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Effective reuse of electroplating rinse wastewater by combining calcined oyster shell powder with H_2O_2/UV process

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ABSTRACT

In this study, the merits of combining the oyster shell powder (OSP) pre-treatment with H_2O_2/UV post-oxidation for the reuse of electroplating rinse wastewater were evaluated. The results showed that the calcined OSP was more effective in removing heavy metals than the original OSP. For the 1,000˚C-calcined OSP of 0.6 g/L, the removals were 98, 94, and 99% for Fe, Ni, and Cr, respectively. That is, a small quantity of the calcined OSP could remove a large quantity of heavy metals due to the large specific surface area and the dramatically increased pH; the former resulted in a better adsorption capability and the latter induced buck precipitation. Further, after the post H_2O_2/UV process, the chemical oxygen demand and total organic carbon were reduced from 1,206 to 41.2 mg/L and from 252 to 12.6 mg/L, respectively, for pH of 8.0, H_2O_2 of 1,000 mg/L, UV of 52 W, and oxidation time of 240 min. That is, the combination of calcined OSP pre-treatment and H_2O_2/UV post-oxidation could not only treat the electroplating rinse wastewater to comply with the Taiwan's effluent standard but could also satisfy the in-house water reuse criteria while resolving the issue of waste oyster shells simultaneously.

Keywords: Electroplating; Rinse wastewater; Oyster shell powder; H_2O_2/UV; Water reuse

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1. Introduction

Electroplating is a common process for modifying material surface properties for desired characteristics and is essential to modern technology. However, the process requires a large quantity of water for rinsing; the resulting rinse water contains heavy metals and organics. Since heavy metals and organics are harmful to the environment and human health, they are prohibited from being directly discharged into rivers and oceans unless they meet Taiwan's strictly enforced effluent standard. Hence, the removal of these harmful materials is critical to the continuous progress of the electroplating industry.

Recently, removal technology of heavy metal ions by biosorption using agricultural waste is becoming popular because of the need for further environmental protection. For example, Cd(II) adsorption by orange peel powder [1], Cr(VI) adsorption by coir pith [2] and fruit peel of litchi [3], and Cu(II) adsorption by crop straws [4,5] and gooseberry fruit [6] have been investigated. Moreover, Ni(II) removal by sugarcane bagasse pith [7], pineapple and bamboo stem [8], and sawdust [9] has also been conducted.

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In addition to the agricultural waste, the mariculture waste also poses environmental concerns due to the rapid expansion of mariculture worldwide which results in the drastic depletion of natural marine resources. Among the various types of mariculture, oyster farms are popular in Asia; consequently, an enormous amount of oyster shells is produced. In Taiwan alone, the quantity of oyster shells produced exceeds 0.16 million tons per year; the oyster shell waste is generally either dumped into coastal waters or land-filled.

Using the oyster shell waste as an adsorbent for heavy metals to benefit both mariculture and the environment has been explored [10–13]. However, none of these studies focused on treating real electroplating wastewater for heavy metal removal by oyster shell powder (OSP).

On top of heavy metals, the electroplating wastewater also contains recalcitrant organics such as surfactant, cyanide, and oil which are very difficult to be biodegradable. In general, advanced oxidation processes (AOPs) are commonly adopted to treat the recalcitrant organics [14,15]. Among the AOPs, H_2O_2/UV is less pH-dependent and generates no chemical sludge. Its performance is generally brought about by the presence of hydroxyl radicals ($HO^{\bullet}$) by direct photolysis of H_2O_2 under UV irradiation as shown by Eq. (1). This process has been effectively employed to oxide recalcitrant organics [15–20]. Therefore, considering the potentials of OSP and H_2O_2/UV, we combined them to remove heavy metals and organics in the electroplating rinse wastewater in this study:

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \quad (1)$$

2. Materials and methods

2.1. Electroplating rinse wastewater

Electroplating rinse wastewater was sampled from an electroplating factory, located in Kaohsiung City, Taiwan. The main products of the factory are electroplated screws and nuts for exporting to Europe. The electroplating process includes passivation, electrolysis, acid treatment, solvent cleaning, and hot degreasing. In these procedures, trivalent chromium, luster agents, surfactants, acid solution, and organic solvent were used without employing any hexavalent chromium. The resulting rinse wastewater contained about 250–300 CMD (m^3/d); the details of the composition are listed in Table 1. The concentrations of Cu and Pb of the wastewater sample were 0.07 mg/L and 0.03 mg/L which were below Taiwan's effluent standard of 3 and 1.0 mg/L, respectively. Thus, the removal of Cu and Pb was not considered in the study.

