Microwave-Assisted Synthesis of trans-Cinnamic Acid for Highly Efficient Removal of Copper from Aqueous Solution

Nancy E. Dávila-Guzmán,† Yhoana B. Medina-Almaguer, † Miguel A. Reyes-González, † Margarita Loredo-Cancino, § Sandra Pioquinto-García, † David A. De Haro-Del Río, † Marco A. Garza-Navarro, ‡,§ and Eugenio Hernández-Fernández*†

Universidad Autónoma de Nuevo León, †Facultad de Ciencias Químicas and ‡Facultad de Ingeniería Mecánica y Eléctrica, San Nicolás de los Garza, 66455 Nuevo León, Mexico
§Universidad Autónoma de Nuevo León, Centro de Innovación y Desarrollo en Ingeniería y Tecnología, Apodaca, 66600 Nuevo León, Mexico

ABSTRACT: trans-Cinnamic acid was synthesized under microwave irradiation, and it was used for the removal of copper, a toxic metal found in industrial wastewater, from synthetic polluted aqueous solutions. Copper removal is more favorable at pH 5 and was enhanced by increasing the copper initial concentration, reaching a maximum uptake capacity of 389.5 mg/g, which is higher than those reported in the literature. Temperature exhibited a negligible effect on the removal of copper by trans-cinnamic acid. The isotherm equilibrium uptake data were found to be described by the Langmuir model. In addition, the study of the removal kinetics shows that the uptake of copper by trans-cinnamic acid follows pseudo-first order kinetics, and equilibrium is attained at approximately 30 min. Based on the X-ray photoelectron spectroscopy, X-ray diffraction, scanning transmission electron microscopy, and Fourier-transform infrared spectroscopy studies, a copper–cinnamic acid complex [Cu(CA)₂] is formed during the removal process. The reusability of this coordination compound was investigated using HCl, HNO₃, and NaOH 0.1 M as desorption eluents; HCl was capable of completely desorbing copper from [Cu(CA)₂], and trans-cinnamic acid was recovered as the trans-isomer. Alternatively, the [Cu(CA)₂] was used to remove octamethylcycloptetrasiloxane from gaseous streams for biogas purification, obtaining an adsorption capacity of 3.37 mg/g. These promising results demonstrate the feasibility of copper removal by trans-cinnamic acid because of its high uptake capacity and potential reusability.

INTRODUCTION

Nowadays, removal of heavy metals from wastewater is a significant environmental concern. Heavy metals have been discharged into water bodies because of the rapid growth of industries such as metal-plating facilities, mining operations, fertilizers, batteries, tanneries, pulp and paper mills, and pesticide manufacturers. Not only are heavy metals non-degradable and toxic even at very low concentrations but they will also form complexes with natural organic matter and will be bio-accumulated in animals, plants, and the human body, causing serious diseases and disorders. According to the United States Environmental Protection Agency (USEPA), copper is one of the most widespread heavy metals in the environment. Therefore, the treatment of heavy metal containing wastewater is required prior to its discharge. The methods that have been commonly used to remove toxic metals from wastewater are coagulation/precipitation, ion exchange, liquid–liquid extraction, cementation, electro-dialysis, adsorption, and membrane separation. To select a specific treatment method, several parameters should be considered, such as the operation cost, environmental impact, initial concentration of the copper ions, and pH values, among others.

Recently, researchers have been interested in new materials that are easily synthesized, exhibit selectivity for heavy metals, and that can be used in a wide range of physicochemical conditions. trans-Cinnamic acid (3-phenyl-2-propenoic acid) derivatives compose a relatively large family of organic acids...
isomers conventionally synthesized by the Perkin reaction and the Knoevenagel condensation,11,12 or by the environmentally friendly methods using ultrasound and microwave irradiation through the Knoevenagel condensation.13,14,15 Besides, the trans-cinnamic acid possesses antibacterial, antifungal, and parasite fighting abilities,15 and it is used in the production of flavors, dyes, and pharmaceuticals, as well as in the production of its methyl, ethyl, and benzyl esters, which are perfume components. Additionally, trans-cinnamic acid is a precursor to the sweetener aspartame.16 In wine, trans-cinnamic acid and its derivatives join benzoic acid derivatives and flavonoids in creating pigments and tannin agents that give each harvest its characteristic bouquet and color.17 Several compounds of trans-cinnamic acid with copper have been prepared in aqueous solution,18,19 thus, this material has demonstrated affinity for heavy metals.

In addition to the affinity for the solute of interest, it is desirable that the material be easily regenerated and/or reused. Chemical regeneration is usually recommended because it allows the possibility to recover valuable solutes that can be reused in adsorption/desorption cycles. On the other hand, spent materials can be recycled as raw materials for ceramic,20 catalyst21 and fertilizer22 production, or as an adsorbent for chemical regeneration is usually recommended because it allows the possibility to recover valuable solutes that can be reused in adsorption/desorption cycles. On the other hand, spent materials can be recycled as raw materials for ceramic,23 catalyst24 and fertilizer25 production, or as an adsorbent for purification processes. For instance, adsorbent materials have been used for the purification of biogas to remove siloxane compounds that causes deposits on the combustion surfaces or gas processing equipment.26

