ABSTRACT: Based on the characteristic that Ca$^{2+}$ can react with 4-ethyl-2-methoxyphenol (EMP) to form a complexation with a phenol−calcium ratio of 4:1, a new extraction and purification method of EMP is developed for the first time in this work. At an optimum purification condition, 99.60% purity of EMP can be obtained through a reaction and decomposition operation. By combining a variety of characterizations, which consist of in situ Fourier transform infrared spectrometer (FTIR), nuclear magnetic resonance (NMR), inductively coupled plasma optical emission spectrometer (ICP-OES), gas chromatography−mass spectrometry (GC−MS)/flame ionization detector (FID), elemental analysis, and thermogravimetric analysis, the reaction mechanism of the coordination process is studied. It is demonstrated that there are three stages of the coordination reaction between Ca$^{2+}$ and EMP. A neutralization reaction occurs in the first stage, while the second stage is a mixing reaction stage including neutralization and coordination reaction. When the reaction proceeds to the third stage, another coordination reaction occurs. Furthermore, phenol and ethanol are added as impurities in EMP. EMP with a purity of more than 99.50% can be obtained using this purification method. It confirms that this efficient method can achieve a good purification effect even for EMP solutions with complicated components.

1. INTRODUCTION

The chemical 4-ethyl-2-methoxyphenol (EMP) is extensively used in pharmaceutical intermediates, health products, and food additives because of its excellent anticancer and antioxidant properties. EMP is mainly obtained from the pyrolysis oil of biomass such as pinewood, bamboo, and soft/hardwood. The composition of pyrolysis oil is extremely complicated due to the diversity and characteristics of biomass itself. Meanwhile, the EMP product is mainly used in the food and pharmaceutical industry, which put forward higher requirements for the safety and high purity of raw materials. Thus, highly efficient EMP extraction and purification methods are very important for ensuring and improving the quality of downstream products.

The current extraction methods of high-purity EMP and/or most of the phenolic compounds mainly consist of distillation/rectification, organic solvent extraction, resin adsorption, porous material adsorption, ionic liquid extraction, and supercritical fluid extraction. However, some of them have various degrees of defects including insufficient purity, high cost, or safety issues. For example, the applicability of distillation and rectification was reduced because of the thermal instability of many phenolic compounds, not to mention that the purity of products can only reach about 95%.

In addition, organic solvent extraction produces a large amount of organic waste during the production process, facing extremely severe environmental problems. As one of the most emerging technologies, ionic solution extraction and supercritical fluid extraction can achieve high purity of about 99%, while their high cost and strict technical and environmental requirements make it difficult to be applied on a large scale in the industry. Therefore, much more efficient extraction methods of EMP or other phenolic substances are urgently required.

The researchers found that several metal ions, which consists of Zn(II), Al(III), Fe(III), Cu(II), Ca(II), Ge(IV), and Ag(I), can react with tea polyphenols, apple polyphenols, guaiacol, etc. to form a coordination product. Based on this characteristic, several extraction and separation methods were studied in various application scenarios. For example, Golbaz et al. researched the reaction mechanism of ferric chloride with...
phenol, cyanide, and chromium ions in the water solution to improve the removal rate of the latter three substances.\textsuperscript{17} The binding mechanism of Cu(II) and Zn(II) ions with phenol in red wine was studied via electrochemical methods, which were used to characterize the compositions of red wine.\textsuperscript{18} Furthermore, a safe metal ion for human health, Ca\textsuperscript{2+}, was used as the complex precipitant to extract guaiacol,\textsuperscript{23} syringol,\textsuperscript{24} and other phenolic compounds.\textsuperscript{25} In our previous study, three stages were revealed for the reaction between Ca\textsuperscript{2+} and guaiacol, in which the final molar ratio of guaiacol to Ca\textsuperscript{2+} reached 4.\textsuperscript{16} Furthermore, 1 mole of the final complexation can release 2 mole pure guaiacol when it was heated at 200 °C. Considering the similar chemical characteristic of guaiacol and EMP, whether these two chemical compounds follow the same coordination reaction mechanism with Ca\textsuperscript{2+} deserves further study. Meanwhile, the extraction and purification method of high-purity EMP was explored based on the reaction mechanism study.

