Porous Fe@C Composites Derived from Silkworm Excrement for Effective Separation of Anisole Compounds

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ABSTRACT: Silkworm excrement is a very useful biomass waste, composed of layer-structured fats and proteins, which are great precursors for carbon composite materials. In this work, new porus composites derived from silkworm excrement were prepared for selective separation of flavor 4-methylanisole from the binary 4-methylanisole/4-anisaldehyde mixture. In particular, the silkworm excrement, possessing a unique nanosheet structure, is converted into a graphite-like carbon by a simple calcination strategy followed by a metal-ion-doping procedure. This Fe@C composite exhibits a special nano-spongy morphology, anchoring Fe,C/Fe5C2 on the carbon nanosheets. Density functional theory simulations showed that 4-methylanisole presents a stronger π−π interaction and attraction forces with sp2 carbon nanosheets in Fe@C composites than 4-anisaldehyde. The selective adsorption experiments further confirmed that the Fe@C composites exhibited a 4-methylanisole capacity of 7.3 mmol/g at 298 K and the highest selectivity of 17 for an equimolar 4-methylanisole/4-anisaldehyde mixture among the examined adsorbents including MOFs and commercial activated carbon materials, which demonstrates the potential of this low-cost and eco-friendly porous carbon material as a promising sustainable adsorbent.

1. INTRODUCTION

Anise compounds are popular flavor gradients used as additives in the food industry and medical intermediates,1 mainly containing anisaldehyde, anisole, anethole, estragole, and 4-methylanisole, and so forth.2 Some of these species are high value-added flavor compounds, which are usually found in small amounts in natural plants or crop oils, whereas pure anise oil has been explored as a very sustainable solvent for the hydrogenation process.3 However, the complex composition and low concentration have posed difficulties for their industrial extraction and purification.4−5 Separation of each species is even more challenging considering that some of them have similar sizes and chemical properties, which is normally carried out by the liquid−liquid extraction coupled with distillation methods.6,7

Certainly, more energy-efficient separation processes including adsorption and membrane separation are preferred technologies because of their ease of operation, high efficiency, and low energy consumption.8 In adsorption, porous materials are the key factors determining the extraction and separation efficiency.9 Because of this critical role, developing new porous adsorbents with superior capacity and fast kinetics with targeted species has gained considerable interest in the scientific community10 as well as in industrial applications.11 Among these, porous carbon materials and zeolites, because of their good chemical and thermal stability, food-grade safety, and cost-effective nature, have been widely used for purification of flavored chemicals.12−15 However, improvements of adsorption capacity and selectivity for targeted flavor molecules are always needed. For example, Xiao16 employed an anisole-modified hyper-crosslinked polystyrene resin and almost doubled the adsorption capacity of vanillin, that is, from 140.5 to 240.3 mg/g. Medellin-Castillo17 studied ozone-modified activated carbon and found enhanced adsorption ability toward diethyl phthalate. Besides the adsorption capacity, improvement of adsorption selectivity has also been reported. Molecular imprinting and affinity separation have been used to recognize target molecules and realize great selectivity for larger biomolecules such as peptides and proteins.18 However, separation of anisole or anisaldehyde...
from anise is still very challenging because of their similar molecular size, high boiling points, and diverse concentrations in industrial processes. As far as we are aware, there are rarely published reports about this separation.

Silkworm excrement (SE) is an abundant agricultural waste produced from the silk reeling industry in China and Southeast Asia.\textsuperscript{19} Most of the waste is discarded and its improper disposal can cause severe environmental issues.\textsuperscript{20} SE is mainly composed of cellulose and proteins with an ordered structure,\textsuperscript{21} in which a high content of carbon with a unique nanosheet morphology has been found.\textsuperscript{22} In this work, a “one-pot” calcination of the SE can produce a nano-spongy porous carbon structure loaded with iron ions. The obtained Fe@C composites demonstrated high adsorption selectivity toward 4-methylanisole from the 4-methylanisole/4-anisaldehyde (MA/AY) mixture, in which the synergistic effects of pore size and functional groups have played an import role, causing a strong interaction with MA through the possible sp$^3$ C π–π stacking and weak polar interactions.