2.2. Experimental methods

2.2.1. OSP preparation and experiment

Oyster shells were obtained from a local seashore area in Tainan City, Taiwan. The shells were cleaned with brushes after discarding the attached fresh remnant; they were then washed with deionized water (DI water), air-dried, and pulverized in a grinder (Yue Cherh, Taiwan). The pulverized powders were further sieved by a 42-mesh sieve (355 μm) to obtain the OSP for subsequent experiments. The sieved OSP was divided into two parts. One was heated at 105℃ for 2 h for removing moisture and was designated as the original OSP. The other was calcined in a programmable furnace (DF-202, Deng Yng, Taiwan) at 1,000℃ for 2 h and was referred to as the calcined OSP. A scanning electron microscope (SEM/EDS) (S-3000N, Hitachi, Japan) was used to analyze the surface structure and elements of the OSP. Batch experiments were performed in a sealed, 250-mL conical flask at 150 rpm in a temperature-controlled mechanical shaking incubator (SB-7D Model, Deng Yng, Taiwan). The flask contained 200 mL of the electroplating rinse wastewater. The OSP treated water

Table 1
Electroplating rinse wastewater composition and regulatory standards

Item	pH	COD (mg/L)	TOC (mg/L)	Total Fe (mg/L)	Total Cr (mg/L)	Ni(II) (mg/L)	Cu(II) (mg/L)	Pb(II) (mg/L)	Conductivity (μS/cm)
Row water	2.3	1,206	252	352	6.5	12.4	0.07	0.03	9.52×10^3
Effluent standard	6–9	100	–	10	2.0	1.0	3.0	1.0	–
In-house reuse criteria	6–8	50	20	–	–	–	–	–	3,000

Note: "–" no regulatory standard.

was precipitated for 30 min. The resulting supernatant was filtered through a 1-μm glass fiber filter (ADVANTEC®, Japan) and then used for the post H_2O_2/UV process.

Each experiment was repeated three times to obtain the average removal (%). Prior to measuring the concentration of heavy metals, the wastewater samples were centrifuged (CN-1040, Hsiangtai, Taiwan) and filtered through a 0.45-μm cellulose acetate membrane filter (ADVANTEC®, Japan).

2.2.2. H_2O_2/UV process

A stainless-steel batch photo reactor (rectangular cylinder), as shown in Fig. 1, was set up for this study (Chensun Engineering Co., Ltd). Its dimensions were 17.4 cm (width) by 17.4 cm (depth) by 20 cm (height) with a total volume of about 6.0 L. Four low-pressure UV lamps (PHILIPS, 12.8 cm in height) with a total power of 52 W (i.e. 4 by 13 W), irradiating mostly 254 nm wavelength, were installed 90° apart with a radial distance of 3.5 cm from the reactor center. A quartz tube (15.4 cm in height and 4.3 cm in diameter) was used to enclose each lamp for lamp protection and complete light penetration. The wastewater sample was 5.0 L for each experiment. After adding a predetermined amount of H_2O_2 (Merck, Germany) into the sample, the solution within the UV-irradiated reactor was stirred by a motor-driven mixer (at the center of the reactor) at 100 rpm to ensure homogeneous mixing. The pH was controlled by either NaOH or HNO_3. All of the experiments were conducted at the room temperature.

2.3. Chemical analysis

The pH, chemical oxygen demand (COD), total organic carbon (TOC), conductivity, Fe, Cr, Cu, Zn, and Ni were measured according to the procedures of standard methods [21]. TOC was determined by the total organic carbon analyzer (Model 700; O.I. Cooperation); Fe, Cr, Ni, Cu, and Pb were measured by an atomic absorption spectrometry (Hitachi, Z-8200, Japan). The stock solutions of heavy metals were obtained from Merck (Germany).