The new complexation extraction method was proposed and studied in this work by utilizing the characteristic that Ca\textsuperscript{2+} can react with 4-ethyl-2-methoxyphenol (EMP) to form a complexation with a phenol–calcium ratio of 4:1. The objectives of this study were (1) to develop a new method for the extraction and purification of EMP, (2) to reveal the reaction mechanism between EMP and Ca\textsuperscript{2+}, and (3) to verify whether the method is suitable for more complicated solutions containing many components.

2. MATERIALS AND METHODS

2.1. Materials. Chemical reagents used in this work including 4-ethyl-2-methoxyphenol (98.0%), phenol (99.5%), Ca(OH)\textsubscript{2} (99.0%), NaOH (99.0%), KBr (spectrographic pure), DMSO-d\textsubscript{6} (99.9%, with 0.03% TMS), and CDCl\textsubscript{3} (99.9%) were purchased from Aladdin Industrial Co. (Shanghai, China). 4-Ethyl-2-methoxyphenol with analytical standard (≥98.0%) was purchased from Sigma-Aldrich Co. (St. Louis). Among these, KBr was used for infrared spectrum measurement, while CDCl\textsubscript{3} and DMSO-d\textsubscript{6} were used for nuclear magnetic resonance (NMR) characterization.

2.2. EMP Purification. The complex extraction process for the purification of EMP is described in Figure 1. The chemical agent Ca(OH)\textsubscript{2} of 4 mmol was dissolved into 200 mL of deionized water in a three-necked flask. Accurately weighed 3.04 g (20 mmol) of 98% EMP as a reactant was slowly added into the three-necked flask at a dropping rate of 0.8 mmol/min using a microperistaltic pump with a 0.2 mm caliber needle under the magnetic stirring at 750 rpm. With the continuous addition of EMP, a white flocculent solid gradually formed in the flask. After all of the reactants had been added, the solid produced in the flask was collected by vacuum filtration with a medium-speed filter paper and further washed three times alternately with 100 mL of absolute ethanol and 100 mL of deionized water. Then, the solid product was dried in a vacuum at 60 °C/20 kPa for 12 h and stored in a drying oven. The collected solid product was named Prod-R4.

The decomposition of the complex Prod-R4 and the recovery of EMP were carried out in a tube furnace. Under a nitrogen purge of 200 mL/min, the tube furnace was heated to 200 °C at a rate of 8 °C/min. In this process, the gas product generated was blown out with a N\textsubscript{2} purge, which was collected by cooling equipment at −10 °C. The solid residue and the liquid product were named TR200 and LP200, respectively. Meanwhile, TR200 was further decomposed at 400 °C, and the solid residue and the liquid product were, respectively, named as TR400 and LP400.

2.3. Qualitative and Quantitative Analysis. Qualitative analysis of LP200 was performed by gas chromatography–mass spectrometry (GC–MS, QP2010SE Shimadzu, Japan) with the capillary column model named Rtx-5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness). It was equipped with a quadrupole analyzer operating in electronic impingement (70 eV) mode at a range of m/z from 30 to 500. The GC–MS was performed under the following conditions: carrier gas, helium; flow rate, 1 mL/min; split ratio, 50:1; injection volume, 1 μL; temperature program, from 323 to 523 K at 10 K/min; and injector temperature, 543 K. Quantitative analysis was performed using a gas chromatography flame ionization detector (GC-FID, 7890A Agilent Technologies, America), which was equipped with a capillary column coated with PEG (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The GC-FID was performed under the following conditions: carrier gas, helium; flow rate, 30 mL/min; split ratio, 19:1; injection volume, 1 μL; temperature program, from 313 to 523 K at 10 K/min; and injector temperature, 523 K.

The external standard method was carried out for the quantitative analysis of the products. EMP (0.5 g) standard
Ca(OH)₂ was performed in a 250 mL three-neck flask, the study of the reaction mechanism between EMP and Ca(OH)₂ was investigated using thermogravimetric analysis (TGA) with a STA-449 F5 synchronous thermal analyzer. The carbon and hydrogen contents were determined by an Elementar Analysen system (Vario Micro Cube, Germany). The ¹³C and ¹H NMR spectrum of the compounds were measured by a 600 MHz nuclear magnetic resonance spectrometer (AV600 BRUKER, Germany). The thermal decomposition of Prod-R₄, TR200, and TR400 was studied in the dark. As expected, the purity of EMP reached up to 99.60% when the light was far away from the decomposition device. As the decomposition temperature increased to 400 °C, the purity of EMP decreased to 190, 180, and 170 °C, indicating that a relatively low temperature was beneficial for improving the purity of EMP because a higher decomposition temperature led to EMP peroxidation. Considering that light is one of the factors that lead to phenol oxidation, 27 the decomposition process of EMP was studied in the dark. As shown in Figure 3, the reaction can be divided into three stages including the first stage (0–6 min), the second stage (6–13 min), and the third stage (13–20 min), which was named as Prod-S₁, Prod-S₂, and Prod-S₃, respectively. These three reaction stages will further be analyzed in the following sections.

