20℃, and the reaction time was 24 h. The results are shown in Fig. 6. The influence of $SO_4^{2-}$ on the adsorption with $HPO_3^{2-}$ was less than $HPO_3^{2-}$ under the coexisting conditions. In the mixed solution of $HPO_3^{2-}$ and $SO_4^{2-}$, $HPO_3^{2-}$ was prior ion and exchanged $SO_4^{2-}$ from HT adsorbed $HPO_3^{2-}$. But these ions were adsorbed together by the coexisting solution.

## 4. Conclusions

The properties of the HT-Cl as a selective adsorbent for $HPO_3^{2-}$ and $SO_4^{2-}$ were examined for the purpose of regeneration of electroless Ni–P plating bath. The HT-Cl indicated very low adsorption capacity for $H_2PO_2^-$ in the pH region of 7–12. On the other hand, both $HPO_3^{2-}$ and $SO_4^{2-}$ were effectively adsorbed in the range of pH 7–10. The $q_e$ of $HPO_3^{2-}$ and $SO_4^{2-}$ was the similar values from the examination of effect on the solution pH and adsorption isotherm. On the coexisting adsorption, the $q_e$ of $HPO_3^{2-}$ was decreased with $SO_4^{2-}$. The maximum adsorption amounts were in the order of $SO_4^{2-} > HPO_3^{2-} > PO_4^{3-} >> H_2PO_2^{-}$ at pH 10: the pH is common pH condition of the electroless Ni–P plating bath. The adsorption amounts increased slightly with the increase in water temperature, and the result indicated that a hot plating bath is preferable to the HT-Cl treatment. The results obtained in this work indicated that the HT-Cl is a useful adsorbent for $HPO_3^{2-}$ and $SO_4^{2-}$ removal in order to regenerate the exhausted electroless Ni–P plating bath.

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