In the present work, trans-cinnamic acid was synthesized under microwave irradiation and it was used as a new material that exhibits a remarkable uptake capacity of copper from aqueous solution. trans-Cinnamic acid was characterized by X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), Fourier-transform infrared spectroscopy (FTIR), and proton and carbon-13 nuclear magnetic resonance spectroscopy (1H NMR and 13C NMR). The effect of pH, initial concentrations, and temperature on the uptake capacity was studied in batch experiments. Furthermore, the uptake equilibrium and kinetics were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetrasiloxane (D4) in gaseous streams. Finally, the uptake and desorption mechanisms were also comprehensively investigated, as well as the reusability of the spent material for the removal of octamethylcyclotetra...
increases too, causing an increase on the affinity for the copper ions (Cu$^{2+}$). A further pH augmentation of aqueous solution could lead to copper precipitation. In addition, the zeta potential of CA was determined to investigate the surface potential in aqueous solutions with pH values between 3 and 6 (Figure 3). Herein, it is observed that Z-potential varies from 1.4 to $-9.38$ mV as pH approaches to 6. It is also noticed that the isoelectric point is about at pH = 3.3, which means that above this point the CA surface is negatively charged. This result is congruent with that observed from removal experiments, where the highest uptake capacity was obtained at pH 5 corresponding to a higher negative surface charge compared to the experiments carried out at pH 2, 3, and 4, indicating that the ability of CA to remove Cu$^{2+}$ depends on its deprotonation.

**Effect of Temperature and Initial Concentration on Uptake Capacity.** The effect of the temperature on the uptake capacity of trans-cinnamic acid was evaluated from 25 to 60 °C (Figure 4). The results showed that the uptake capacity was not affected by the temperature.

Additionally, the effect of the initial copper concentration on the uptake capacity was evaluated from 0.1 to 11 mmol/L. As shown in Figure 5, the uptake capacity increases with the augmentation of the initial copper concentration. The increase of the initial copper concentration leads to a higher driving force for the copper removal as well as a major occupancy of the active sites. On the other hand, an analysis of the total organic compounds before and after copper removal was carried out to determine the amount of CA that remains in the solution after copper removal. The results indicated an increase of the total organic content from 1.41 to 90.76 mg/L. These results are an indication that less than 9% of the trans-cinnamic acid remain in the solution after the copper uptake.

**Equilibrium Uptake Capacity.** The relationship of uptake capacity of trans-cinnamic acid and copper concentration at equilibrium is depicted in Figure 6. As the equilibrium concentration rises, the equilibrium uptake capacity also
increases until a plateau is reached. The isotherm form is convex which refers to a favorable removal. Langmuir and Freundlich models were used to fit the equilibrium data, where the Langmuir isotherm model fitted the experimental data better than the Freundlich isotherm model according to the higher value of the determination coefficient $R^2$ (Table 1). For comparison purposes, maximum uptake capacity ($q_m$) of copper onto trans-cinnamic acid is shown along with the maximum uptake capacity of various adsorbents reported in the literature, showing that cinnamic acid has a better removal capacity (389.5 mg/g) than other adsorbents previously reported in the literature (Table 2).

### Table 1. Isotherm Model Parameters for the Copper Removal by trans-Cinnamic Acid

| model          | parameters | $R^2$ |
|---------------|------------|-------|
| Langmuir      | $b=0.218$  |       |
|               | $q_m (mg/g)=389.5$ | 0.97  |
| Freundlich    | $K_F (mg1^{-1/g} L^{1/2})=103.04$ | 0.89  |
|               | $n=3.90$   |       |

### Table 2. Maximum Uptake Capacity of Various Materials of Copper Ions

| adsorbent                  | pH | adsorbent dose (g/L) | $q_m (mg/g)$ | references                        |
|----------------------------|----|----------------------|--------------|----------------------------------|
| granular-activated carbon  | 4.5| 100                  | 7.03         | Almohammadi and Mirzae 30        |
| treated laterite           | 5.0| 10                   | 7.25         | Rani et al. 31                   |
| multi-walled carbon        | 7.0| 0.8                  | 12.34        | Mobasherpour et al. 32          |
| nanotubes                  |    |                      |              |                                  |
| barley straw ash           | 6.5| 5.0                  | 17.89        | Arshadi et al. 33                |
| pomegranate peel           | 5.8| 2.5                  | 30.12        | Ben-Ali et al. 34                |
| $XG_gP(AMPS)$ hydrogel     | 5.2| 4.0                  | 39.06        | Jalali et al. 35                 |
| grape-based activated      | 5.0| 2.0                  | 43.47        | Demiral and Gungör 36            |
| carbon                    |    |                      |              |                                  |
| benzidine-based adsorbent  | 4.5| 1.5                  | 45.45        | Taskin et al. 37                 |
| CB                         | 6.0| 5.0                  | 46.95        | Mohammed and Samaka 38          |
| MIA                       | 5.0| 2.0                  | 48.78        | Thanh et al. 39                  |
| GB10-activated carbon      | 9.56| 0.8                | 66.79        | Mondal and Majumder 30          |
| geopolymer                 | 6.0| 2.0                  | 83.13        | Al-Harashbeh et al. 41          |
| $Gg-clP(AAm-co-AN)$ hydrogel| 5.0| 0.3                  | 203.7        | Mittal et al. 42                 |
| palygorskite               | 5.0| 1.0                  | 210.64       | Wang et al. 43                   |
| carbon foam                | 5.0| 0.6                  | 212.00       | Lee et al. 44                    |
| MCa@Mg/Fe-LDHs carbon     | 6.3| 0.25                 | 338.17       | Xie et al. 45                    |
| spheres trans-cinnamic acid| 5.0| 1.0                  | 389.50       | this work                        |

### Figure 7. Copper removal kinetics of trans-cinnamic acid. Conditions: 25 °C, 400 min$^{-1}$ stirring speed, 1 g/L, initial copper concentration 1 mM. Solid line represents PS-1 model and dashed line represents PS-2.