2. EXPERIMENTAL SECTION

2.1. Materials. SE was purchased from a farmer’s market (Yizhou, China). MA (99.0%) and AY (99.0%) were supplied by Guangdong Hua Fang spice Co. Ltd. (Guangzhou, China). Analytical grade absolute ethanol (C$_2$H$_5$OH, 99.7%), FeCl$_2$-4H$_2$O (99.0%), and ZnCl$_2$ (99.0%) were supplied by Aladdin Industrial Co. Ltd. (Shanghai, China). All the other materials were commercially available and were purchased at analytical grade and used directly without further purification. Chemical properties of MA and AY are shown in Table S1.

2.2. Synthesis of Fe@C Composites. SE was first washed in deionized (DI) water to remove ash from the raw materials and then dried at 130 °C for 8 h. Then, it was crushed into small particles with an average diameter of 1–2 mm. After that, the crushed SE particles (10.0 g) were immersed in a water solution of mixed ZnCl$_2$ and FeCl$_3$ for 12 h, and then freeze-dried to maintain the three-dimensional structure. The frozen SE was heated to 1200 °C at a rate of 5 °C/min and held at this temperature for 1.0 h under N$_2$ atmosphere. After cooling down to room temperature, the final samples were washed using 10 mmol/L HCl solution to remove any loosely bonded species. More DI water was then used to wash the samples until pH 7. These samples were designated as Fe@C-1 and Fe@C-2, representing weight ratios of Fe/Zn at 1.0/1.0 and 2.0/1.0, respectively. For comparison, calcined SE without Fe loading was also prepared and named as SE-C.

2.3. Material Characterization. Fourier transform infrared (FTIR) spectra were recorded with a Bruker TENSOR II FTIR spectrophotometer in a range of 4000–400 cm$^{-1}$. Powder X-ray diffraction (PXRD) measurements were performed on an X-ray spectrometer (Rigaku) with Cu Kα radiation (λ = 1.5406 Å). Raman spectra were carried out on a microscopic confocal Raman spectrometer (Renishaw, RW1000-inVia) with an excitation of laser light at 514.5 nm. Analytical grade absolute ethanol (C$_2$H$_5$OH, 99.7%) was transferred into a 100 mL conical flask, continuously shaken on a thermostatic oscillator, and incubated at 298 K for 20 min. Then, 50 mg of adsorbents were added into the flask, and the concentration of the solution components was determined at the given intervals of time until equilibrium was reached. The binary adsorption kinetics of MA and AY were performed following the same protocol at a 1:1 ratio of MA/AY. The equilibrium adsorption capacity $q_e$ (mmol/g), transient fractional adsorption capacity $q_t$ (mmol/g), and selectivity (aMA/AY) were calculated according to eqs 1–3, respectively.

$$q_t = \frac{(C_0 - C_t)V}{m}$$ \hspace{1cm} (1)

$$q_e = \frac{(C_0 - C_e)V}{m}$$ \hspace{1cm} (2)

$$\alpha_{MA/AY} = \frac{q_{t,MA}}{q_{t,AY}}$$ \hspace{1cm} (3)

where $C_0$, $C_t$, and $C_e$ (mmol/L) are the concentrations of the examined component at the initial condition, the equilibrium condition, and a time $t$ (min) after adsorption started, respectively; $V$ is the volume of the solution (L), and $m$ is the weight of the dried adsorbents (g); $C_{t,MA}$ and $C_{t,AY}$ are the concentrations of MA and AY (mmol/g) at adsorption time $t$, respectively; $q_{t,MA}$ and $q_{t,AY}$ are the adsorbed amounts of MA and AY at time $t$, respectively.

The concentrations of MA and AY were analyzed by a gas chromatography instrument, installed with a HP-INNOWAX column (30 m × 0.32 mm×0.25 μm) and a flame ionization detector (FID). Samples were injected into a 1.0 μL loop, at a N$_2$ gas flow of 24 mL/min. The temperatures of the oven and FID were 180 and 300 °C, respectively. Under these conditions, linear regression of MA and AY concentration vs. peak area ($x_1$ and $x_2$) was performed to obtain a standard curve: $y_1 = 189599x_1 + 763620$ ($R^2 = 0.999$, 10.0–80.0 mmol/L) and $y_2 = 147165x_2 - 632200$ ($R^2 = 0.999$, 10.0–80.0 mmol/L). All measurements were performed in triplicate and average values were reported.

