New Way to Analyze the Adsorption Behavior of Flavonoids on Macroporous Adsorption Resins Functionalized with Chloromethyl and Amino Groups

Song Lou,†‡ Zhenbin Chen,§ Yongfeng Liu,†‡ Helin Ye,†‡ and Duolong Di†‡

†Key Laboratory of Chemistry of Northwestern Plant Resources and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
‡Graduate University of the Chinese Academy of Sciences, Beijing 100049, PR China
§State Key Laboratory of Gansu Advanced Non-ferrous Metal Materials, Lanzhou University of Technology, Lanzhou, 730050 Gansu, China

ABSTRACT: A series of macroporous adsorption resins (MARs) with novel structure were synthesized on the basis of the Friedel–Crafts catalyzed and amination reaction. Adsorption feature of the synthetic resins with respect to the purification effect were investigated systemically by employing rutin as the adsorbate. Different from traditional adsorption patterns, the results showed interesting conclusions: (1) With the increase in the temperature of the experiment, the adsorption capacity increased gradually; with the increase in the concentration of the initial solution, the adsorption capacity increased to the maximum and then decreased gradually. (2) The classical models that the inductive effect transmitted to the first layer and the adsorption process contained in one compartment could not explain our experimental results reasonably. Thus, a new adsorption isotherm model that the inductive effect passed to a higher layer and a new adsorption kinetics model in which the adsorption process contained more compartments were created according to the multiparameter theory and Karickhoff’s theory by investigating the regression of the experimental results. The conclusion that the inductive effect passed to the fourth layer and the adsorption process contained four compartments was drawn.

1. INTRODUCTION

Macroporous adsorption resins (MARs) have been shown to be potentially powerful separation materials and have been developed into a novel technique in many fields, such as chromatographic analysis,1 treatment,2 medical,3 and wastewater disposal.4 Except for the general advantage of that of the common adsorbent, MARs possess many special characteristics such as high mechanical strength, good acid and alkali resistance, porous availability, high surface area, and a long lifetime that make them more promising.5–7 To gain a greater adsorption capacity and a higher adsorption selectivity for some specific organic compounds, chemical modification of MARs is often undertaken by introducing special functional groups into the matrix of the polymeric adsorbents,8,9 which would modify the chemical composition of the adsorbent surface and hence improve its adsorption for organic compounds.10 Thus, investigations of the adsorption features of organic compounds on MARs are of great importance.11,12

However, researchers all over the world have always paid attention to the application of MARs, and theoretical research on the adsorption features of MARs lags severely at present. Although there are several reports about the adsorption feature of MARs,13–18 many simply attributed the adsorption of MARs to the patterns usually used, such as Langmuir and Freundlich. Moreover, many researchers have investigated the factors controlling the adsorption properties of MARs, although little is known about their extensional adsorption–desorption kinetics and isotherms with respect to purification treatment.19–22 A number of adsorption systems have been observed to exhibit multiphasic behavior with two distinct timescales: a rapid release on the order of minutes followed by a slow timescale on the order of hours.23,24 In most cases, nonlinearity was observed in the adsorption isotherms and was described by the empirical Freundlich model.25 However, little has been done to determine the impacts of the pore size distribution and the functional groups of polymer resins. As a result, the state of theoretical research was not improved, which resulted in a lack of pertinence in the molecular design with respect to the synthesis and modification process of MARs and a further hampering of the development of MAR research and applications. An understanding of the features will benefit the development of an efficient, successful purification process.

Our interest was focused on the adsorption of MARs to flavonoids from sea buckthorn leaves and in further investigating

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the influence of the structure parameters’ degree of matching with respect to synthetic MARs and flavonoids and the adsorption feature. Considering the inadequacy of previous reports and by combining our research interests, in this article a series of adsorption MARs with novel matrix and hydrogen-bonding groups were synthesized. A macroporous styrene-co-divinylbenzene copolymer with chloromethyl groups (DDM-1) was prepared by Friedel–Crafts catalysis, and then a novel adsorption resin with amino groups (DDM-2) was obtained by following the amination reaction via pendant chlorine groups, which have high surface areas. One solute, rutin, which is one of the classical flavonoids whose structure is shown in Figure 1, possesses the representative structure of flavonoids and is cost-efficient; it was adopted as the adsorbate in this work used to investigate the adsorption features of MARs системически. Experimental results showed that the adsorption capacity would present an interesting trend with increasing experimental temperature; the results also showed that the adsorption of MARs was different from that in the Langmuir and Freundlich patterns. To probe the adsorption behavior of the synthetic resins, the adsorption features were analyzed accurately by using patterns such as Langmuir, Freundlich, and three-parameter adsorption isotherms, and the results proved that the pattern of Freundlich and the three-parameter adsorption isotherms were more suitable for expressing the adsorption feature of rutin on the resins. However, the goodness of fit ($R^2$) was less than 0.99 for all of the resins. Through analysis and investigation, we hypothesized that the inductive effect transmitted to the first layer and the adsorption process containing one or two compartments were unreasonable. Considering the deficiency of the existing models, the pattern in which the inductive effect passed to a higher layer and the adsorption process contained more compartments was proposed according to the multiparameter theory and Karickhoff’s theory. The real terminated layer of the inductive effect and the real terminated compartments of the adsorption process were investigated through regression of the experimental results.

On the basis of the above work, a novel and more reasonable adsorption pattern of MARs was brought up as follows: (1) With the increase in the temperature of the experiment, the adsorption capacity increased gradually; with the increase in the concentration of initial solution, the adsorption capacity increased to the maximum and then decreased gradually. (2) The inductive effect passed to the fourth layer, and the adsorption process contained four compartments according to the new adsorption model.