The removal capacity at equilibrium predicted by the PS-1 was similar to the experimental data; meanwhile, the value predicted by the PS-2 was 45% higher than the experimental value. Some satisfactory fits of removal kinetics data with the PS-1 model have been reported elsewhere. 35,47,48

### Uptake Mechanism of Copper.

The XRD patterns of trans-cinnamic acid and [Cu(CA)$_2$] are presented in Figure 8. The pattern of synthesized trans-cinnamic acid can be related to the presence of the (alpha) polymorph of ortho-ethoxy-trans-cinnamic acid 49 because of the highest peak in 26° and a

### Table 3. Parameters and Determination Coefficient of PS-1 and PS-2 Kinetics Models

| pseudo-first order kinetic model | pseudo-second order kinetic model |
|---------------------------------|----------------------------------|
|                                |                                |
| $K_1 (min^{-1})$               | $q_e (mg/g)$ | $R^2$ | $K_2 (g mg^{-1} min^{-1})$ | $q_e (mg/g)$ | $R^2$ |
| 0.1133                          | 58                     | 0.965                        | 9.24 × 10$^{-4}$ | 84.47 | 0.945 |

### Removal Kinetics of Copper Ions by trans-Cinnamic Acid.

Removal kinetics provides valuable information about the performance of a material in the process and offers insights about the possible uptake mechanisms. For instance, the residence time, which is determined by the solute uptake rate, is relevant for pilot-scale applications. 46 Thus, the evolution of the uptake capacity through time was determined and it is shown in Figure 7, where it can be noticed that the equilibrium is reached after 30 min of contact time. Two common kinetic models, pseudo-first order (PS-1), and pseudo-second order (PS-2) kinetic models, were used to predict the removal kinetics of copper onto trans-cinnamic acid. The PS-1 kinetic model showed a higher determination coefficient for fitting the
smaller peak that appeared in 21°. It is noticeable that after the removal process, any crystallographic evidence of the trans-cinnamic acid in the \([\text{Cu(CA)}_2]\) pattern cannot be seen, suggesting the formation of a completely different structure.

In addition, the thermal stability of trans-cinnamic acid before and after copper removal was evaluated by TGA. trans-Cinnamic acid is thermally stable at temperatures lower than 105 °C, and then a progressive weight loss is observed up to 177 °C where trans-cinnamic acid loses 97% of its initial weight. After copper removal, an increase of the thermal stability of \([\text{Cu(CA)}_2]\) was observed because only a weight loss of 20% was registered at 300 °C.

FTIR was used to identify differences between trans-cinnamic acid before and after the removal process. The spectra obtained are shown in Figure 9, where the disappearance of the stretch −OH is found at 2645−2627 cm⁻¹. Also, the other bands shifted to lower wavenumbers in the spectrum of trans-cinnamic acid after the copper removal \([\text{Cu(CA)}_2]\) (Table 4). The influence of copper as an electron-rich atom causes an increase in the density charge around the double bond in the carboxylate, so in the black spectra, the bands −C==C− are intensified. Approximately between 1300 and 1230 cm⁻¹, another case of vibration −C==C− of the aromatic group is observed, this time, the bands are at similar wavenumbers, however, the intensity decreased. This decrease is considered as evidence of the increase in the perturbation of the aromatic system in the ring, which is caused by the effect of the double bond in the carboxylate.

In order to get further insight regarding Cu removal by the functional groups of trans-cinnamic acid, we proceed to measure C 1s, O 1s, and Cu 2p XPS spectra from trans-cinnamic acid, as well as \([\text{Cu(CA)}_2]\). Figure 10 shows C 1s and O 1s spectra recorded from trans-cinnamic acid, where three peaks can be recognized at 284.6, 285.7, and 288.9 eV, attributed to C in C−C, C−O, and O−C=O, respectively (Figure 10a); along with two peaks at 532.5 and 533.6 eV, related to O in C−O and O−C==O, respectively (Figure 10b).

Figure 11 displays C 1s, O 1s, and Cu 2p spectra recorded from \([\text{Cu(CA)}_2]\). Likewise, the C 1s spectrum shows peaks related to C−C, C−O, and O−C==O, although they depict a change in their binding energies, which is more obvious for the emission associated with O−C==O (∆BE = 1 eV) (Figure 11a). Moreover, the O 1s spectrum shows a remarkable shift in the binding energy related to photo-emission from O−C==O (∆BE = 0.9 eV) (Figure 11b). It is also observed that the Cu 2p spectrum, where it is possible to identify two prominent peaks at 954.4 and 934.3 eV, corresponds to photo-electrons emitted from 2p3/2 and 2p1/2 core levels, respectively; those related to their satellite at 962.8 and 943.7 eV correspond to shake-up-like of Cu²⁺ at higher binding energies than the Cu 2p3/2 and Cu 2p1/2 edge, respectively (Figure 11c)50,51 Accordingly, shifts in the binding energy associated to C and O at O−C==O and the presence of shake up satellites at Cu 2p spectra confirms the efficient removal of Cu²⁺ cations from carboxylic moieties of trans-cinnamic acid molecules.52,53

Moreover, there is a remarkable change in the morphological features of CA particles before and after copper removal (Figure 12). This change involves a turn from an acicular-like morphology to the formation of square plates of CA.

Based on these results, an uptake mechanism for the formation of the coordination compound \([\text{Cu(CA)}_2]\) is proposed. This is carried out, from 2 mol of trans-cinnamic acid with NaOH to form the corresponding carboxylate and the subsequent nucleophilic substitution with copper nitrate hemi(pentahydrate) by double substitution of the oxygen atom with the negative charge, and then with the interaction of one of the pairs of free electrons of the second oxygen toward the metal to generate the copper complex \([\text{Cu(CA)}_2]\) (Scheme 2).