2.5. Simulation Method. Calculations were performed via density functional theory (DFT) following the gradient-corrected hybrid density functional B3LYP method.\textsuperscript{23} Chemical structures of MA and AY were optimized with the polarized continuum model and dielectric constant of ethanol condition.\textsuperscript{24} All calculations were conducted with a 6-311g + (d) basis set as implemented in a Gaussian 09 package (revision C.01). The net charge on the atoms was assigned through the analysis of natural bonding orbitals. By using highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy values for a
molecule,\(^\text{eqs 4–6}\) electronegativity (\(\chi\)), chemical hardness (\(\eta\)), and softness (\(\delta\)) can be calculated using

\[
\chi = \frac{(I + A)}{2} \tag{4}
\]

\[
\eta = \frac{(I - A)}{2} \tag{5}
\]

\[
\delta = \frac{1}{2\eta} \tag{6}
\]

where \(I = -E_{\text{HOMO}}\) and \(A = -E_{\text{LUMO}}\) are ionization potential and electron affinity.\(^{26}\)

3. RESULTS AND DISCUSSION

3.1. Structure, Surface Area, and Porosity. FTIR spectra of SE-C, Fe@C-1, and Fe@C-2 are Shown in Figure 1A, in which all have peaks at 1590 and 670 cm\(^{-1}\) associated with \(\text{C} = \text{O}\) stretching vibration and \(\text{N} - \text{H}\) bending vibration, respectively.\(^{27}\) Also, a very broad peak near 3426 cm\(^{-1}\) and a sharp spike at 1015 cm\(^{-1}\) were shown in these samples, corresponding to stretching and bending vibrations of \(-\text{OH}\) groups, respectively;\(^{28}\) however, their lower intensity of FTIR peaks indicates a significant decrease of O-containing groups from the original SE. Moreover, two narrow vibration peaks at 750 and 820 cm\(^{-1}\), representing bending vibration of \(\sigma_{\text{CH}}\) bonding from ortho- and meta-groups in a benzene ring, had disappeared in both Fe@C-1 and Fe@C-2 samples.\(^{29}\) It means that the graphitization degrees of these Fe@C samples were increased after Fe-catalytic calcination.

The PXRD patterns of original SE, calcined SE-C, and Fe@C composites are shown in Figures 1B and S1. Original SE has diffraction peaks at \(2\theta = 15.2/24.6^\circ\) and 26.79/29.32\(^\circ\) indexed to \(\text{CaCO}_3\) and \(\text{SiO}_2\) species,\(^{30}\) respectively, which might have come from silkworms’ food components.\(^{31}\) After being calcined at a high temperature, the diffraction peak in all spectra appearing around 25.5\(^\circ\) corresponded to the (002) plane of a partially graphitized structure.\(^{32}\) After doping Fe species, new peaks at \(2\theta = 36.0/45.1\) and 41.3/46.1\(^\circ\) in Fe@C-1 and Fe@C-2 represent \(\text{Fe}_3\text{C}\) and \(\text{Fe}_7\text{C}_2\) structures, respectively,\(^{33}\) and the peak intensity increases with the increased Fe loading amounts. We believe that these iron carbides are formed by the reduction of Fe ions during the high-temperature carbonization process, which also provide weak polar adsorption sites on the surface of Fe@C composites.\(^{34,35}\)

The effect of Fe loading contents on the graphitization extent of SE-C was tested via Raman analysis, as shown in Figure 1C, which suggests that all samples exhibited two overlappings of the D peak and the G peak (\(I_D/I_G\)) as listed in Table S2. These values can determine their degree of graphitization.\(^{36}\) The \(I_D/I_G\) values of Fe@C-2 (1.14) and Fe@C-1 (1.08) are obviously lower than that of the SE-C sample (1.77), confirming a higher degree of graphitization in the Fe@C samples because of the introduction of Fe species during the calcination.\(^{37,38}\) This enriched graphitic carbon in the newly designed Fe@C composites may also have catalytic properties.\(^{39}\)