2. EXPERIMENTAL SECTION

2.1. Chemical Reagents and Samples. Analytical grade ethanol, methanol, sodium chloride, dichloromethane, triethylenetetramine, zinc chloride, and sodium chloride were purchased from Tianjin Chemical Reagent Co., Inc. (Tianjin, China). Pharmaceutical grade chloromethyl methyl ether was purchased from Jinan Leqi Chemical Reagent Co., Inc. (Shandong province, China), and distilled water was used.

Sea buckthorn leaves were obtained from Gansu Greenness Biotech Co., Ltd. (Gansu province, China), and they were employed after washing and drying. The standards were purchased from the National Institutes for Food and Drug Control (Beijing, China).

2.2. Pretreatment of Commercial Adsorbents. The initial beads, which were nonpolymer styrene-co-divinylbenzene copolymer (DDM-0) with no functional groups, were purchased from Xi’an Sunresin Technology Co., Ltd. (Shanxi province, China). Before the adsorption experiments, the weighed resins were pretreated by soaking in ethanol overnight and subsequently washing thoroughly with distilled water to remove the monomers and porogenic agents trapped inside the pores during the synthesis process.

2.3. Synthesis of Adsorbents with a Functional Group. 2.3.1. Preparation of MARs with Chloromethyl Groups. MARs with chloromethyl groups (DDM-1) were prepared using an electroplating substitution method. The initial beads were soaked in dichloromethane for 24 h. An organic solution composed of dichloromethane, zinc chloride initiator, sodium chloride, and initial beads was mixed with chloromethyl methyl ether in a 1000 mL three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. The round-bottomed flask was heated with a programmed heater. The mixture was stirred to give a suspension of beads of a suitable size in the solution (100–120 rpm) and then held at 323 K for 20 h. The synthetic MARs were filtered out, packed in an extractor, and washed with a large amount of distilled water and then methanol until there was no white precipitate while an aqueous solution of silver nitrate was added to the filtrate. The variation of the proportion between the initial beads and chloromethyl methyl ether in the synthesis process can produce MARs with different numbers of chloromethyl groups.

2.3.2. Preparation of MARs with Amino Groups. The DDM-1 MARs were dried at 313 K under vacuum, swelled with methanol for 24 h, and mixed with excess triethylenetetramine in a 500 mL three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. The mixture was held at 303 K for 9 h, and beads with amino group were synthesized through an amination reaction. Then the beads were filtered out and washed with distilled water until there was no white precipitate while an aqueous solution of silver nitrate was added to the filtrate. MARs with different numbers of amino groups (DDM-2) can be obtained by varying the reaction time and the proportion of DDM-1 beads with respect to aminating agent in the synthesis process.

2.4. Determination of the MARs’ Physical Parameters. 2.4.1. Analysis. The swelling ratio in water, defined as the ratio of the volume occupied by the resin when swollen in water to its volume in the dry state at room temperature, was determined using a small measuring cylinder. The specific surface area and the pore size distribution of the adsorbents were calculated by the BET and BJH methods, respectively, via the nitrogen adsorption and desorption curves at 77 K using a Micromeritics ASAP 2020 automatic surface area and porosity analyzer (Micromeritics Instrument Corp., USA). Before the BET surface area measurement, the adsorbents were outgassed at 333 K for 24 h on the degas port of the analyzer. Infrared spectra of the adsorption resin were obtained from a Nexus-670 FT-IR spectrometer (Nicolea, USA) with a pellet of powdered potassium bromide and adsorbent in the range of 500–4000 cm$^{-1}$. X-ray photoelectron spectroscopy (XPS) was used to evaluate the chlorine and nitrogen content of modified resins. The spectra were recorded on an Escalab...
<table>
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<th>DDM-0</th>
<th>DDM-1</th>
<th>DDM-2</th>
</tr>
</thead>
<tbody>
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<td>P(St-DVB)</td>
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210 Axis Ultra photoelectron spectrometer (VG Scientific, U.K.) using a Mg Kα excitation source.

2.4.2. Determination of the Number of Chloromethyl and Amino Groups in Adsorbents. The number of chloromethyl and amino groups before and after reactions was determined by an electrochemistry method. The accuracy of the weight of the synthetic beads was 0.2 g, and heat digested a sample in a nickel crucible at 873 K for 8 h with 0.5 g of melting sodium hydroxide. The melted masses were diluted in distilled water to 250 mL, and then the electric potential of the sample aqueous solution was determined by an electrochemistry workstation. The electrochemistry workstation was composed of a potentiometer (PHS-3D, Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) at 383 K until the mass was constant. The following equation was used to calculate the moisture content of the adsorbent

\[
d = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100\%
\]

where \(d\) (%) is the moisture content of the adsorbent, \(W_{\text{wet}}\) (g) is the weight of the hydrated adsorbent, and \(W_{\text{dry}}\) (g) is the weight of the dry adsorbent.

2.4.4. Preparation of Sample Solutions. Sea buckthorn leaves (1 kg) were extracted with 12 L of distilled water in a bath at 353 K for 2 h; this extraction was repeated with 8 L of distilled water. The double extracts were mixed and negative-pressure filtered, the filtrate was evaporated to yield the fluid extract, 6 L of ethanol (95%, v/v) added with standing for 24 h, and the supernatant of the solution was evaporated to yield the fluid extract by removing the ethanol under reduced pressure in a rotary evaporator (RE-52C, Gongyi City Yuhua Instrument Co., Ltd., China) at 323 K. The extract of sea buckthorn leaves was photophobically stored in a refrigerator at 253 K. Then the extract was thawed at ambient temperature before use and diluted to an appropriate concentration (5.57 g/L) with distilled water to produce sample solutions.

2.5. Analytical Procedure for Rutin Solution. Rutin in the aqueous solution was determined by using a UV spectrophotometer (T-6, Beijing Purkinje General Instrument Co., Ltd., Beijing, China) at a wavelength of 500 nm. The method was in accordance with Chinese pharmacopoeia. The concentration of rutin was determined by the obtained standard plotted in the range of 0.007–0.04 mg/mL: \(A = 11.42C - 0.0065\) (R² = 0.9998), where \(A\) and \(C\) are the absorbency and the concentrations of rutin (mg/mL), respectively.