3. Results and discussion

3.1. Effect of OSP dose on removing organics and heavy metals

3.1.1. Original OSP

For evaluating the effectiveness of the original OSP, its dose was varied from 1 to 5 g/L. The results are shown in Fig. 2. By increasing the OSP dose, the removals of COD and TOC increased slightly. The

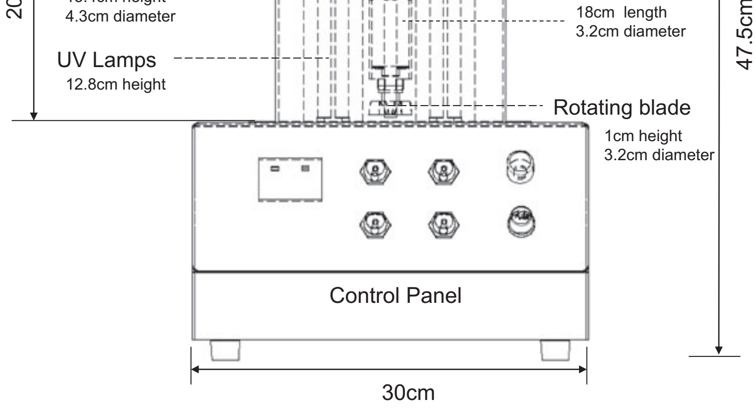

Fig. 1. Experimental setup of the batch photo reactor.

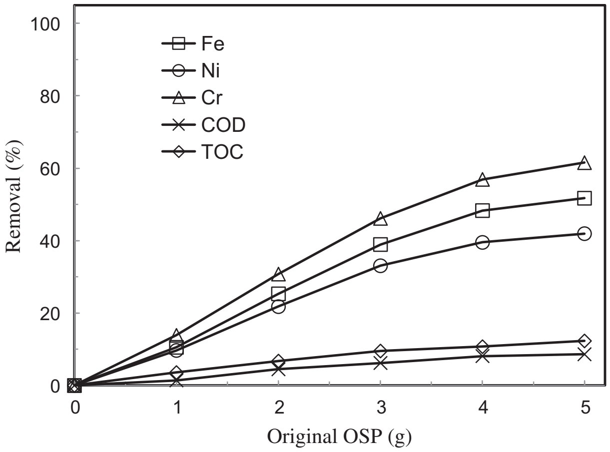

Fig. 2. Effect of original OSP dose on removing organics and heavy metals.

removal efficiency for both COD and TOC was about 10% for the original OSP of 5 g/L; the residuals of COD and TOC were 1,102 and 221 mg/L, respectively. That is, the original OSP could not effectively remove the organics in the electroplating rinse wastewater. On the other hand, more heavy metals were removed by increasing the original OSP dose; the maximum removals, for the original OSP of 5 g/L, were 52, 62, and 42% for Fe, Ni, and Cr, respectively. That is, the corresponding concentrations of Fe, Ni, and Cr reduced from 352 to 170 mg/L, from 12.4 to 7.2 mg/L, and from 6.5 to 2.5 mg/L. However, none of the resulting water qualities complied with the effluent standards.

3.1.2. Calcined OSP

The dose of the calcined OSP was from 0.2 to 1.0 g/L. The results are shown in Fig. 3. By increasing the dose of the calcined OSP, the removals of COD and TOC increased; for the calcined OSP of 1 g/L, they were 24 and 28.2%, respectively, which were better than those by the original OSP. The residuals of COD and TOC were 917 and 181 mg/L, respectively. However, the former still did not meet the effluent standard of 100 mg/L. In contrast, heavy metals were removed completely as compared to organics. For the calcined OSP of 0.6 g/L, the removals were 98, 94, and 99% for Fe, Ni, and Cr, respectively; the corresponding concentrations were from 352 to 9 mg/L, from 12.4 to 0.8 mg/L, and from 6.5 to 0.1 mg/L. That is, all of them complied with the respective effluent limits of 10, 1.0, and 2.0 mg/L of Fe, Ni, and Cr, respectively. In addition, for the conditions of the calcined OSP of 0.8 and 1 g/L, Fe, Ni, and Cr were reduced almost completely. In other words, the calcined OSP was effective for removing heavy metals in the electroplating rinse wastewater.