![Figure 9. IR spectrum of trans-cinnamic acid (a) before removal and (b) after removal.](image)

![Figure 10. (a) C 1s and (b) O 1s spectra recorded by XPS from trans-cinnamic acid.](image)

**Table 4. Observed Infrared Band Positions for trans-Cinnamic Acid after and before the Removal Process**

|      | before (cm⁻¹) | band assignment | after (cm⁻¹) | band assignment |
|------|--------------|----------------|--------------|----------------|
| 2845 | O−H         |                | 1641         | C==O           |
| 1670 | C==O        |                | 1552         | C−C            |
| 1627 | C−C         |                | 1279         | C−C            |
| 1314 | =C−H        |                | 860          | =C−H           |

 DOI: 10.1021/acsomega.9b02720
ACS Omega 2020, 5, 317–326
This structure is in agreement with the one proposed by Drew et al.\textsuperscript{54} and Kumar et al.,\textsuperscript{55} where dimeric copper complexes using cinnamate were prepared. On the other hand, physisorption analysis was carried out to estimate the surface area of [Cu(CA)\textsubscript{2}], where a value of 18.06 m\textsuperscript{2}/g was obtained with a significant fraction of the pore volume corresponding to mesopores (89.5%).

**Desorption and Reusability.** Spent materials after removal processes are usually subjected to regeneration to keep the process economic. In this sense, several eluents have been employed to regenerate spent materials, such as acid and basic solutions.\textsuperscript{56} The desorption of copper ions from [Cu(CA)\textsubscript{2}] was evaluated using HCl, HNO\textsubscript{3}, and NaOH 0.1 M as eluents. Figure 13 shows that the copper concentration desorbed from [Cu(CA)\textsubscript{2}] and the desorption percentage. Copper desorption was found to follow the order HCl > HNO\textsubscript{3} > NaOH. The best results were presented under acidic desorption conditions because when using NaOH there was practically no desorption process, on the other hand when comparing the two acids it is observed that the greater the pK\textsubscript{a}, the better the release of the metal ion, this can be explained because of the strong acidic nature that HCl has with a pK\textsubscript{a} of −8.0 compared to HNO\textsubscript{3} that has a pK\textsubscript{a} of −1.3.

**Scheme 2. Proposed Mechanism for the Formation of the Coordination Compound [Cu(CA)\textsubscript{2}]**

![Scheme 2](https://example.com/scheme2.png)
With respect to the desorption mechanism, the protonation of one of the oxygen atoms of the \([\text{Cu(CA)}_2]\) is first carried out and subsequently the nucleophilic attack by the chloride anion of HCl on the copper atom, promoting the rupture of the covalent bond, and recovering the electron pair of the originally protonated oxygen atom. This new species formed, presents an equilibrium with the carboxylic acid of trans-cinnamic acid and with the species of partial coordination with copper metal, finally this same process occurs to generate a second molecule of trans-cinnamic acid in addition to copper chloride (CuCl2) as final products of the process (Scheme 3).

The solid obtained after the desorption process by \(^1\text{H}\) NMR was analyzed, and it showed four signal groups, the first one appeared at 6.5 ppm like a doublet with \(J = 16.0\) Hz, the second one appeared in the region from 7.3 to 7.4 ppm, which was assigned for three aromatic hydrogens, at 7.6 ppm was possible to observe another doublet with \(J = 16.0\) Hz, and finally multiple signals were observed from 7.65 to 7.70 ppm, which were assigned for two aromatic hydrogens. The \(J = 16.0\) Hz value indicates that the trans-cinnamic acid was recovered like the trans-isomer. Further, the analysis by high-resolution mass spectroscopy showed an \((M + H) m/z\) 149.05891 value, which is in agreement with the calculated exact mass for the trans-cinnamic acid \((M + H) m/z\) 149.06025.

Finally, the reusability of \([\text{Cu(CA)}_2]\) in the removal of octamethylcyclotetrasiloxane (D4) from gaseous streams was evaluated. D4 is a common siloxane in biogas streams which causes severe damages to the engine parts of combustion motors when the biogas is used as the biofuel. Accordingly, preliminary adsorption tests were carried out using \([\text{Cu(CA)}_2]\), where an adsorption capacity of 3.37 mg/g was obtained when the initial concentration of D4 was 400 mg/Nm\(^3\). This result herald a potential application for \([\text{Cu(CA)}_2]\) in biogas purification. In fact, experiments for the simultaneous removal of several siloxanes using \([\text{Cu(CA)}_2]\) are in progress.

### CONCLUSIONS

In this work, the properties of trans-cinnamic acid for the removal of copper from aqueous solution have been studied for the first time. The removal process was examined under different conditions including pH, contact time, initial copper concentrations, and temperature, and the maximum uptake capacity obtained was 389.5 mg/g at pH 5, 25 °C, and 400 min\(^{-1}\). The kinetic data of the copper removal were adequately predicted with the pseudo-first-order kinetic model, and the equilibrium state was obtained after 30 min. Moreover, Langmuir and Freundlich isotherms were employed to represent the equilibrium isotherm, and the Langmuir model fitted the experimental data with better determination coefficient. Characterization of \([\text{Cu(CA)}_2]\) revealed that a mesoporous coordination compound is formed as a result of the removal of copper by trans-cinnamic acid. Experiments show that copper can be completely desorbed from \([\text{Cu(CA)}_2]\) using HCl as the eluent, and the CA was recovered as its trans-isomer. Additionally, \([\text{Cu(CA)}_2]\) might be used to adsorb D4 because an adsorption capacity of 3.37 mg/g was achieved in preliminary experiments at 400 mg/Nm\(^3\) D4 initial concentration. These results suggest that trans-cinnamic acid synthesized under microwave irradiation could be a promising material for the removal of copper from wastewater.