2.6. Adsorption/Desorption Experiments. 2.6.1. Adsorption Experiment. The adsorption/desorption experiment of rutin were carried out as follows: preweighed amounts of hydrated resins (equal to 1.2 g of dry resin) and a 100 mL sample solution with a known concentration were added to a 250 mL conical flask with a stopper. Subsequently, the flasks were continually shaken in a SHA-B incubator (100 rpm, Jintan Zhengji Instrument Co., Ltd., Jiangsu province, China) at 308 K for 6 h. The final concentrations of rutin were analyzed with a UV spectrophotometer. The desorption experiments were carried out as follows: after the adsorption equilibrium was reached, the adsorbate-laden resins were desorbed with 50 mL of ethanol (70%, v/v). The flasks were shaken (100 rpm) at a constant temperature of 303 K for 6 h. Then corresponding concentrations of rutin were analyzed with a UV spectrophotometer. The ratios and adsorption/desorption capacities were calculated with the following equations:

\[
a(\%) = \frac{C_{\text{D}} - C_{\text{e}}}{C_{\text{D}}} \times 100\% \tag{4}
\]

adsorption ratio:

\[
b_{\text{e}} = \left( C_{\text{D}} - C_{\text{e}} \right) \times \frac{V_{\text{i}}}{(1 - W)W} \tag{5}
\]

adsorption capacity:

\[
D(\%) = \frac{C_{\text{D}} - C_{\text{D}}}{(C_{\text{e}} - C_{\text{e}}) V_{\text{i}}} \times 100\% \tag{6}
\]

Desorption ratio:

\[
p_{\text{e}} = \frac{V_{\text{d}}}{(1 - M)W} \tag{7}
\]

where \(A\) is the adsorption ratio (%) and \(b_{\text{e}}\) is the adsorption capacity (mg/g of dry resin) at adsorption equilibrium. \(C_{\text{e}}\) and \(C_{\text{D}}\) are the initial and equilibrium concentrations of the sample solutions, respectively (mg/L). \(M\) is the moisture content of the resin (%). \(W\) is the weight of the resin used (g). \(V_{\text{i}}\) is the volume of sample solution used in the study (mL).

2.6.2. Determination of Accuracy and Precision. In this experiment, the coefficient of recovery (P) and the relative standard deviation (RSD)
were adopted to test the accuracy and precision, respectively, of our experimental methods. \( P \) was determined as follows: After adsorption was finished, the concentration of rutin \((C_t)\) in raffinate was first investigated as that in section 2.6.1; thereafter, 10.00 mL of the sample solution was added to a flask loaded with 50.00 mL \((C_s)\) of the raffinate and the concentration of rutin \((C_s)\) was determined again. This process was conducted in six randomly selected adsorption experiments, and \( P \) was calculated with the following equation:27

\[
P = \frac{50 + 10}{C_s} \times 100% \tag{8}
\]

As for RSD, it was obtained from three parallel experiments, and its value was calculated from the following equation:

\[
\text{RSD} = \frac{S}{C} \tag{9}
\]

where \( C_s \) is the concentration of solution in the added sample, \( C_s \) is denoted the concentration of raffinate, \( S \) is the standard deviation, and \( C \) represents the arithmetic mean of three parallel experiments.

The values of \( P \) and RSD in the experiment were 93.46 and 0.35%, respectively, which indicated that the accuracy and precision could satisfy the needs of the experiment.

2.6.3. Adsorption Kinetics. Subsequently, the adsorption kinetics curves of rutin on the selected primal resins and modified ones with chloromethyl and amino groups were studied according to the following process: adding 3.16 g of pretreated resin (equal to 1.2 g of dry resin) and 1000 mL of the sample solution to each flask with a lid. Then the rutin concentrations in the adsorption process were determined with a UV spectrophotometer at different time intervals until equilibration.

2.6.4. Adsorption Isotherms and Thermodynamics. After the 50 mL sample solutions with different concentrations were placed in contact with 3.16 g of pretreated resin (equal to 1.2 g of dry resin) in shakers at temperatures of 303, 308, 313, 318, and 323 K, the equilibrium adsorption isotherms of rutin on the selected resins were obtained at different temperatures.

2.6.5. Adsorption Isotherm Model. The adsorption isotherm was fitted to the Langmuir and Freundlich equations using the nonlinear least-squares analysis. The equations can be presented for the adsorption processes as

\[
q_e = \frac{q_m C_e}{K_r + C_e} \tag{10}
\]

\[
q_e = K_0 C_e^{1/n} \tag{11}
\]

where \( q_m \) is the maximum adsorption capacity for forming a monolayer \((\text{mg/g})\), \( K_r \) is the parameter relative to the adsorption energy \((\text{mg/L})\), \( K_0 \) reflects the adsorption capacity of the adsorbent \( (\text{mg/g})(\text{L/mg})^{1/n} \), \( n \) represents the adsorption affinity of the adsorbent for the adsorbate, and \( q_e \) \((\text{mmol/g})\) is the equilibrium concentration in the solid phase.

2.5.6. Exploration of the Termination of the Inductive Effect. In this work, considering the restriction of the Langmuir and Freundlich models, a new adsorption isotherm model was created according to the multi-parameter theory.28 Through analysis, it was determined that the isotherm parameters were different from those in classical models. Considering the deficiency of this theory, the pattern in which the inductive effect passed to a higher layer was proposed. The real terminated layer of the inductive effect was investigated through regression of the experimental results.