The sodium salt of EMP (EMP-Na) was prepared by reacting EMP with NaOH solution to analyze whether the acid–base reaction occurred in the first stage. As shown in Figure 4a, the hydroxyl absorption band of EMP in the IR spectrum was chosen as the decomposition temperature of EMP product recovery.

**Table 1. EMP Purity Based on the Purification Method**

| decomposition temperature (°C) | theoretical injection concentration (mg/mL) | detection concentration (mg/mL) | purity (%) | yield (%) |
|-------------------------------|---------------------------------------------|---------------------------------|------------|----------|
| 170 (without light)           | 16.31                                       | 16.24                           | 99.60      | 46.88    |
| 170                           | 15.63                                       | 15.32                           | 98.02      | 46.72    |
| 180                           | 15.50                                       | 15.70                           | 98.73      | 46.07    |
| 190                           | 16.67                                       | 16.96                           | 98.30      | 45.19    |
| 200                           | 16.11                                       | 15.72                           | 97.58      | 47.79    |
| 400                           | 14.80                                       | 11.48                           | 77.57      | 67.84    |

98.30, 98.73, and 98.02% with the decomposition temperature decreasing to 190, 180, and 170 °C, respectively. This indicated that a relatively low temperature was beneficial for improving the purity of EMP because a higher decomposition temperature led to EMP peroxidation. Considering that light is one of the factors that lead to phenol oxidation, 27 the decomposition process of EMP was studied in the dark. As expected, the purity of EMP reached up to 99.60% when the light was far away from the decomposition device. As the decomposition temperature increased to 400 °C, the purity of EMP decreased to 77.57% because of the thermal instability and photolysis properties of EMP. Although 99.60% purity of EMP can be easily obtained through the easy reaction and decomposition devices, the mechanism of the coordination reaction between EMP and Ca²⁺ deserved to be further investigated to expand the application of this technology.

**3. RESULTS AND DISCUSSION**

**3.1. Thermochemical Properties.** The thermal decomposing characteristic of Prod-R₄, TR200, and TR400 was measured by TGA. As shown in Figure 2, the complex Prod-R₄ kept stable for a time when the temperature reached 200 and 400 °C, indicating that three different reaction stages occurred in the coordination reaction process. The decomposition of the complex should be divided into three stages: the first stage, 60–220 °C (50.66% reduction); the second stage, 330–450 °C (21.20% reduction); and the third stage, 700–910 °C (residual weight 7.52%). The mass loss in the first stage was the largest among the three stages, indicating that more EMP could be released in this stage. On the other hand, the mass loss trend of the complex decreased smoothly when the temperature increased to above 400 °C. This is because the decomposition of EMP generated low-molecule alkanes and aromatics, such as methane, ethane, ethylene, phenol, etc., when the decomposition temperature was too high. Therefore, around 200 °C was chosen as the decomposition temperature of EMP product recovery.

**3.2. Quantitative Analysis.** According to the TGA analysis of Prod-R₄, almost 50% weight loss can be observed when it was decomposed at about 200 °C. The released material was verified to be EMP from the GC–MS analysis. Meanwhile, the purity of EMP reached 97.58%, as shown in Table 1. Compared with that, the purity of EMP reached

![Figure 2. Thermal analysis of Prod-R₄, TR200, and TR400.](https://dx.doi.org/10.1021/acs.omegajdx.0c05483)
stage $\delta_{(C-OH)}$ was located at 1366.73 cm$^{-1}$, while it disappeared in the spectra of EMP-Na and Prod-S1. 28 It indicated that a neutralization reaction occurred in the first stage. To further illustrate the occurrence of the acid–base reaction, the infrared spectra of EMP, Prod-S1, and EMP-Na were further compared in Figure 4a. It was not difficult to find that the absorption bands of 1311.74 and 1310.91 cm$^{-1}$ appeared in the EMP-Na and Prod-S1 spectra, respectively. They did not appear in EMP, verifying that the modified absorption peak should be the absorption peak of the hydroxyl oxygen atom $\nu_{(C-O)}$.29,30 In addition, EMP-Na and Prod-S1 spectra had 11 similar absorption bands, thus the reaction that took place in the first stage is the neutralization reaction.