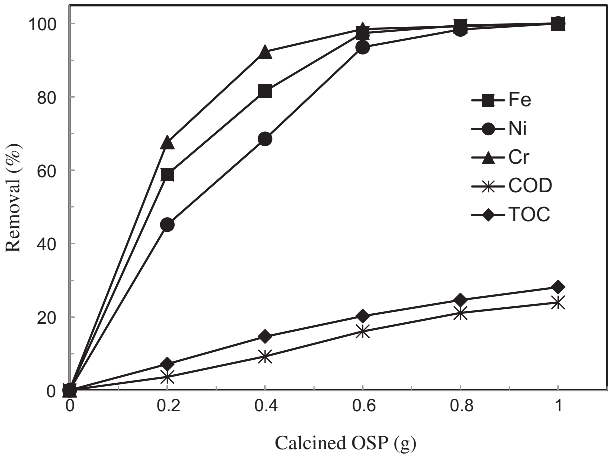

Fig. 3. Effect of calcined OSP dose on removing organics and heavy metals.

3.2. Mechanism of heavy metals removal by OSP

3.2.1. Solution pH

The solution pH is an important factor in governing either adsorption or precipitation for removing heavy metals by the OSP. The dominant metal species of solution are $M(OH)_2$ for $pH > 6.0$; M^{2+} and $M(OH)^+$ for $pH < 6.0$ [22,23]. In order to clarify the removal mechanism of heavy metals by the OSP, the pH effect was examined. The results depicted in Fig. 4 show that by increasing the OSP dose, the pH of electroplating rinse wastewater increased from its raw value of 2.3–7.7 when the original OSP dose of 5 g/L

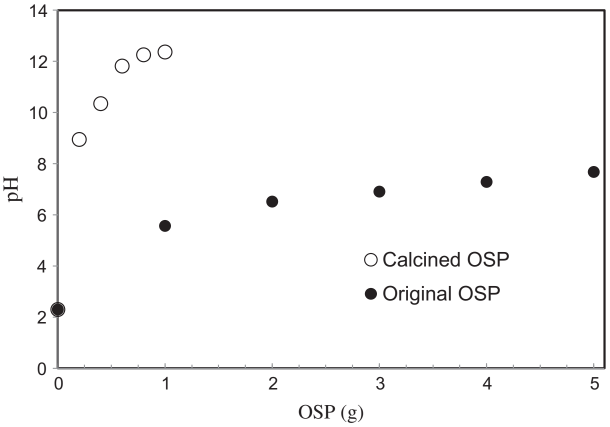

Fig. 4. Solution pH after adding OSP.

was added. In contrast, the pH dramatically increased to 11.8 from 2.3 by only adding the calcined OSP dose of 0.6 g/L; thus, heavy metals were significantly removed as illustrated in Fig. 3.

3.2.2. OSP structure

The 5000X surface micrographs of the original OSP and the calcined OSP analyzed by SEM are shown in Fig. 5(a) and (b), respectively. As portrayed in Fig. 5(a), the surface of the original OSP consisted of large plates without any porosity, indicating that metal adsorption was limited to only a thin surface layer. By contrast, as shown in Fig. 5(b), at the calcination temperature of 1,000°C the structure of the calcined OSP became thin fragmental sheets with cavities. That is, a large surface area for adsorption was created and resulted in the dramatic increase in the removal of heavy metals.

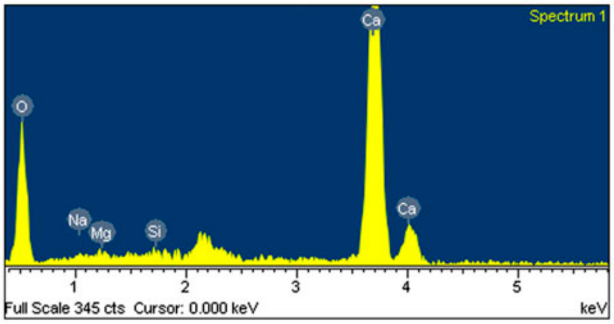

Fig. 6. Element analysis of 1,000°C-calcined OSP.