The investigation of the termination because of the inductive effect was carried out by using Origin 8.1 software. The process was conducted as follows: (1) Equations that the inductive effect probably terminated at different layers were deduced. (2) The results obtained were regressed with the above obtained equations one by one, and the regression results contained the related coefficient \( (R_2) \), the equilibrium constant \( (K_1, K_2, ..., K_n) \), and the \( \chi^2 \) distribution \( (\chi^2/\text{DoF} = \chi^2/\text{DoF}, \chi^2 \text{ per degree of freedom } \) where \( \chi^2 = (\Delta_1/\sigma_1)^2 + (\Delta_2/\sigma_2)^2 + (\Delta_3/\sigma_3)^2 + ... + (\Delta_N/\sigma_N)^2) \). \( \Delta \) represented the deviation from an experimental point to the fit curve, \( \sigma \) stood for the standard error, and the degrees of freedom \( \text{DoF} = (\text{number of data points} - \text{number of adjustable parameters}) \) was obtained. (3) The above values were conscripted to determine the transmission of the inductive effect until the values satisfied the following conditions: \( R^2 > 0.99, \chi^2/\text{DoF} \) reached the minimum, the regression ended, and the termination layer of the inductive effect was obtained.

2.5.7. Adsorption Kinetics Model. A phenomenological first-order, two-component, four-parameter model comprising both fast and slow adsorption steps was often used to describe the desorption rate of absorbate from adsorbents

\[
\frac{q_e}{q_{le}} = F_1 \exp(k_1 t) + F_2 \exp(k_2 t) \tag{12}
\]

where \( F_1 \) and \( F_2 \) are the rapidly and slowly adsorbing fractions, respectively. The rate constants of rapid and slow adsorption are designated as \( k_1 \) and \( k_2 \) \((\text{min}^{-1})\). This model is widely applied in various adsorption systems because of its simplicity and was found to be adequate in describing the adsorption of various samples with different characteristics. The parameters from the model are useful for distinguishing between rapidly and slowly desorbing fractions. Furthermore, results from the models gave the biphasic nature of adsorption data in this study. However, it should be noted that this model does not necessarily consider the reasonable procedures of adsorption. The model defining the adsorption process contained just two steps without taking into account the differences between fast adsorption, slow adsorption, and even slower adsorption. Moreover, all of the models of adsorption kinetics overlook the extensional delivery parameter and use a constant instead. Mean-
In this work, considering the restriction above, a new adsorption kinetics model was created according to Karickhoff’s theory. The pattern in which the adsorption process should contain more compartments was proposed. The real sections were investigated through regression of the experimental results.

The investigation of the termination about the adsorption compartments was carried out by using Origin 8.1 software. The process was conducted as follows: (1) Equations that the adsorption effect probably terminated at different compartments were deduced. (2) The results obtained were regressed with the above obtained equations one by one, the regression results contained the related coefficient ($R^2$), and the $\chi^2$ distribution were obtained. (3) The above values were conscripted to determine the transmission of the inductive effect until the values satisfied the following conditions: $R^2 > 0.99$, $\chi^2$/DoF reached the minimum, the regression ended, and the termination compartments of the adsorption were obtained.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Adsorption Resins. Figure 2 displays the FTIR spectra of starting resins DDM-0 and synthetic resins DDM-1 and DDM-2. In the spectrum of DDM-1, there is an absorption band in the vicinity of 576 cm$^{-1}$ that belongs to the stretching vibrations of the C–Cl bond. There were also some other new absorption bands at 1246 and 2073 cm$^{-1}$. They were the in-plane bending vibrations of the benzene ring after binary substitution caused by the substitution of hydrogen atoms at the para position of benzene rings by –CH$_2$Cl. In the spectrum of DDM-2, the N–H structure was disclosed by the occurrence of bands at 860 cm$^{-1}$ as a result of out-of-plane bending vibrations of N–H and at 925 cm$^{-1}$ as a result of the rocking vibration of N–H. There were also some other new absorption bands at 1126, 1221, and 1382 cm$^{-1}$. They were the stretching vibrations of C–N.

Figure 3 shows XPS spectral changes of MARs before and after modification. The characteristic XPS substrate signal for unmodified MARs (left) at 285 eV was attributed to C 1s, and the peak at 200 eV for resins functionalized with chloromethyl-groups (middle) was from Cl 2p and was attributed to the matrix of –CH$_2$Cl. Chlorine (∼200 eV), carbon (∼285 eV), and nitrogen (∼399.5 eV) photoelectron peaks (in order from low to high binding energy) were observed for resins functionalized with amino groups (right). The existence of amino was confirmed by the signal at a binding of 399.5 eV, which is N 1s. Therefore, the signal evidently showed that chloromethyl- and amino groups had been grafted onto the MARs.

3.2. Adsorption Isotherms. To illustrate better the adsorption properties of the synthetic copolymer, equilibrium adsorption isotherms of rutin on synthetic resins DDM-0, DDM-1, and DDM-2 were investigated at five different temperatures of 303, 308, 313, 318, and 323 K, as shown in Figure 4. Point B in Figure 4 indicated that equilibrium adsorption isotherms of rutin on the synthetic copolymer were consistent with II equilibrium adsorption isotherms classified by Brunauer, which were considered to be due to the multilayer reversible adsorption process taking place on the solid adsorbent. Point B is the first precipitous part in Figure 4 and represents the saturated adsorption capacity of the first monolayer of coverage on the resin.

Additionally, an increase in the reaction temperature from 303 to 323 K observably augmented the adsorption. The high temperature would make the resins swells better. The larger the
of rutin that would enter the resins. Meanwhile, the stereospecific volume and aperture that the resins possess, the more molecules of rutin would get into the aperture of the resins. Therefore, the reaction temperature may play a dominant role in rutin adsorption on the spent adsorbents.