\(\text{N}_2\) isotherms and the pore size distribution of SE-C and Fe@C composites are shown in Figures 1D and S2, whereas their porosity parameters are listed in Table 1. The SE-C sample showed a type IV isotherm with a clear hysteresis loop (H4) in its \(\text{N}_2\) isotherm at 77K, indicating a typical hierarchical structure with micro/mesopores,\(^{40}\) and it has the highest \(\text{N}_2\) capacity and surface area (1560.2 m\(^2\)/g), and a larger hysteresis loop among the three samples. The hierarchical structure of SE-C was composed of micropores and mesopores in its pore structure. After Fe doping, \(\text{N}_2\) uptake and the surface area, mesopore surface area, and pore volume of Fe@C-1 (1104.1 m\(^3\)/g) and Fe@C-2 (904.3 m\(^3\)/g) decreased as seen in Figure 1D and from Table 1. These changes could be caused by the shrinkage of pore structure, blockage of pore by Fe species during calcination, and possible density increase compared to the SE-C sample. Moreover, the pore size distribution of all these samples were calculated by employing DFT as shown in Figure 1.
Figure S2, suggesting similar pore-size distribution at 5.0−6.0, 6.7−8.1, 12.0−15.0, and 20.0−25.0 Å.

3.2. Morphology Analysis. Scanning electron microscopy (SEM) and TEM images of SE, SE-C, and Fe@C composites are shown in Figures 2 and S3. The original SE presents an interesting wrinkled structure with a smooth surface as shown in its SEM images (Figure S3A). Further examination by TEM (Figure 2A) shows that SE actually possesses very thin nanosheet structures, which are not commonly seen on carbon materials derived from biomass.41,42 It is attributed to a special reconstruction of lamellar structures from mulberry leaf cellulose by silkworms through intestinal absorption.43,44 After being calcinated with Fe species, SE was transformed into a 3D nano-spongy network packed with nanosheets (Figures S3B and 2B). This new Fe@C composite possesses many porous channels, providing a great diffusion pathway for molecules. Some nanosheets in the original SE were broken during high-temperature calcination and Fe/Zn activation, which were reconstructed into a spongy network through self-assembly. Figure 2C shows that Fe species are uniformly dispersed over the Fe@C-1 composites. Furthermore, a high-resolution TEM image shows that the clear lattices’ fringe spacing in Fe@C-1 is around 0.183, 0.201, 0.205 and 0.307 nm, among which 0.183 and 0.205 nm are assigned to the 312 and 510 planes of Fe5C2, 0.201 and 0.307 nm are assigned to the 211 and 210 planes of Fe3C, respectively.45,46 These Fe–C lattices can be seen embedded into the carbon layer, whereas Fe–C bonds were in accordance with the PXRD results as shown in Figure 1B. The carbon layer with \( d = 0.345 \) nm can be easily assigned to (002) plane of the graphitic carbon,47 confirming the catalytic role of Fe species in the formation of graphitic carbon in SE.

3.3. Composition Analysis. In order to study the effects of Fe species on the surface properties of the SE-derived carbons, XPS elemental analysis was performed on SE-C and Fe@C-1 as shown in Figures 3, S4, and Table S3, in which the oxygen atomic percentage was decreased from 11.88% in SE-C to 3.96% in Fe@C-1 (Figure S4 and Table S3). Thus, we believe that through Fe catalysis and activation, larger amounts of oxygen in SE were removed during the calcination of Fe@C-1 compared to SE-C, making the surface of Fe@C-1 more hydrophobic. Meanwhile, 0.56% atomic percentage of Fe in the full survey spectrum of the Fe@C-1 sample indicates the successful grafting of iron on the carbon surface.

The high-resolution XPS spectra of C 1s from the SE-C and Fe@C-1 samples present peaks at binding energies of 284.8, 285.6, and 286.7 eV, which are assigned to sp\(^2\) C, sp\(^3\) C, and O=C–O bands, respectively, as shown in Figure 3A.38 Clearly, the intensity of the sp\(^3\) C peak in Fe@C-1 was significantly lower than that in SE-C, as shown in Table S4, whereas the intensity of sp\(^3\) C was increased to 75.3%. The reduction of sp\(^3\) C in Fe@C-1 was due to its transformation into sp\(^2\) graphite carbon with Fe catalysis, which in turn can also enhance the hydrophobicity of Fe@C-1.49,50 Moreover, the presence of Fe in the form of the Fe\(_3\)C band (284.3 eV) would weaken the polarity of graphitic carbon as well.