### EXPERIMENTAL SECTION

**Procedure for the Synthesis of trans-Cinnamic Acid.**

All commercial materials were used as received unless otherwise noted. In a round bottom flask with a reflux condenser, malonic acid (1 equiv), triethylamine (1 equiv), benzaldehyde (1 equiv), piperidine (0.2 equiv), and toluene (20 mL) were mixed. The flask was positioned in the irradiation cavity and the mixture was heated with stirring under microwave irradiation at 110 °C and held for 60 min.
Then, the flask was cooled to room temperature and the residue was dissolved in methanol and then concentrated under reduced pressure. The crude was cooled at room temperature and 10 mL of 5% sodium bicarbonate was added slowly, next it was stirred for 20 min. The mixture was washed with ethyl acetate and aqueous layer was collected, cooled at 0 °C, and then the pH was adjusted with HCl until pH 4. The solid was filtered and washed with ether and hexanes. (68%) It was obtained as a white solid, mp 130–131 °C; 1H NMR (400 MHz, DMSO-d6): δ 6.53 (d, J = 16.0 Hz, 1H), 7.30–7.43 (m, 3H), 7.59 (d, J = 16.0 Hz, 1H), 7.67–7.69 (m, 2H), 13C NMR (100 MHz, DMSO-d6): δ 119.2, 128.2, 128.9, 130.2, 134.2, 143.9, 167.6 (C=O).27

Characterization. In order to characterize the structure of the material, the XRD patterns were collected using a Siemens D5000 diffractometer with Cu Kα radiation (λ = 1.5406 Å) operated at 35 kV and 25 mA in the 2θ range of 2–50° at 0.02°/min with a step time of 4 s. FTIR was employed to allow the identification of chemical functional groups onto the materials surface where a PerkinElmer instrument (spectrum one model) from 500 to 4000 cm⁻¹ was used.

Melting point was registered using an Electrothermal Mel-Temp apparatus. Thin-layer chromatography was performed on pre-coated sheets of silica gel 60 F254 (E. Merck). The spectra were obtained in the DMSO-d6 solution. 1H NMR data were acquired on an Inova 300 MHz and on a Bruker 400 MHz NMR spectrometer. Chemical shifts (δ) are reported in parts per million and coupling constants were expressed as (J) and reported in Hertz (Hz). 13C NMR data were acquired on a Bruker NMR spectrometer at 100 MHz. Mass spectral data were obtained using ESI techniques (Agilent, 6210 TOF). Reactions carried out with stirring under microwave irradiation in open-vessels were all performed with a CEM Discover.

XPS was performed at room temperature for measuring C 1s, O 1s, and Cu 2p spectra from the sample of trans-cinnamic acid loaded with Cu²⁺ ions [Cu(CA)₂]²⁻, as well as pure trans-cinnamic acid in a Thermo-Scientific, K-Alpha spectrometer with monochromatized Al Kα radiation (E = 1.5 keV), X-ray spot of 400 μm and flood gun for charge compensation. Peaks of the recorded XPS spectra were deconvoluted and fitted using a Gaussian approach and nonlinear baseline. The specific surface area was obtained using the N₂ physisorption analysis into contact with 100 mg of [Cu(CA)₂] during 24 h until the capacity (mg1/g) was obtained by a mass balance as follows

\[ q = (C_o - C)V/m \]  

where \( q \) is the uptake capacity at the time \( t \) (mg/g), \( C_o \) is the initial copper concentration (mg/L), \( C \) is the copper concentration at the time \( t \) (mg/L), \( V \) is the volume of the metal solution (L), and \( m \) is the mass of the CA (mg).

Desorption Experiments. Desorption experiments were carried out using HCl, HNO₃, and NaOH 0.1 M as eluents. First, the removal of copper by trans-cinnamic acid was conducted in 1 L flasks at room temperature, 1 g of CA per liter of the solution, 400 min stirring speed, and pH 5. After the equilibrium was reached (40 min), the spent CA ([Cu(CA)₂]) was separated from the copper solution by filtration. Then, 100 mg of [Cu(CA)₂] was placed in 250 mL flask containing 100 mL of HCl, HNO₃, or NaOH 0.1 M and allowed to equilibrate for 24 h in an orbital shaker at 200 rpm. After, aliquots were taken for further copper concentration analysis by means of atomic absorption spectrometry.

Reusability Experiments. The [Cu(CA)₂] was subjected to an adsorption test for the removal of octamethylcyclotrisiloxane (D4) from gaseous streams. The adsorption experiment was carried out using a mass/volume ratio of 1 g/L, D4 initial concentration of 400 mg/Nm³, 25 °C, 1 atm. First, a volume of D4 (analytical grade, 98% of purity, provided by Sigma-Aldrich) was volatilized into a 1.48 L glass flask to obtain a D4 gaseous solution. Then, the mixture was diluted to obtain a concentration of 400 mg/Nm³. This solution was put into contact with 100 mg of [Cu(CA)₂] during 24 h until the equilibrium was reached. Several aliquots were taken and analyzed by a Nexis GC 2030 gas chromatograph with a flame ionization detector to monitor the siloxane concentration. The column used was an SH-Rxi-5ms SHIMADZU (15.0 m × 0.25 mm inner diameter × 0.25 μm film thickness). The temperature of the injector port, oven, and detector were set at 150, 110, and 250 °C, respectively. Helium was used as the carrier gas at a constant flow rate of 1.50 mL/min and pressure of 12.08 psi. Gas samples of 500 μL were injected to the GC. The duration of the method was 1.4 min. Finally, the uptake capacity was obtained by mass balance following eq 1.