Table 2
Results of the element analysis of original and calcined OSP

Element	Original OSP	Calcined OSP
C (%)	9.79	1.53
O (%)	47.63	49.35
Na (%)	0.20	0.04
Mg (%)	0.29	0.21
Si (%)	0.36	0.30
Ca (%)	41.73	48.57

Further, the analysis of elements by EDS revealed that the original OSP and the calcined OSP had the same elements, except in the proportions. Therefore, only the result of the latter is illustrated in Fig. 6, whereas the detailed compositions of the elements are listed in Table 2, including those of the original OSP. For the original OSP, the compositions of oxygen, calcium, and carbon were 47.63, 41.73, and 9.79%, respectively, whereas those corresponding to the calcined OSP were 49.35, 48.57, and 1.53%. That is, after calcination, the proportions of oxygen and calcium increased and that for carbon decreased. According to the literature, as the calcined temperature rises, the proportion of minerals in the oyster shell matrix changes; $CaCO_3$ can be completely converted to almost pure CaO at 900°C [11,24]. Therefore, our observation of the fact that a small quantity of 1,000°C-calcined OSP could remove a large amount of heavy metals is due to the following: (1) the large specific surface area which resulted in a better adsorption capability; (2) the large amount of CaO in water increased the pH enormously and induced buck precipitation of heavy metals according to the following reactions:

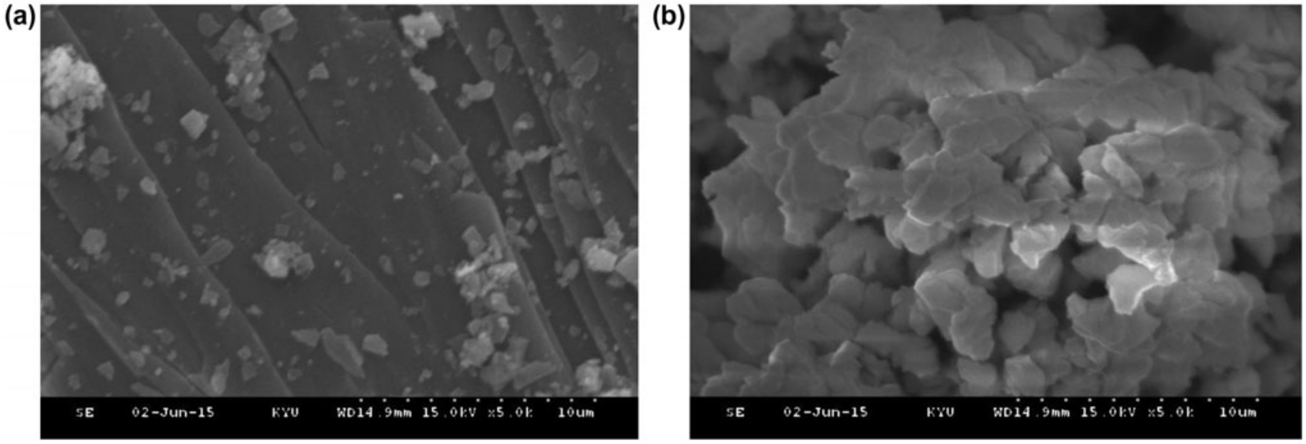

Fig. 5. (a) SEM image of original OSP and (b) SEM image of 1,000°C-calcined OSP.

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} \tag{2}$$

$$\mathrm{Ca(OH)_2} \leftrightarrow \mathrm{Ca^{2+}} + \mathrm{OH^-} \tag{3}$$

$$\mathrm{M^{2+}} + 2\mathrm{OH^-} \rightarrow \mathrm{M(OH)_{2(S)}} \tag{4}$$

3.3. H_2O_2/UV process

After pre-treating the electroplating rinse wastewater by the calcined OSP dose of 0.6 g/L, the contents of heavy metals in the wastewater were obviously lower than those of the effluent standards. On the other hand, the pH was 11.8; the residual COD and TOC were 1,012 and 201 mg/L, respectively. Therefore, the pre-treated electroplating rinse wastewater was further post-treated by H_2O_2/UV oxidation. It is worthy to point out that the initial pH of the H_2O_2/UV process was controlled at either 11.8 or 8.0; the latter was for meeting the effluent standard of pH 6.0–9.0 and reuse criteria of 6.0–8.0. The results are shown in Fig. 7. By increasing the oxidation time and H_2O_2 dose, the mineralization efficiency of the organics increased. Moreover, the removals for pH 8.0 were always better than those for pH 11.8. Generally, lowering the pH value is beneficial to the removal of organics in the H_2O_2/UV process [20,25–27]. At pH of 11.8 and the oxidation time of 240 min, the TOC removals were 61 and 89% for H_2O_2 of 500 and 1,000 mg/L, respectively. On the other hand, at pH 8.0, the corresponding TOC removals were 75 and 95%.