The higher adsorption capacity and a significantly higher adsorption capacity and a close correlation coefficient (R^2) of 0.985 for the Langmuir isotherm could reasonably explain the adsorption process, suggesting the multilayer coverage of rutin in the adsorption process, because of their different physical and chemical structures. All of the information showed that DDM-1 and DDM-2 exhibited a higher adsorption capacity than starting copolymer DDM-0, which resulted from its high specific surface area and polarity. This can be explained by the fact that the specific surface area of the starting copolymer was greatly increased after the synthetic reaction. The surfaces of synthetic resins contain polar groups, with the polarity between that of the resin and flavones partially accounting for the increase in the adsorption capacities. However, DDM-2 exhibited a higher adsorption capacity than DDM-1 because hydrogen bonding interactions occurred between the amino group and the hydroxyl group of the flavones. The result showed that the selectivity of the adsorbent toward rutin was remarkably enhanced after hydrogen groups were introduced. The Langmuir and Freundlich equations are used to reveal the linearity fitting and to describe the equilibration relationship between the concentrations of adsorbate in the fluid phase and the adsorbent at a given temperature. The correlation coefficients were calculated according to the Langmuir and Freundlich equations mentioned above, as listed in Table 4. It could be seen that the correlation coefficients (R^2) estimated from the Freundlich equation were high, the R^2 values were larger than 0.9, and the exponent (n) was larger than 1 in all cases, which demonstrates that the adsorption of rutin onto adsorbents is favorable. The R^2 values were much higher than those from the Langmuir equation, implying that the Freundlich isotherm could reasonably explain the adsorption process, suggesting the multilayer coverage of flavones onto the resin. However, the R^2 from Freundlich, which could not reach 0.99, was still not ideal.

Adsortion and desorption isotherms were compared to assess the degree of reversibility of the adsorption reaction. A comparison of these isotherms does provide an assessment of the structural characteristics of the adsorbent with respect to the desorption

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<th>Langmuir</th>
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Table 3. Isotherm Parameters of Rutin Desorption on DDM-0, DDM-1, and DDM-2 at 308 K

<table>
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<th>adsorbent</th>
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"H = n_f/d / n_L."
behavior of rutin. We calculated the hysteresis index ($H$), defined as the $n_{H2}/n_{H1}$ ratio, to quantify the degree of apparent adsorption—desorption hysteresis. The $H$ values for all of the adsorbents with different rutin loadings are listed in Table 3.

The value of $H$ provides evidence of apparent adsorption—desorption hysteresis ($H > 2$) on DDM-2. Isotherm results showed that no hysteresis was observed for synthetic polymeric adsorbent DDM-1, and the adsorption was reversible in aqueous solution ($H \approx 1.4$). That is because there is a relatively small proportion of micropores on DDM-1, but the number of pores existing as micropores of <2 nm width was large in DDM-2. These micropores probably entrapped the loaded rutin molecule and made a slow and prolonged adsorption—desorption process, which may lead to the apparent adsorption—desorption hysteresis resulting from nonequilibrium processes. Yu et al.36 showed that a good relationship between the microporosity and apparent desorption hysteresis in Diuron adsorption—desorption on soils. Braida et al.2 noted the swelling of an adsorbent during benzene desorption hysteresis in Diuron adsorption.

3.2. Determination of the Polarity Inductive Effect Termi-
nation. On the basis of the study of Wang and conclusions in our previous research with a consideration that the induction force could be transmitted to a higher layer, an application program, Origin 8.1, was adopted to probe the information about the transmission of the inductive effect.

The adsorption process is viewed as consisting of initial first layer adsorption followed by multilayer attachment to previous layers. For multilayers, the adsorption of each layer could be expressed using the following general expressions.

$$
S + M \leftrightarrow M_1S; \quad K_1 \text{ first layer adsorption}
$$

$$
M_1S + M \leftrightarrow M_2S; \quad K_2 \text{ second layer adsorption}
$$

$$
M_2S + M \leftrightarrow M_3S; \quad K_3 \text{ third layer adsorption}
$$

$$
\vdots
$$

$$
M_{n-1}S + M \leftrightarrow M_nS; \quad K_n \text{ nth layer adsorption}
$$

where $M$ is the adsorbate (e.g., rutin); $S$ is the free adsorbent surface site; $M_1S$ is the surface complex; and $K_1, K_2, K_3, \ldots, K_n$ are the equilibrium adsorption constants (M$^{-1}$) for the first layer, second layer, $\ldots$, nth layer, respectively.

The above equilibrium adsorption reaction can be expressed as

$$
K_i = \frac{[MS]}{[S][M]} \quad \text{first layer}
$$

$$
K_2 = \frac{[M_2S]}{[MS][S]} \quad \text{second layer (13)}
$$

$$
K_n = \frac{[M_nS]}{[M_{n-1}S][M]} \quad \text{nth layer}
$$

For multilayer adsorption, the adsorbate partially adsorbed by the previous layer was also covered by the subsequent layer adsorbate. This covered adsorbate did not participate in the previous layer adsorption/desorption process. For the previous layer adsorption, only the uncovered part of the adsorbate participates in the equilibrium adsorption/desorption reaction. Thus, $[MS] = XQ_{m-1}((\theta_1 - \theta_2); [S] = XQ_m(1 - \theta_1)$ by eq 13

$$
K_i = \frac{[M_1S]}{[S][M]} = \frac{XQ_m(1 - \theta_1)}{XQ_m((\theta_1 - \theta_2))}
$$

$$
= \frac{\theta_1 - \theta_1}{{(\theta_2 - \theta_1)}C_e}
$$

(14)

where $X$ is the total solid concentration (g/L); $C_e$ is the equilibrium adsorbate concentration (M); $Q_m$ is the surface site (monolayer)
density \((\text{mol/g})\); and \(\theta_1, \theta_2, \ldots, \theta_n\) are the fractions of surface coverage at the first layer, second layer, \ldots, nth layer, respectively.