### Table 1. Physical Properties of SE-C, Fe@C-1, and Fe@C-2

| Sample      | \( S_{\text{BET}} \) (m\(^2\)/g) | \( S_{\text{mic}} \) (m\(^2\)/g) | \( S_{\text{meso}} \) (m\(^2\)/g) | \( V_t \) (cm\(^3\)/g) | \( V_{\text{mic}} \) (cm\(^3\)/g) |
|-------------|---------------------------------|---------------------------------|---------------------------------|-----------------|-----------------|
| SE-C        | 1560.2                          | 164.0                           | 1396.2                          | 0.96            | 0.06            |
| Fe@C-1      | 1104.1                          | 216.2                           | 887.9                           | 0.75            | 0.13            |
| Fe@C-2      | 904.3                           | 280.0                           | 624.3                           | 0.53            | 0.12            |
| Fe-removed  | 1396.1                          | 211.0                           | 1185.1                          | 0.89            | 0.08            |
| MIL-101     | 3163.3                          | 56.7                            | 3106.6                          | 1.51            | 0.01            |
| Uio-66      | 1292.4                          | 1170.5                          | 121.9                           | 0.61            | 0.50            |
| C-CA        | 760.4                           | 668.1                           | 92.2                            | 0.38            | 0.31            |

\( S_{\text{BET}} \) = BET surface area; \( S_{\text{mic}} \) = microporous surface area; \( S_{\text{meso}} \) = mesoporous surface area; \( V_t \) = total volume; \( V_{\text{mic}} \) = microporous volume.

Figure 3. High-resolution C 1s XPS spectra of (A) SE-C and (B) Fe@C-1.
3.4. Adsorption Kinetics. The results of adsorption kinetics of MA and AY on SE-C, Fe@C-1, and Fe@C-2 at 298 K are shown in Figure 4, in which the adsorption capacity of MA is much higher than that of AY on these samples. MA and AY have similar molecular structures, except for a methyl (−CH3) group in MA and an aldehyde group (−CHO) in AY. The faster adsorption rate by MA also suggests a stronger interaction between the adsorbents and MA than AY, and the order of capacity of MA follows Fe@C-1 > Fe@C-2 > SE-C, which is not consistent with the trend of their specific surface areas (Table 1). These results demonstrate that the surface properties and surface areas are at least equally important in the adsorption of MA. Fe@C-1 composites exhibited not only the highest adsorption capacity, but also the highest adsorption density per surface area because of the synergistic effect of iron sites and carbon sites. However, excessive loading of Fe species may block the pores of porous carbon and lower the surface area as shown in the nitrogen isotherm (Figure 1D and Table 1), leading to a slight decrease in adsorption capacity of MA.

To further understand the effects of Fe species on the adsorption efficiency of MA and AY on Fe@C composites, an HCl (1.0 mol/L) solution was used to completely remove Fe species on Fe@C-1 (Fe-removed Fe@C-1). The adsorption kinetic curves of MA and AY were measured again as shown in Figure 4B and porosity parameters of Fe-removed Fe@C-1 are listed in Table 1, in which the specific surface area increases greatly. However, the adsorption equilibrium capacity of MA on Fe-removed Fe@C-1 does not change much compared to that of Fe@C-1, whereas the kinetics is slower after Fe is removed, though it is still higher than the SE-C sample. Apparently, the Fe species played an important role in facilitating the diffusion and adsorption kinetics of MA on Fe@C composites. On the contrary, the adsorption uptake of AY on the Fe-removed Fe@C-1 samples increased majorly because of the increase of its surface area (SBET from 1273.9 to 1396.1 m²/g) rather than the Fe species. This further suggests that in the absence of Fe species, the surface area is a major factor to determine the adsorption properties of AY.

Moreover, kinetics data of the three samples show that 60% adsorption uptake for both MA and AY occurs within 30 min and the adsorption equilibrium is generally achieved after about 100 min. These adsorption kinetic profiles can be fitted to the linear driving force (LDF) model, expressed in eq 7.

\[
q_t = q_e (1 - e^{-kt})
\]

where \( q_e \) (mmol/g) and \( q_t \) (mmol/g) are the adsorption capacities at equilibrium and adsorption time \( t \) (min), respectively, and \( k \) (1/min) is the adsorption rate constant. The fitting curves of the LDF model are shown in Figure 4C,D, and the fitting parameters are listed in Table 2. The \( R^2 \) values of the model is above 0.99, indicating a high degree of agreement between the experimental data and the model. The slightly higher rate constant of MA than that of AY is consistent with the observed kinetic curves as described above. Moreover, Fe@C-2 and Fe@C-1 showed a higher rate constant for MA and a lower rate constant for AY compared
to the bare SE-C sample, indicating that the Fe-doped surface with enriched sp² carbon exhibited higher affinity of MA than that of AY.