As shown in Figure 4b, the infrared spectra of EMP, Prod-S2, and TR200 were compared in the second stage. Hydroxyl absorption band of 1366.73 cm$^{-1}$ was not found in the spectra of Prod-S2 and TR200, indicating that the neutralization reaction was still in process at this stage. Furthermore, the benzene ring skeleton vibration $\nu_{(C=C)}$ absorption band was red-shifted from 1514.39 cm$^{-1}$ for EMP to 1500.76 cm$^{-1}$ for EMP-Na and 1503.12 cm$^{-1}$ for Prod-S2, indicating that a group with a stronger electron-donating effect was generated in the second stage. This was because a hydroxyl oxygen atom caused the vibration absorption of the benzene ring skeleton.31,32 The combined frequency of the absorption bands of aromatic hydrogen atoms $\delta_{(CH)}$, $\rho_{(CH)}$ and $\delta_{(C-OH)}$ at 1206.10 cm$^{-1}$ was not found in the spectra of Prod-S2 and TR200, while it was red-shifted to 1196 cm$^{-1}$. This suggested that the coordination reaction happened in this stage. Thus, it showed that a mixed stage of neutralization reaction and the complexation reaction simultaneously occurred in the second stage.

The aromatic ring skeleton vibration absorption bands of EMP at 1514.39, 1463.47, and 1453.09 cm$^{-1}$ were found in the spectrum of Prod-R4 and Prod-S3 (Figure 4c), indicating that EMP molecules were present in the third stage. Furthermore, the weak signal of the hydroxyl absorption band at 1370 cm$^{-1}$ again appeared in the spectrum of Prod-R4, indicating the presence of the unreacted hydroxyl group in this stage. It showed that the type of complexation reaction in this stage was completely different from that in the second stage. The new absorption bands were observed at 930 and 985 cm$^{-1}$, which corresponded to Prod-R4 and Prod-S3. The former belonged to the out-of-plane wagging vibration $\omega_{(C-H)}$ absorption of hydrogen atoms of 1,2,3,4-substituted benzene ring, while the latter represented 1,2,3,5-substituted benzene ring hydrogen atom.34 Meanwhile, the hydrogen atom sites in EMP corresponding to these two substituents were HA and HC (Figure 6), indicating that the coordination sites in the third stage should be these two sites.

3.4. NMR Analysis. Based on in situ FTIR analysis, the coordination site in the third stage was located on the hydrogen atom of the benzene ring, while the exact location was still unclear. Therefore, $^{13}$C and $^1$H NMR techniques were used to characterize the reaction products to further determine the coordination sites.

The hydrogen atoms were located on the benzene ring, which were named as $H_A$, $H_B$, and $H_C$. The corresponding carbon atoms were named as $C_A$, $C_B$, and $C_C$ respectively. As shown in Figure 5, compared to the EMP spectrum, the signal strengths of $C_A$ and $C_C$ in the Prod-R4 spectrum almost disappeared. Meanwhile, the signal of $C_B$ was significantly stronger than those of $C_A$ and $C_C$. The signal of $C_D$, $C_E$, and $C_P$ carbon atoms attached to other groups in the aromatic ring also became very weak in the spectrum of Prod-R4. The signal intensity of those carbon atoms that were not attached to other groups, such as $C_{DG}$, $C_{DP}$, and $C_P$, remained unchanged before

\[ \text{Figure 3. In situ FTIR spectra of the coordination reaction: (a) three-dimensional (3D) FTIR spectra and (b) two-dimensional (2D) FTIR spectra of three different reaction stages.} \]