Equation 14 could be recast as

\[
\theta_i - \theta_{i-1} = K_i C_e (\theta_{i-1} - \theta_i) \tag{15}
\]

Thus, the adsorption equation of the polaritide inductive effect transmitted to different layers could be expressed, respectively, as follows:

1. If there was no transmission of induction force, then the adsorption energies for multilayer adsorption would be equal to each other and the equilibrium constants would be \(K_1 = K_2 = \ldots = K_n\). From eq 15, the following equation could be obtained:

\[
\theta_1 - \theta_2 = K_1 C_e (1 - \theta_1)
\]

\[
\theta_2 - \theta_3 = K_1 C_e (\theta_1 - \theta_2)
\]

\[
\ldots
\]

\[
\theta_{n-1} - \theta_n = K_1 C_e (\theta_{n-2} - \theta_{n-1})
\]

By summing both sides of eq 16, we have

\[
\theta_1 = K_1 C_e + (\theta_n - K_1 C_e \theta_{n-1}) \tag{17}
\]

Because \(\theta_n\) and \(\theta_{n-1}\) represent the surface coverage at the two outmost layers and they were small, the term \((\theta_n - K_1 C_e \theta_{n-1})\) could be neglected. As a result,

\[
\theta_1 = K_1 C_e \tag{18}
\]

By substituting eq 18 into eq 16, we obtain

\[
\theta_2 = K_1 C_e \theta_1 = (K_1 C_e)^2 \tag{19}
\]

With the same procedure as that of eq 19, the following expression was obtained:

\[
\theta_3 = K_1 C_e \theta_2 = (K_1 C_e)^3 \tag{20}
\]

\[
\theta_4 = K_1 C_e \theta_3 = (K_1 C_e)^4
\]

\[
\ldots
\]

\[
\theta_n = K_1 C_e \theta_{n-1} = (K_1 C_e)^n
\]

The total adsorption fraction \(\theta\) was

\[
\theta = \theta_1 + \theta_2 + \theta_3 + \ldots + \theta_n \tag{21}
\]

By substituting \(\theta_1, \theta_2, \ldots, \theta_n\) into eq 21, the relationship between \(K_1\) and \(C_e\) was obtained:

\[
\theta = K_1 C_e + (K_1 C_e)^2 + \cdots + (K_1 C_e)^n \approx 0 \quad \text{and eq} 22 \text{could be simplified to}
\]

\[
\theta = \frac{K_1 C_e}{1 - K_1 C_e} \tag{23}
\]

By replacing the surface coverage with the adsorption density, eq 23 could be rewritten as

\[
Q_e = \frac{Q_m K_1 C_e}{1 - K_1 C_e} \tag{24}
\]

Equation 24 presents the expression of no transmission of the inductive effect, and it is a two-parameter adsorption isotherm pattern.

2. Correspondingly, if the induction force of the adsorbent is transmitted to the second layer, then \(K_3 = K_4 = \ldots = K_n\) and the adsorption could be expressed as follows:

\[
\begin{align*}
\theta_1 - \theta_2 &= K_1 C_e (1 - \theta_1) \\
\theta_2 - \theta_3 &= K_3 C_e (\theta_1 - \theta_2) \\
\theta_3 - \theta_4 &= K_3 C_e (\theta_2 - \theta_3) \\
\theta_4 - \theta_5 &= K_3 C_e (\theta_3 - \theta_4) \\
\ldots \\
\theta_{n-1} - \theta_n &= K_3 C_e (\theta_{n-2} - \theta_{n-1})
\end{align*} \tag{25}
\]

By summing both sides of eq 25, the following equation was obtained:

\[
\begin{align*}
\theta_1 &= K_3 C_e \theta_2 + (\theta_n - K_n C_e \theta_{n-1}) \\
\theta_3 &= K_3 C_e \theta_4 + (\theta_n - K_n C_e \theta_{n-1}) \\
\ldots \\
\theta_n &= K_3 C_e \theta_{n-1} + (\theta_n - K_n C_e \theta_{n-1})
\end{align*} \tag{26}
\]

For the same reason, the \((\theta_n - K_n C_e \theta_{n-1})\) term could be ignored. As a result,

\[
\theta_3 = K_3 C_e \theta_2 \tag{27}
\]

Because of the same procedure, the following equation could be obtained after eq 27:

\[
\begin{align*}
\theta_4 &= K_3 C_e \theta_3 = (K_3 C_e)^2 \theta_2 \\
\theta_5 &= K_3 C_e \theta_4 = (K_3 C_e)^3 \theta_2 \\
\ldots \\
\theta_n &= K_3 C_e \theta_{n-1} = (K_3 C_e)^{n-2} \theta_2
\end{align*} \tag{28}
\]

Now the total adsorption fraction \(\theta\) can be expressed as eq 21. The following equation can be obtained by substituting eqs 27 and 28 into eq 21:

\[
\theta = \theta_1 + \theta_2 + K_3 C_e \theta_2 + (K_3 C_e)^2 \theta_2 + \ldots + (K_3 C_e)^n \theta_2
\]

\[
\theta = \theta_1 + \theta_2 + \frac{1 - (K_3 C_e)^{n-1}}{1 - K_3 C_e} \tag{29}
\]

With the same method, eq 29 can be simplified to

\[
\theta = \theta_1 + \frac{\theta_2}{1 - K_3 C_e} \tag{30}
\]

According to the hypothesis of multilayer adsorption, the adsorption capacity of higher layers was smaller than that of lower layers. Thus, \(\theta_3 < \theta_2 < \theta_1\) was certain, and \(K_3 C_e < 1\) could be acquired effortlessly. Under the same condition as that of eq 14, \((K_3 C_e)^n \approx 0\) and eq 30 could be simplified to

\[
\theta = \theta_1 + \frac{\theta_2}{1 - K_3 C_e} \tag{31}
\]

By substituting eq 27 into eq 2S, \(\theta_2\) could be calculated from eq 32:

\[
\theta_2 = \frac{K_3 C_e \theta_1}{1 + K_2 C_e - K_3 C_e} \tag{32}
\]

By introducing the expression \(\theta_2\) into eq 2S, \(\theta_1\) was obtained as eq 33:

\[
\theta_1 = \frac{K_1 C_e (1 + K_2 C_e - K_3 C_e)}{(1 + K_2 C_e - K_3 C_e) - K_3 C_e} \tag{33}
\]
Table 5. Regression Result Based on the Induction Force Transfer Effect

