



Phosphate removal during Fe(II) oxidation in the presence of Cu(II): Characteristics and application for electro-plating wastewater treatment



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ABSTRACT

This study investigated the potential contribution of co-present Cu(II) on the phosphate removal by the addition of Fe(II), and compare Fe(II) with conventional lime dosing in phosphate removal from real-plating wastewater originally containing Cu(II). Though the phosphate removal during Fe(II) oxidation by DO was notable, the co-present Cu(II) remarkably promoted the phosphate removal by adding Fe(II). The process of phosphate removal during Fe(II) oxidation was affected by DO, [Fe(II)]₀ and pH, respectively. The catalytic effect of Cu(II) as little as 0.5 mg/L significantly weakened the suppressed effect of the above mentioned factors on phosphate precipitation. Such enhanced phosphate removal was considered due to the facilitated generation of Fe(III) through catalytic oxidation of Fe(II) in the presence of Cu(II). For the real electro-plating wastewater, in contrast with lime, the process of phosphate removal by dosing Fe(II) combined with the original Cu(II) showed efficient performance, produced less sludge and demanded lower economic cost. These results announced that in the presence of co-existing DO and Cu(II) the Fe(II) may have application in the electro-plating wastewater treatment and important implication for its utilization.

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1. Introduction

The accumulation of phosphate compounds led by untreated discharge of municipal and industrial wastewater resulted in eutrophication in water bodies such as lakes and rivers [1]. Chemical precipitation is one of the most efficient and well-stable method to remove the phosphate from the wastewater [2]. Chemicals reagents, such as Fe(II), Fe(III), Al(III) and Ca(II)-based salts, are most widely used in the wastewater treatment [3]. Although Al(III) is effective for the phosphate precipitation, it is expensive and has received adverse public attention due to its unproven links with Alzheimer's senile dementia [4]. On the contrary, iron salts are relatively cheaper (<http://net.chemnet.com>) and of less environmental concern [5].

Aqueous Fe occurs in one of two principle oxidation states, Fe(II) and Fe(III). Both of their interactions with phosphate involve the following mechanism: precipitation of iron phosphate, complexation of phosphate with iron (oxy)hydroxides, phosphate adsorption onto the (oxy)hydroxides, crystallization, coagulation

and flocculation phenomenon [5–7]. Although Fe(III) is more commonly used due to its higher effectiveness in precipitating phosphate, it is readily to hydrolyze and would precipitate rapidly at the pH range above 5, leading to lower iron utilization efficiency [8]. In addition to its cost benefits over Fe(III), Fe(II) hydrolyzation does not proceed as readily as that of Fe(III) at the same pH condition. This makes Fe(II) an increasingly attractive option for precipitating phosphate [9,10]. Furthermore, several studies have indicated that in oxygenated wastewater treatment systems, such as BAF, MBR, and A/O system, phosphate precipitation by the Fe(III) generated through in situ Fe(II) oxidation was even more effective than by the directly added Fe(III) [11–13]. It is thought that in an oxygenated environment the in situ oxidation of Fe(II) could generate Fe(III) which in turn forms stronger complexes with phosphate [9,10,14,15]. Li et al. investigated the use of H₂O₂ as an additional oxidant for Fe(II) dosed in a secondary effluent, and observed better performance for phosphate removal [16]. This result indicated that the performance of phosphate removal by dosing Fe(II) might relate to the extent in situ Fe(II) oxidation which could be promoted through the ways of advanced oxidation process or catalytic oxidation process.

Cu(II) is an efficient oxidation reaction catalyst whose favorable effect for Fe(II) oxidation has been demonstrated in previous studies [17–19]. Cu(II) showed better catalytic performance for

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Fe(II) oxidation than many other metal ions [20], and good applicability in widely ranged pH and temperature conditions [21,22]. Cu(II) is therefore speculated can be used for enhancing the phosphate removal process with adding Fe(II), since it might be able to catalytically accelerate the in situ Fe(II) oxidation and ultimately promote phosphate precipitation. It is not environmental friendly to add external Cu(II) in wastewater treatment process. But when Cu(II) originally exists in the wastewater stream such as wastewater generated in electro-plating processing and mining activities, attempts of utilizing its catalytic effect for wastewater treatment will be environmental sound practice.

Phosphate and Cu(II) are often found co-present in electro-plating wastewater. As the discharge limit for phosphate became more stringent in China (0.5–1.0 mg/L), much effort is being paid on treating phosphate in electro-plating wastewater to comply with the discharge standard. Regarding the conventional electro-plating wastewater process, advanced oxidation such as ozonation is often firstly applied for removing refractory organic pollutants, and followed by phosphate precipitation with adding lime [23]. Thus, the advanced oxidation treated effluent not merely contains co-present phosphate and Cu(II), but also include high level of dissolved oxygen (DO). In such cases there will be certain advantages to carry out phosphate removal using Fe(II) and employ the originally existing Cu(II) as catalysts. It is practically meaningful to examine phosphate removal by adding Fe(II) and the enhancement by originally co-present Cu(II) in electro-plating wastewater treatment. Therefore, a series of batch scale experiments were carried out in this study to (1) examine the potential contribution of co-present Cu(II) on the phosphate removal by adding Fe(II); (2) investigate the effect of operating parameters including Fe(II)-dose, initial DO, and initial pH on the phosphate removal by adding Fe(II) and with co-present Cu(II); (3) compare the Fe(II) dosing option with conventional lime coagulation method in phosphate removal from real electro-plating wastewater.