\[ \text{Figure 4. 2D FTIR spectra of (a) EMP, Prod-S1, and EMP-Na; (b) EMP, Prod-S2, and TR200; and (c) Prod-R4 and Prod-S3.} \]
and after the reaction just as in the case of CB. It indicated that HA and HC were most likely to be coordination sites in the third stage because the signals of CA and CC were shielded. Based on the $^{13}$C NMR spectral analysis, the most likely coordination sites for the third-stage reaction should be HA and HC on the benzene ring. To further determine which one of them was the coordination site, $^1$H NMR was used to study the structure of the final product and the intermediate product of this complexation reaction. Compared with the HB and HC signals of the EMP spectrum, that of EMP-Na was transferred to a higher field due to the disappearance of neutralized hydrogen atoms on the hydroxyl group as shown in Figure 6a,b. According to Moreno-Villoslada et al., the electron-donating effect of the phenoxide ion led to an increase in the density of the proton–electron cloud, which favored hydrogen atoms signal toward the high field in $^1$H NMR. It again showed that the neutralization reaction occurred in the first stage as well as the metal phenoxide Ca(OH)(EP$_O$) (EP$_O$), EMP with ionic bond) was produced. In addition, the signal of TR200 (Figure 6c) was further transferred to a higher field because the neutralization of phenolic hydroxyl hydrogen atoms occurred continuously in the second stage. With an increase in the molecular weight of the complex, its solubility in deuterated reagents decreased gradually. When the reaction continued to the third stage, the molecular weight of the complex further increased. Its molecular rotation frequency gradually decreased, resulting in the gradual widening and stacking of the proton signals of HA and HC. It should be noted that the signal integrals of three aromatic hydrogen atoms HB, HB, and HC of EMP were respectively 32.99, 33.33, and 33.68%, which were almost the same (Figure 6a). Nevertheless, it can be observed from Figure 6d that the peak area integrals of HA and HC almost disappeared for Prod-R4, indicating that the chemical state around two hydrogen atoms HB and HC were significantly changed. It showed that a complexation reaction occurred at these two positions.

$^1$H NMR detection was further conducted for Prod-R4 at variable temperatures. As depicted in Figure 7a, the molecular rotation rate of this complex was improved with increasing the test temperature, making the stacked peak signal clearer. The peak areas of HB, HB, and HC were further integrated and fitted with the total peak areas of three hydrogen atoms as shown in Figure 7b. The signal of HB always maintained a relatively stable peak area ratio with the increasing test temperatures. The signal of HA showed an increasing trend, while that of HC decreased. This unusual trend indicated that HA and HC had a completely different chemical state from that of HB in the final product of the complexation reaction, verifying that the coordination sites of the third stage of the complexation reaction were HA and HC on the benzene ring.

### 3.5. Coordination Number

To determine the coordination number of the complexes, the elemental compositions of the intermediate and the final product were analyzed by ICP-OES. Due to this fast and sequential reaction, it was almost impossible to segment the reaction accurately, suggesting that the products of Prod-S1 and Prod-S2 cannot be obtained directly from the reaction process. Fortunately, the thermal decomposition product TR200 and TR400 had the same structure as those of the corresponding reaction stage from TGA analysis, indicating that these two compounds could represent the product of Prod-S2 and Prod-S1, respectively. As shown in Table 1, 1 mole EMP reacted with one mole Ca$^{2+}$ because the R value of TR400 was about 1 (≈0.91) in the first stage. With the continuation of the reaction to the second stage, the R value increased to 1.5 (≈0.91).
stage, one mole EMP was bonded with the intermediate produced in the first stage to produce a product that had an R value of 2 (≈2.03). Furthermore, the R value of Prod-R4 reached 4 (≈4.16), indicating that another two moles EMP were further coordinated with the intermediate produced in the second stage. Thus, the coordination number of the complex should be 4 (Table 2).

| compound    | w_C (%) | w_Ca (%) | R   |
|-------------|---------|----------|-----|
| TR200       | 37.90   | 15.487   | 0.91|
| TR200       | 60.67   | 11.092   | 2.03|
| Prod-R4     | 66.16   | 5.891    | 4.16|

$R = \frac{w_C}{(M_C \cdot N_C)} \cdot \frac{w_C}{(M_C \cdot N_C)}$, $w_C$ the mass content of carbon; $M_C$, molecular weight of carbon, 12.01 g/mol; $N_C$, the number of carbon atoms of EMP; $w_Ca$, the mass content of calcium; $M_Ca$, molecular weight of calcium, 40.078 g/mol.

3.6. Reaction Mechanism. According to the characterization of the reaction process between Ca$^{2+}$ and EMP, the mechanism of calcium–phenol complexation reaction was clearly demonstrated as shown in Figure 8. The reactions can be divided into three stages. The first stage was the neutralization stage, in which Ca$^{2+}$ was neutralized with EMP to produce the phenolate Ca(OH)(EP_O). The second stage was a mixing stage, in which the hydroxide in Ca(OH)(EP_O) continued to neutralize with OH$^-$ of EMP, and the generated phenolate ion was combined with Ca$^{2+}$ to produce the complex of Ca(EP_O)(EP_O) (EP_O, EMP phenolate ion with coordination bond at oxygen atom of its hydroxyl group). In this complex, the coordination site was a hydroxyl oxygen atom. When the reaction proceeded to the third stage, two moles of EMP were combined with Ca(EP_O)(EP_O) using a hydrogen atom as the coordination site to form the final product Ca(EP_O)(EP_O)(EP_H)$_2$ (EP_H, EMP molecule with coordination bond at hydrogen atom of its aromatic ring).