<table>
<thead>
<tr>
<th>resins</th>
<th>layer</th>
<th>$\chi^2$/DoF</th>
<th>$Q_m$(mg/g)</th>
<th>$K_1$(L/mg)</th>
<th>$K_2$(L/mg)</th>
<th>$K_3$(L/mg)</th>
<th>$K_4$(L/mg)</th>
<th>$K_5$(L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDM-0</td>
<td>1</td>
<td>1.2531</td>
<td>28.369</td>
<td>0.0392</td>
<td>0.0375</td>
<td>0.0410</td>
<td>0.9340</td>
<td>0.976</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.2112</td>
<td>63.290</td>
<td>0.0230</td>
<td>0.0392</td>
<td>0.0410</td>
<td>0.9340</td>
<td>0.985</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.9811</td>
<td>5.0607</td>
<td>0.4197</td>
<td>0.0201</td>
<td>0.01677</td>
<td>0.0261</td>
<td>0.986</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.2665</td>
<td>4.6079</td>
<td>1.13 x 10^{-3}</td>
<td>5.74 x 10^{-2}</td>
<td>2.64 x 10^{-2}</td>
<td>0.6437</td>
<td>0.6265</td>
<td>0.994</td>
</tr>
<tr>
<td>DDM-1</td>
<td>1</td>
<td>1.7017</td>
<td>40.093</td>
<td>0.0222</td>
<td>0.0195</td>
<td></td>
<td></td>
<td></td>
<td>0.975</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.6434</td>
<td>102.915</td>
<td>0.0073</td>
<td>1.64 x 10^{-4}</td>
<td>3.84 x 10^{-3}</td>
<td></td>
<td></td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.0867</td>
<td>3.2373</td>
<td>0.1403</td>
<td>0.0045</td>
<td>0.3109</td>
<td>2.56 x 10^{-3}</td>
<td></td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.5987</td>
<td>9.90 x 10^{3}</td>
<td>6.18 x 10^{-4}</td>
<td>6.21 x 10^{-2}</td>
<td>1.70 x 10^{-4}</td>
<td>0.1295</td>
<td>0.1094</td>
<td>0.993</td>
</tr>
<tr>
<td>DDM-2</td>
<td>1</td>
<td>4.8509</td>
<td>50.010</td>
<td>0.0486</td>
<td>0.0497</td>
<td></td>
<td></td>
<td></td>
<td>0.933</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.4904</td>
<td>50.174</td>
<td>0.0520</td>
<td>7.89 x 10^{-6}</td>
<td>7.17 x 10^{-3}</td>
<td></td>
<td></td>
<td>0.981</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.7449</td>
<td>0.5509</td>
<td>4.1373</td>
<td>0.0187</td>
<td>0.0252</td>
<td>0.0300</td>
<td></td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.7547</td>
<td>1.89 x 10^{0}</td>
<td>1.3425</td>
<td>2.48 x 10^{-7}</td>
<td>8.27 x 10^{-3}</td>
<td>0.3782</td>
<td>0.3582</td>
<td>0.990</td>
</tr>
</tbody>
</table>

Figure 7. Regression curves of the relationship between the equilibrium concentration ($C_e$) and adsorption capacity ($Q_m$).

By substituting the values of $\theta_1$ and $\theta_2$ into eq 31, the relationship between $\theta$ and $C_e$ was obtained as eq 34:

$$\frac{\theta}{K_1} = \frac{(1 - K_3 C_e)(1 + K_2 C_e - K_3 C_e) + K_2 C_e}{(1 - K_3 C_e)(1 + K_1 C_e)(1 + K_3 C_e - K_3 C_e) - K_2 C_e}$$ (34)

Similarly, by replacing the surface coverage with the adsorption density, eq 34 could be changed to

$$Q_e = \frac{Q_m K_1 C_e}{K_1 C_e \sum_{i=3}^{i \text{th layer}} [K_1 C_e + 2K_1 K_2 C_e^2 + \ldots + (i - 3)K_1 K_2 \ldots K_{i-2} C_e^{i-1}] + (i - 2)K_1 K_2 \ldots K_{i-1} C_e^{i-1} (1 + K_3 C_e - K_{i-1} C_e)}{(1 + K_{i+1} C_e)[(1 + K_{i-1} C_e)] \sum_{i=3}^{i \text{th layer}} (1 + K_1 C_e - K_{i+1} C_e^2) + K_1 K_2 \ldots K_{i-2} C_e^{i-2} (1 + K_{i-1} C_e - K_{i-2} C_e)}$$ (36)

Equation 36, which was an $(i + 2)$-parameter equation, denoted a general formula that the inductive effect transmitted to a certain layer. Thus, the transmission of the induction force could be investigated from the data of $Q_e$ and $Q_m$ obtained from the adsorption equilibrium by Origin 8.1. The regression did not end until the corresponding $R^2 > 0.99$, and the results are shown in Table 5 and Figure 7. It could be found that $R^2$, $Q_m$, and $\chi^2$/DoF were all satisfied with the rules above after regressed to the fourth layer. Furthermore, the value of $\chi^2$/DoF was much lower than the beginning value. All of this showed that the induction force of the adsorbent would transmit to the fourth layer, which is in accordance with the transmission of the inductive effect in a chemical bond.38,39

3.4. Adsorption Thermodynamics. To illuminate better the adsorption mechanism of rutin with respect adsorption resins and give evidence of the polarity inductive effect termination, the adsorption thermodynamic parameters and free energy ($\Delta G^0$) were evaluated. The change in the free energy of adsorption can be calculated from the equilibrium adsorption constants

$$\Delta G^0 = -RT \ln K$$ (37)

where $\Delta G^0$ is the standard free energy change, $R$ is a constant, $T$ is the absolute temperature, and $K$ is the equilibrium constant. The values of $\Delta G^0$ for the adsorption of rutin onto resins are also listed in Table 6. It could be found that the difference value...
Table 6. Thermodynamic Results of the Transmitted Induction Force