Isotherm Models. The equilibrium data were fitted by using the well-known Langmuir and Freundlich isotherm models. Equation 2 refers to the Langmuir isotherm model where \( q_e \) and \( b \) are the Langmuir parameters, maximum uptake capacity (mg/g) and equilibrium constant (L/mg), respectively.

\[ q_e = q_m bC_e / (1 + bC_e) \]  

The Freundlich parameters, \( K_F \) and \( n \), are related to uptake capacity (mg⁻¹/g L¹/²) and intensity (dimensionless), respectively.

DOI: 10.1021/acsomega.9b02720

ACS Omega 2020, 3, 317–326
The parameters were obtained from nonlinear regression using the generalized reduced gradient (GRG2) algorithm, where the coefficient of determination, $R^2$, were maximized.

**Uptake Kinetics Models.** The uptake kinetics data were analyzed by using the pseudo-first order (PS-1) kinetic model and the pseudo-second order (PS-2) kinetic model. The most popular form used for the PS-1 rate equation is

$$q = q_\infty (1 - \exp(-kt))$$

where $q$ and $q_\infty$ are the amounts of copper uptake per gram of trans-cinnamic acid (mg/g) at time $t$ (min) and at equilibrium, respectively, and $k_1$ (min$^{-1}$) is the rate constant of the PS-1 model.

The PS-2 rate equation is

$$q = \frac{q_\infty k_t}{1 + q_\infty k_t t}$$

where $k_2$ (g/mg min) is the rate constant of the PS-2 model. The PS-1 and PS-2 parameters were obtained from nonlinear regression the generalized reduced gradient (GRG2) algorithm by maximizing the coefficient of determination $R^2$ similarly to equilibrium data.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: eugenio.hernandezfr@uanl.edu.mx. Phone: +52-81 83 29 40 00 ext. 6293. Fax: +52-81 83 76 29 29.*

**ORCID**

Nancy E. Dávila-Guzmán: 0000-0002-9362-4458

Eugenio Hernández-Fernández: 0000-0001-6769-9125

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors thank CONACYT of Mexico for the financial support via project CB-2015/256359, and Y.B.M.-A. for the participation on the preliminary removal experiments.

**REFERENCES**

(1) Davila-Guzman, N. E.; Cerino-Cordova, F. J.; Loredo-Cancino, M.; Rangel-Mendez, J. R.; Gomez-Gonzalez, R.; Soto-Regalado, E. Studies of Adsorption of Heavy Metals onto Spent Coffee Ground: Equilibrium, Regeneration, and Dynamic Performance in a Fixed-Bed Column. *Int. J. Chem. Eng.* 2016, 1.

(2) Selvi, A.; Rajasekar, A.; Theerthagiri, J.; Ananthaselvam, A.; Sathishkumar, K.; Madhavan, J.; Rahman, P. K. S. M. Integrated Flocculation Methods from Aqueous Solutions. *Front. Environ. Sci.* 2019, 7, 66.

(3) Johnson, P. D.; Girinathnannair, P.; Ohlinger, K. N.; Ritchie, S.; Teuber, L.; Kirby, J. Enhanced Removal of Heavy Metals in Primary Treatment Using Coagulation and Flocculation. *Water Environ. Res.* 2008, 80, 472–479.

(4) Pang, F. M.; Teng, S. P.; Teng, T. T.; Omar, A. K. M. Heavy Metals Removal by Hydroxide Precipitation and Coagulation-Flocculation Methods from Aqueous Solutions. *Water Qual. Res. J.* 2009, 44, 174–182.

(5) Edelbali, S.; Pehlivan, E. Evaluation of chelate and cation exchange resins to remove copper ions. *Powder Technol.* 2016, 301, 520–525.

(6) Meterfi, S.; Meniai, A.-H.; Chikhi, M. Elimination of Cu(II) from Aqueous Solutions by Liquid-Liquid Extraction. Test of Sodium Diethylthiocarbamate (SDDT) as an Extracting Agent. *Energy Procedia* 2012, 18, 1165–1174.

(7) Nassef, E. Removal of Copper From Wastewater By Cementation From Simulated Leach Liquors. *J. Chem. Eng. Process Technol.* 2015, 06, 1–6.

(8) Dong, Y.; Liu, J.; Sui, M.; Qu, Y.; Ambuchi, J. J.; Wang, H.; Feng, Y. A combined microbial desalination cell and electrodialysis system for copper-containing wastewater treatment and high-salinity wastewater desalination. *J. Hazard. Mater.* 2017, 321, 307–315.

(9) Davila-Guzman, N. E.; Cerino-Cordova, F. J.; Soto-Regalado, E.; Loredo-Cancino, M.; Loredo-Medrano, J. A.; Garcisè-Redes, R. B. A mass transfer model for the fixed-bed adsorption of ferulic acid onto a polymeric resin: axial dispersion and intraparticle diffusion. *Environ. Technol.* 2016, 37, 1914–1922.

(10) Ferrer, O.; Gibert, O.; Cortina, J. L. Reverse osmosis membrane composition, structure and performance modification by bisulphite, iron(III), bromide and chloride exposure. *Water Res.* 2016, 103, 256–263.

(11) Chavan, H. V.; Bandgar, B. P. Aqueous Extract of *Accacia concinna* Pods: An Efficient Surfactant Type Catalyst for Synthesis of 3- Carboxycoumarins and Cinnamic Acids via Knoevenagel Condensation. *ACS Sustainable Chem. Eng.* 2013, 1, 929–936.