Base on this reaction mechanism, 2 moles of EMP were released when 1 mole final product Ca(EP_O)(EP_O)(EP_H)$_2$ was heated at 170–200 °C; meanwhile, the final product was converted to the intermediate product Ca(EP_O)(EP_O). Thus, the theoretical maximum yield should be 47.06% using the purification method reported in this study. It showed that 46.88% yield was close to the maximum, indicating the high efficiency of this purification technology. Another 2 moles of EMP can be released through the regular acid dissolution and organic solvent extraction. Furthermore, it is deserved to be noticed that the intermediate product (Ca(EP_O)(EP_O)) can be used as a circulating complexing agent to react with EMP again to form Ca(EP_O)(EP_O)(EP_H)$_2$, indicating that the purification method had high application potential.

3.7. Extended Applications. To further expand the application range of the complex extraction method, its performance for the extraction of lower-purity EMP was further explored. Phenol is the most common phenolic compound in the industry and is also a byproduct in the production process of many phenolic compounds. Meanwhile, phenol has a benzene ring and a hydroxyl group, which is similar to the molecular structure of EMP. Therefore, phenol was added to EMP as an impurity to investigate the effect of the complex extraction method on the purification of EMP. First, the initial purity of EMP was fixed at 80, 85, 90, 95, and 98%, (n/n, mole fraction) by adding EMP into phenol. As shown in Figure 9b, the EMP purity ranged from 99.62 to 99.77%, suggesting that this highly efficient extraction method could achieve an ideal extraction effect for the mixture of EMP and phenol.

Figure 8. Coordination reaction mechanism between Ca$^{2+}$ and EMP.
in the complexation mode to generate Ca(EPO)[EPO]. In the third stage, another coordination reaction occurred, in which 2 moles of EMP were further combined with Ca(EPO)[EPO]. The complex sites were located in the benzene ring hydrogen atoms H<sub>a</sub> and H<sub>c</sub>, generating the final product Ca(EPO)[EPO][EPH]<sub>2</sub>. The separation and purification method proposed in this study can achieve high-purity EMP through simple operation steps. This purification method could open up a new route for fine chemical industries.

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**Notes**

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**ABBREVIATIONS**

EMP, 4-ethyl-2-methoxyphenol; [EPH], EMP molecule with coordination bond at hydrogen atom of its aromatic ring; (EPO), EMP with ionic bond; EMP-Na, the reaction product of EMP and Na<sup>+</sup>; [EP O], EMP phenolate ion with coordination bond at oxygen atom of its hydroxyl group; FTIR, Fourier transform infrared spectrometer; GC-FIR, gas chromatography flame ionization detector; GC−MS, gas chromatography−mass spectrometry; ICP-OES, inductively coupled plasma optical emission spectrometer; LP200, liquid product collected when Prod-R4 decomposed at 200 °C; LP400, liquid product collected when Prod-R4 decomposed at 400 °C; NMR, nuclear magnetic resonance; Prod-R4, the final product of EMP reaction with Ca<sup>2+</sup> when EMP was excessive; Prod-S1, the first stage in the reaction of EMP and Ca<sup>2+</sup>; Prod-S2, the second stage in the reaction of EMP and Ca<sup>2+</sup>; Prod-S3, the third stage in the reaction of EMP and Ca<sup>2+</sup>; R value, the molar ratio of EMP and Ca<sup>2+</sup>; TGA, thermogravimetric analysis; TR200, solid product collected when Prod-R4 decomposed at 200 °C; TR400, solid product collected when TR200 decomposed at 400 °C

![Figure 9](image-url). (a) Standard curve of EMP. (b) Effect of EMP concentrations in phenol on EMP purity. (c) Effect of EMP concentration in the solution mixing 3.2 mmol phenol and 10 mL ethanol on EMP purity. (d) Effect of ethanol content on EMP purity in the solution mixing 3.2 mmol phenol and 12.8 mmol EMP.
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