3.5. Adsorption Equilibrium. In order to compare the adsorption capacity of MA molecules on the new adsorbents, adsorption isotherms of MA were measured on SE-C, Fe@C composites, and several typical adsorbents including two MOFs and a commercial activated carbon XFNANO C-AC (Table 1). The experimental data were also fitted using Langmuir and Freundlich models given by eqs 8 and 9.

\begin{equation}
\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}
\end{equation}

\begin{equation}
Q_e = K_F C_e^{1/n}
\end{equation}

where \(Q_m\) and \(Q_e\) (mmol/g) are the maximum and equilibrium adsorption capacity and \(K_L\) (L/(mmol)) is a constant related to the adsorption energy; \(K_F\) (mmol/(1-1/n)/g/L^1/n) is defined as the adsorption or distribution coefficient, and \(n\) is an indicator of the adsorption intensity.

The Langmuir model provides a better fitting to the experimental data than the Freundlich model, indicating that adsorption of MA may be preferentially occurring via monolayer formation over the surface of these adsorbents. Among the examined samples, Fe@C-1 has the highest \(K_L\) value, indicating the highest adsorption affinity toward MA molecules. Fe@C-1 also exhibited much higher adsorption capacity (7.3 mmol/g) than MOFs, in which MIL-101 has mesoporous cages, whereas UiO-66 possesses a microporous structure with hydrophilic metal sites (Zr⁴⁺) and a hydrophobic surface. In particular, at the feeding concentration lower than 5.0 mmol/L of MA (the inset of Figure SB), Fe@C-1 exhibited about 38% higher adsorption uptake than MIL-101 with \(S_{BET} = 3163.3\) m²/g and UiO-66 with \(S_{BET} = 1292.4\) m²/g (Table 1), which strongly indicates that the high capacity of MA on Fe@C composites is dominated by the surface properties rather than by the surface areas of the examined adsorbents. In addition, the adsorption capacity per unit surface area of these samples, as depicted in Figure S5, in which Fe@C-1 has an adsorption capacity of \(7.9 \times 10^{-3}\) mmol/(g·m²), is about 3.6 and 1.8 times higher than that of MIL-101 and UiO-66, respectively.

3.6. Selective Separation of Binary MA/AY Mixture. Multicomponent adsorption is important to evaluate the real performance of new adsorbents. In particular, the effects of adsorption time, adsorbate concentration, and molar ratio in the multicomponent mixture on the adsorption selectivity are examined in this work, as shown in Figure 6. The selectivity changes on SE-C and Fe@C-1 show a clear decreasing trend with the adsorption time, whereas the examined MOFs and C-AC adsorbents show much lesser change in their selectivity with the adsorption time. However, these MOFs and C-AC have a much lower selectivity ranging from 4 to 2, indicating again that the surface property is more important than the surface area affecting the selectivity of binary adsorption of MA and AY. Fe@C-1 exhibits the highest selectivity (17.3) for MA/AY at the beginning of adsorption, which is 5.8–2.7 times higher than the examined MOFs and C-AC. This could be mainly attributed to the unique nano-spongy morphology and high porosity (Figure 2B,C), which effectively accelerated the MA diffusion (Table 2) in Fe@C composites. This leads to the preoccupation of adsorption sites by MA rather than AY, resulting in a higher MA selectivity at the beginning of the adsorption process. Then, MA selectivity decreases with the adsorption time, suggesting that more AY molecules are getting adsorbed onto the adsorbent surface so that the selectivity dropped. The selectivity of MA/AY on the Fe-removed Fe@C-1 sample is lower than Fe@C-1 (Figure 6A), which further suggests the important role that the Fe species has played in the adsorption of MA.

The effects of adsorbate concentration and the molar ratio of MA/AY on selectivity were also studied under the condition of 298 K and 60 s adsorption time, as shown in Figure 6B,C. The results clearly show that the selectivity on Fe@C-1 increases with the molar ratio between MA and AY, giving selectivity as high as 43.7 when the molar ratio is 9:1 in the mixture, as shown in Figure 6B. However, the selectivity on Fe@C-1 decreases with the absolute concentration of MA and AY in an
equimolar mixture solution, changing from 17.2 at 12 mmol/L to 5.9 at 96 mmol/L of MA and AY, as shown in Figure 6C. The decrease in selectivity is possibly due to the quick saturation of limited adsorption sites or a concentration-dependent diffusion rate at higher concentrations.