(12) Rabbani, G. A Concise Introduction to Perkin Reaction. *Org. Chem.* 2018, 07, 2.

(13) McNulty, J.; Steele, J. A.; Wolf, S. The ultrason promted Knoevenagel condensation of aromatic aldehydes. *Tetrahedron Lett.* 1998, 39, 8013–8016.

(14) Fioritto, S.; Taddeo, V. A.; Genovese, S.; Epifano, F. A green chemical synthesis of coumarin-3-carboxylic and cinnamic acids using crop-derived products and waste waters as solvents. *Tetrahedron Lett.* 2016, 57, 4795–4798.

(15) Gupta, M.; Wakhloob, B. P. Tetra-Butylammoniumbromide mediated Knoevenagel condensation in water: Synthesis of cinnamic acids. *Arkivoc* 2007, 2007, 94–98.

(16) Mogliaiah, K.; Reddy, G. R. Microwave-Assisted Solvent-Free Synthesis of trans-Cinnamic Acids Using Lithium Chloride as Catalyst. *Synth. Commun.* 2004, 34, 205–210.

(17) Ortega-Villareal, A. S.; Hernández-Fernández, E.; Jensen, C.; Valdivia-Berroeta, G. A.; Garrard, S.; López, I.; Smith, S. J.; Christensen, K. A.; Reyes-Gonzalez, M. A.; Michaelis, D. J. Synthesis and characterization of ethyl benzotriazolyl acrylate-based D-R-A fluorophores for live cell-based imaging applications. *RSC Adv.* 2019, 9, 8759–8767.

(18) Lee, J.; Lee, D. G.; Park, J. Y.; Chae, S.; Lee, S.; Lee, J.; Lee, D. G.; Park, J. Y.; Chae, S.; Lee, S. Analysis of the trans-Cinnamic Acid Content in Cinnamonom spp. and Commercial Cinnamon Powder Using HPLC. *J. Agric. Chem. Environ.* 2015, 04, 102–108.

(19) American Chemical Society. *trans-Cinnamic Acid*. 2014. Available online: https://www.acs.org/content/acs/en/molecule-of-the-week/archive/1/trans-cinnamicacid.html (accessed May 14, 2019).

(20) Kalinowska, M.; Świslocka, R.; Lewandowski, W. The spectrosopic (FT-IR, FT-Raman and 1H, 13C NMR) and theoretical studies of cinnamic acid and alkali metal cinnamates. *J. Mol. Struct.* 2007, 834–836, 572–580.

(21) Allan, J. R.; Casson, B. R.; Gerrard, D. L.; Hoe, S. Thermal, spectral and magnetic studies of some compounds of cobalt (II), nickel (II) and copper (II) with cinnamic acid. *Thermochim. Acta* 1989, 154, 315–322.

(22) Cabras, M. A.; Zoroddu, M. A. Synthesis and magnetic characterization of some Cu(II) complexes of cinnamic acids. *Inorg. Chem.* 1986, 117, 5–7.

(23) Verbrinnen, B.; Block, C.; Van Caneheum, J.; Vandebeete, C. Recycling of spent adsorbents for oxyanions and heavy metal ions in the production of ceramics. *Waste Manag.* 2015, 45, 407–411.
magnetite Fe3O4 nanoparticles as a novel adsorbent for copper (II) removal: A case study on copper removal.

Characterization and adsorption capacity of raw pomegranate peel biomass adsorbent for copper removal. J. Hazard. Mater. 2016, 326, 238–245.

Qiu, H.; Lv, L.; Pan, B.-c.; Zhang, Q.-j.; Zhang, W.-m.; Zhang, Q.-x. Critical review in adsorption kinetic models. J. Zhejiang Univ., Sci. A 2009, 10, 716–724.

He, D.; Zhang, L.; Zhao, Y.; Mei, Y.; Chen, D.; He, S.; Luo, Y. Recycling Spent Cr Adsorbents as Catalyst for Eliminating Methylmercaptan. Environ. Sci. Technol. 2018, 52, 3669–3675.

Bhattacharjee, A.; Jana, B. B.; Mandal, S. K.; Bhakta, J.; Ghosh, D.; Lahiri, S. Nutrient Depoatration Efficiency of Selected Natural and Synthetic Adsorbents from Municipal Wastewater for Environmental and Economic Benefits. Res. J. Environ. Sci. 2018, 12, 234–246.

Shen, M.; Zhang, Y.; Hu, D.; Fan, J.; Zeng, G. A review on removal of siloxanes from biogas: with a special focus on volatile methylsiloxanes. Environ. Sci. Pollut. Res. 2018, 25, 30847–30862.

Pawar, H. S.; Wagh, A. S.; Lali, A. M. Triethylamine: A potential N-base surrogate for pyridine in Knoevenagel condensation of aromatic aldehydes and malonic acid. New J. Chem. 2016, 40, 4962–4968.

Knight, A. W.; Tiggges, A. B.; Ilgen, A. G. Adsorption of copper (II) on mesoporous silica: the effect of nano-scale confinement. Geochim. Trans. 2018, 19, 13.

Nagai, A.; Michida, W.; Sakuragi, M.; Nishida, M.; Guan, G.; Abudula, A.; Kusakabe, K. International Journal of Biomass and Renewables; Universiti Teknologi Petronas, 2012, Vol. 7.

Almohammadi, S.; Mirzai, M. Removal of copper (II) from aqueous solutions by adsorption onto granular activated carbon in the presence of competitor ions. Adv. Environ. Technol. 2016, 8, 85–94.