In order for COD to be smaller than 100 mg/L, it would be better that the associated TOC was smaller than 30 mg/L. The results shown in Fig. 7 indicate that only three operation conditions of the H_2O_2/UV process met the needed TOC of being smaller than 30 mg/L. Therefore, the COD and TOC concentrations of these three conditions are redrawn as shown in Fig. 8 for which the H_2O_2 doses were all of 1,000 mg/L. For the first condition of pH 11.8 and oxidation time = 240 min, the concentrations of COD and TOC were 96.6 and 27.2 mg/L which met the effluent standard, but the pH had to be adjusted to 6.0–9.0 before discharging. For the second condition of pH 8.0, oxidation time = 210 min, the concentrations of COD and TOC were 78.6, 20.2 mg/L, respectively, which met the effluent standard, including the pH. For the last condition of pH 8.0, oxidation time = 240 min, the concentrations of COD and TOC were 41.2, 12.6 mg/L, respectively, which not only met the effluent standard but also satisfied the in-factory water reuse criteria with COD of 50 mg/L and TOC of 20 mg/L. From these results, it is clear that the calcined OSP removed heavy metals and H_2O_2/UV oxidation reduced organics effectively. Thus, the combination of the calcined OSP pre-treatment and H_2O_2/UV post-oxidation reduced heavy metals and organics not only to comply with the effluent standard but also to satisfy in-house water reuse criteria. In the meantime, the issue of waste oyster shell was also resolved.

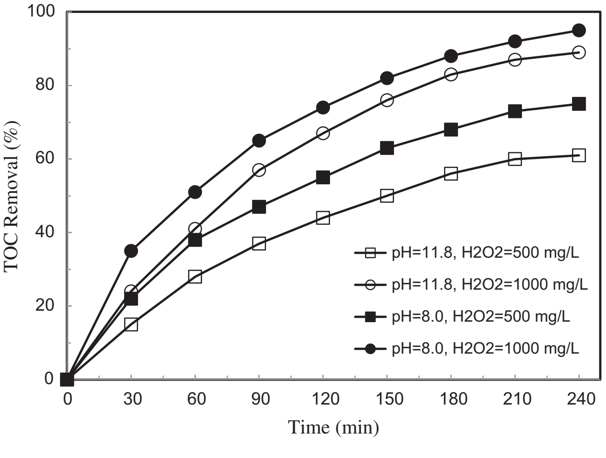

Fig. 7. TOC removal by H_2O_2/UV oxidation.

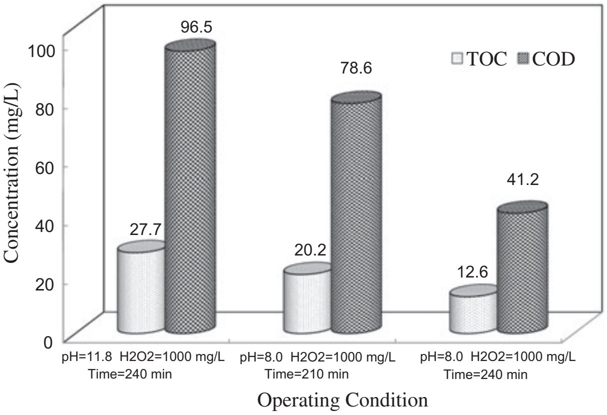

Fig. 8. H_2O_2/UV operating conditions of TOC < 30 mg/L.

4. Conclusion

This study evaluated the performance of removing heavy metals and organics in the electroplating rinse wastewater by combining the OSP pre-treatment with H_2O_2/UV post-oxidation. The results showed that the calcined OSP was more effective in removing heavy metals than the original OSP. The effectiveness of the calcined OSP was due to its large specific surface area to result in a better adsorption capability and its enormously increased pH to induce buck precipitation. Moreover, the subsequent H_2O_2/UV oxidation reduced TOC to 12.6 mg/L to meet the in-house water reuse criteria. That is, the combined process is more efficient, economic, and environmentally friendly.

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