3.7. Electronic Structure of Adsorbate Molecules and Adsorption. DFT simulations were performed to calculate the molecular properties including dipole moment (Figure S6), charge distribution (Figure 7), and frontier molecular orbital (FMO) energies (Figure 8). The data obtained from the calculation for MA and AY are listed in Table S5.

The electrostatic potential of MA and AY was mapped into the constant electron density surface, as shown in Figure 7. The electrostatic potential was increased in the color order of red (−0.05 eV) < orange < yellow < green < blue (+0.05 eV), indicating that electron flows from the blue to the red region, and the highest electron density exists in the red region. In the case of MA, electrons were transferred from alkyl and alkoxy groups to the benzene ring (arrows in Figure 7A), which increased the charge density over the benzene ring (fluorescent yellow). As for AY, electrons were transferred from the alkoxy group to the aldehyde group, and formed the highest charge density shown by the red color (arrows in Figure 7B). This variation in electron redistribution results in a lower electron density in the benzene ring of AY than that of MA, which could be a major reason for the different adsorption behaviors in experiments. The Fe@C composites possess a high amount of sp² C, and its graphitic surface will preferentially form π−π stacking interactions with the benzene ring of MA or AY. However, AY possesses a strong electron-donating (alkoxy) group and a strong electron-withdrawing (aldehyde) group attached to the benzene ring. The decreased electron density on the benzene ring leads to increased polarity of the molecule and thus weakens the affinity of AY with the graphitic surface of the SE-derived carbon composites. These factors result in a decreased adsorption capacity and slower kinetics of AY, thus a high selectivity toward MA in the mixture adsorption.

Moreover, the dipole moments and FMO energies of the two adsorbates were also calculated and are shown in Figure 8. Based on the simulation results, the dipole moments of MA and AY exhibited a great difference, that is, 1.655 and 5.627 D.
New composite adsorbents have been generated from the SE, which is a useful biomass waste commonly found in China and South Asia. A calcination process was used to prepare high-graphitic porous nano-spongy carbon materials (SE-C). A metal-doping procedure was also used to modify the surface of SE-C to create Fe@C composites for anisole separation applications. The microscopy imaging and composition analysis show that Fe@C and FeC$_{3}$ species exist on Fe@C composites. Fe activation and catalysis resulted in carbon surface of Fe-C$_{3}$ composites with a high degree of graphitization having the ratio $I_p/I_g = 1.08/1.14$. In particular, Fe@C composites have demonstrated high adsorption capacity of 7.3 mmol/g 4-methylanisole and fast adsorption kinetics, compared to highly porous MOF MIL-101 and UiO-66. Selectivity of MA/AY on Fe@C-1 reached up to 43.7 and 17.3 times higher than the examined MOF MIL-101 and UiO-66, respectively, which is 5.8-2.7 times higher than the examined adsorbents. Our DFT simulation of MA and AY molecules provides some explanation for the observed adsorption properties by analyzing the electronic structures and electron distribution. We believe that the outstanding selective adsorption of MA was attributed to intensified $\pi-\pi$ interaction from the benzene ring and weak polar alkoxy from MA with sp$^2$ C and Fe species on the surface of Fe@C composites.

4. CONCLUSIONS

The microscopy imaging and composition analysis show that Fe@C and FeC$_{3}$ species exist on Fe@C composites. Fe activation and catalysis resulted in carbon surface of Fe-C$_{3}$ composites with a high degree of graphitization having the ratio $I_p/I_g = 1.08/1.14$. In particular, Fe@C composites have demonstrated high adsorption capacity of 7.3 mmol/g 4-methylanisole and fast adsorption kinetics, compared to highly porous MOF MIL-101 and UiO-66. Selectivity of MA/AY on Fe@C-1 reached up to 43.7 and 17.3 times higher than the examined MOF MIL-101 and UiO-66, respectively, which is 5.8-2.7 times higher than the examined adsorbents. Our DFT simulation of MA and AY molecules provides some explanation for the observed adsorption properties by analyzing the electronic structures and electron distribution. We believe that the outstanding selective adsorption of MA was attributed to intensified $\pi-\pi$ interaction from the benzene ring and weak polar alkoxy from MA with sp$^2$ C and Fe species on the surface of Fe@C composites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02681.

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