Rani, K. S.; Srinivas, B.; GouraNaidu, K.; Ramesh, K. V. Removal of copper by adsorption on treated laterite. Mater. Today: Proc. 2018, 5, 463–469.

Mobasherpour, I.; Salahi, E.; Ebrahimi, M. Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto multi-walled carbon nanotubes. J. Saudi Chem. Soc. 2014, 18, 792–801.

Achar, M.; Amir, M. J.; Mousavi, S. Kinetic and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash. Water Resour. Ind. 2014, 6, 1–17.

Ben-Als, S.; Jaoali, I.; Souissi-Najar, S.; Ouederni, A. Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. J. Cleaner Prod. 2017, 142, 3809–3821.

Jalali, M. A.; Koohi, A. D.; Sheykhan, M. Experimental study of the removal of copper ions using hydrogels of xanthan, 2-acrylamido-2-methyl-1-propane sulfonic acid, montmorillonite: Kinetic and equilibrium study. Carbohydr. Polym. 2016, 142, 124–132.

Demiral, H.; Güngör, C. Adsorption of copper(II) from aqueous solutions on activated carbon prepared from grape bagasse. J. Cleaner Prod. 2016, 124, 103–113.

Taskin, O. S.; Kiskan, B.; Alku, A.; Balkis, N.; Yagci, Y. Copper(II) removal from the aqueous solution using microporous benzidine-based adsorbent material. J. Environ. Chem. Eng. 2016, 4, 899–907.

Mohammed, A. A.; Samaka, I. A. S. Bentonite coated with magnette Fe3O4 nanoparticles as a novel adsorbent for copper (II) ions removal from water/wastewater. Environ. Technol. Innov. 2018, 10, 162–174.

Thanh, D. N.; Novák, P.; Vejpravova, J.; Vu, H. N.; Lederer, J.; Munshi, T. Removal of copper and nickel from water using nanocomposite of magnetic hydroxyapatite nanorods. J. Magn. Magn. Mater. 2018, 456, 451–460.

Mondal, S.; Majumder, S. K. Honeycomb-like porous activated carbon foam derived from phenol resin. Chemosphere 2015, 130, 59–65.

Xie, Y.; Yuan, X.; Wu, Z.; Zeng, G.; Jiang, L.; Peng, X.; Li, H. Adsorption behavior and mechanism of Mg/Fe layered double hydroxide with Fe3O4-carbon spheres on the removal of Pb(II) and Cu(II). J. Colloid Interface Sci. 2019, 536, 440–455.

Qiu, H.; Lv, L.; Pan, B.-c.; Zhang, Q.-j.; Zhang, W.-m.; Zhang, Q.-x. Critical review in adsorption kinetic models. J. Zhejiang Univ., Sci. A 2009, 10, 716–724.

Letina, D.; Letshwemo, W. M. Investigating waste rock, tailings and slag as ash clinker as adsorbents for heavy metals: Batch and column studies. Phys. Chem. Earth, Parts A/B/C 2018, 105, 184–190.

Wang, J.; Zhao, Y.; Zhang, P.; Yang, L.; Xu, H. a.; Xi, G. Adsorption characteristics of a novel ceramsite for heavy metal removal from stormwater runoff. Chin. J. Chem. Eng. 2018, 26, 96–103.

Fernandes, M. A.; Levendis, D. C.; de Koning, C. B. Solvate polymorphs of ortho-ethoxy-trans-cinnamic acid: the crystal and molecular structures. Cryst. Eng. 2001, 4, 215–231.

Dong, H.; Edmondson, J. L.; Miller, R. L.; Chourasai, A. R. Chemical reactivity at Fe/CuO interface studied in situ by X-ray photoelectron spectroscopy. Vacuum 2014, 101, 27–32.

Marković, D.; Deeks, C.; Nunnery, T.; Radovanović, Ž.; Radoičić, M.; Šaponjić, Z.; Radetić, M. Antibacterial activity of Cu-based nanoparticles synthesized on the cotton fabrics modified with polycarboxylic acids. Carbohydr. Polym. 2018, 200, 173–182.

Zheng, J.-C.; Feng, H.-M.; Lam, M. H.-W.; Lam, P. K.-S.; Ding, Y.-W.; Yu, H.-Q. Removal of Cu(II) in aqueous media by biosorption using water hyacinth roots as a biosorbent material. J. Hazard. Mater. 2009, 171, 780–785.

Badruddoza, A. Z. M.; Tay, A. S. H.; Tan, P. V.; Hidayat, J.; Uddin, M. S. Carboxymethyl-β-cyclodextrin conjugated magnetic nanoparticles as nano-adsorbents for removal of copper ions: Synthesis and adsorption studies. J. Hazard. Mater. 2011, 185, 1177–1186.

Drew, M. D. B.; Mullins, A. P.; Rice, D. A. Synthesis, characterization and structural properties of some copper(II) trans-cinnamates and related compounds. Polyhedron 1994, 13, 1631–1637.

Kumar, S.; Sharma, R. P.; Venugopalan, P.; Jerzykiewicz, M.; Starynowicz, P. Synthesis, spectroscopic characterization, single crystal X-ray structure and packing analyses of [Cu(temed)(p-nitro-cinnamate)2] and [Cu(temed)(p-methoxy-cinnamate)2]. J. Mol. Struct. 2018, 1173, 261–267.

Kumar, M.; Singh, A. K.; Sikandar, M. Study of sorption and desorption of Cd (II) from aqueous solution using isolated green algae Chlorella vulgaris. Appl. Water Sci. 2018, 8, 225.

Ho, Y. Review of second-order models for adsorption systems. J. Hazard. Mater. 2006, 136, 681–689.