2. Materials and methods

2.1. Materials and sample preparation

Reagent grade sodium monohydrogen (ortho-) phosphate (Na_2HPO_4), sodium bicarbonate (NaHCO_3), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), lime ($\text{Ca}(\text{OH})_2$) were used to prepare the test solution by dissolving into deionized water. All Fe(II) solutions were freshly prepared immediately before use.

2.2. Apparatus and experimental procedure

2.2.1. Batch experiment using synthesized wastewater

A series of batch scale experiments were conducted to examine the performance of phosphate removal by Fe(II) in the presence of Cu(II) using a 5 L plexi-glass made reactor (shown in Fig. 1). This reactor was equipped with a CO_2 cartridge, an air compressor, and a constant-temperature water bath. In the experiment the reactor was firstly added with 3 L of deionized water. The water inside was then deoxygenated by purging with N_2 gas. After that, the water was added with quantified NaHCO_3 in powder form, and simultaneously purged with gauged CO_2 and air, by which pH and DO in water were adjusted to a designed level and maintained throughout the experiment. In the following step, known amount of KH_2PO_4 solution was added in to achieve an initial phosphate concentration of 11 mg/L. The phosphate removal process was then started by adding quantified Fe(II) and Cu(II) solutions to achieve their designed concentrations. In the experimental time for the phosphate removal process was 60 min. The solution inside the reactor was kept stirred by an agitator (model Eurostar-P1, IKA,

Germany). The agitator was controlled at a speed of 350 rpm for 1 min after the addition of Fe(II) and Cu(II), and subsequently at 200 rpm for another 59 min. Solution samples were withdrawn at regular intervals via syringes, and filtered through syringe filters (0.45 μm , PES, Germany). The filter sample was then split into two parts. One part was used to determining phosphate concentration. The other part was quenched with 25% H_2SO_4 solution and deoxygenated using nitrogen for dissolved iron (Fe(II)) determination.

2.2.2. Batch experiment using real electro-plating wastewater

Another series of batch experiments were conducted using Cu(II) bearing real electro-plating wastewater. The performance of phosphate removal by adding Fe(II) was compared to that of by adding lime in the experiment. The real wastewater was collected from the effluent of an ozonation treatment unit of an electro-plating processing factory in Shenzhen, China. The characteristics of the wastewater were shown in Table 1. The experiment was carried out using a program controlled six paddle stirrer (TA6-4, Wuhan, China) for 20 min. Fe(II) and lime solutions with varied concentrations were added into the water to achieve a desired phosphate removal target, respectively. At the end of the experiment, residual phosphate in the wastewater and sludge produced was determined.

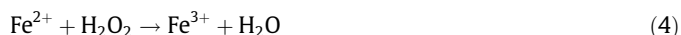
2.3. Analytical methods

Water quality parameters were analyzed following APHA Standard Method (APHA, 1998) [24]. The concentrations of PO_4^{3-} and Fe^{2+} were measured by the colorimetric methods using a UV/visible spectrometer (UV2450, SHIMADZU, Japan). Solution pH was measured using a pH meter (model PB-10, Sartorius, Germany). DO in solution was monitored by a DO meter (model 550A, YSI, USA).

3. Results and discussion

3.1. Phosphate removal by adding Fe(II)

The performance of phosphate removal by adding Fe(II), and the effects of co-present DO and Cu(II) were investigated. The results were shown in Fig. 2. When there was only DO or Cu(II) co-present with phosphate, almost no phosphate removal took place throughout the experiments. In the case of Fe(II) addition in absence of DO and Cu(II), observable but poor phosphate removal was recorded. On the contrary, when Fe(II) was added in a DO containing solution, notable phosphate removal was achieved. The final phosphate removal rate was 62.4% at the end of the experiment. It indicated that phosphate removal should be resulted from precipitating with Fe(III) which was generated through Fe(II) oxidation by DO in solution. Moreover, phosphate removal by adding Fe(II) was observed remarkably promoted in the presence of co-existing DO and Cu(II). The final phosphate removal rate was increased to 91.7%. Such enhanced phosphate removal was considered due to the catalytic oxidation of Fe(II) in the presence of Cu(II) (Eqs. (1)–(4)) [17,18].



These speculations were evidenced by the results of Fe(II) consumption (Fig. 2b). Fe(II) consumption rate only showed observable when there was no DO and Cu(II), but greatly increased in

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