<table>
<thead>
<tr>
<th>resins</th>
<th>layer</th>
<th>$-\Delta G_0^T$ (kJ/mol)</th>
<th>$-\Delta G_0$ (kJ/mol)</th>
<th>$-\Delta G_0$ (kJ/mol)</th>
<th>$-\Delta G_0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDM-0</td>
<td>1</td>
<td>8.2943</td>
<td>8.4079</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.6597</td>
<td>9.5721</td>
<td>8.1794</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.2232</td>
<td>10.0048</td>
<td>10.4686</td>
<td>9.3359</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>17.3758</td>
<td>7.3178</td>
<td>9.3066</td>
<td>1.1281</td>
</tr>
<tr>
<td>DDM-1</td>
<td>1</td>
<td>9.7503</td>
<td>10.0824</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.5984</td>
<td>22.3183</td>
<td>14.2434</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5.0292</td>
<td>13.8373</td>
<td>2.9917</td>
<td>15.2817</td>
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<td></td>
<td>4</td>
<td>18.9212</td>
<td>7.1162</td>
<td>22.2262</td>
<td>5.2343</td>
</tr>
<tr>
<td>DDM-2</td>
<td>1</td>
<td>7.7439</td>
<td>7.7918</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>2</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-3.6363</td>
<td>10.1897</td>
<td>9.4258</td>
<td>8.9793</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-0.7542</td>
<td>38.9480</td>
<td>12.2789</td>
<td>2.4899</td>
</tr>
</tbody>
</table>

between $-\Delta G_0^T$ and $-\Delta G_0$ was lower than that between $-\Delta G_0^T$ and $-\Delta G_0$ and that between $-\Delta G_0^T$ and $-\Delta G_0$ and that $-\Delta G_0$ and $-\Delta G_0$ were almost equal. This also might indicate that the polarity inductive effect would transmit to the fourth layer. It can be seen that the difference between $-\Delta G_0^T$ and $-\Delta G_0$ of DDM-2 was not large because the adsorption process of rutin was controlled by a chemical rather than a physical mechanism on DDM-2. That is to say the adsorption on synthetic resin (DDM-2) could be considered to be chemical adsorption enhanced by the physical force. However, the water molecule could hinder the van der Waals force interaction between rutin and resins in aqueous solution, and the adsorbent had enough intensive hydrophobic force offered by the amino groups that it could help rutin to overcome the interference from water molecules to approach a suitable location on the adsorbent surface. With the increase in the adsorption layer, the inductive effect decreased regularly\(^{40}\) and $\Delta G_0$ and $-\Delta G_0$ decreased correspondingly. In this work, if the adsorption behavior was regressed with a six-parameter equation, then the results were in accordance with the diminishing law of the inductive effect. It also suggested that the induction force of the adsorbent transmitted to the fourth layer was reasonable.

3.5. Adsorption Kinetics. To date, little attention has been paid to developing a model of adsorption kinetics that recognizes highly retarded sorption behavior. Work by DiToro and Horzematsu\(^{31}\) to discriminate reversible from resistant sorption components can be construed as a quasi-kinetic model, but they did not address the temporal behavior of the resistant component. For trace metal sorption in marine sediments, Duursma and Bosch\(^{32}\) found a highly retarded component that they ascribed to diffusive uptake into sediment particles. Their data, fitted to conventional diffusion models (porous spherical particles), gave effective diffusion coefficients. No attempt was made to characterize the active distribution volumes for adsorbate uptake or to extrapolate the measured diffusion coefficients. Karickhoff and Morris\(^{33}\) constructed a particularly simple model offering considerable utility in examining laboratory data. However, there was no consideration of the reasonable procedures of adsorption. The model contains just one step without considering the differences between quick adsorption, slow adsorption, and even slower adsorption. Moreover, all of models of adsorption kinetics overlook the extensional delivery parameter and use a constant instead. Considering the deficiency of Karickhoff’s model, we concluded that the hypothesis for the adsorption process should be divided into more compartments. The real sections were investigated through a regression of the experimental results.

On the basis of the study of Karickhoff and co-workers and attached to the thought that the real adsorption could contain more compartments, an application, Origin 8.1, was adopted to probe the information about the compartments. The derivation process is shown as follows

$$C \rightarrow S_1 \rightarrow S_2$$

(38)

where $C$ is the solution phase and $S_1$ and $S_2$ are two sorption compartments. If states $S_1$ and $S_2$ are assumed to differ only in the kinetics of access from the aqueous phase, then $S_1/X_1 = S_2/(1 - X_1)$ at equilibrium, where $X_1$ is the fractional sorbent mass in fast component $S_1$. Access to and from slow state $S_2$ is given by

$$\frac{1}{1 - X_1} \frac{dS_2}{dt} = -k_2 \left[ \frac{S_2}{1 - X_1} - \frac{S_1}{X_1} \right]$$

(39)

where $k_2$ is the kinetic constant for accessing compartment $S_2$. If exchange between the solution phase and $S_1$ is assumed to be sufficiently fast to maintain equilibrium between these two phases, then sorption can be described with one kinetic coefficient ($q_2$) and for closed systems is given by

$$\theta C - RT = \frac{\rho S - (1 - R)T}{\rho S^0 - (1 - R)T} = \frac{\rho S_1 - X_1(1 - R)T}{\rho S_1 - X_1(1 - R)T}$$

$$= \cdots = \frac{\rho S_2 - (1 - X_1)(1 - R)T}{\rho S_2^0 - (1 - X_1)(1 - R)T} = \exp \left[ -q_1 q_2 R_1 (t - t_0) \right]$$

(40)

where $T$ is the total concentration of rutin ($T = \theta C + \rho S$); $S$ is the total concentration adsorbed ($S = S_1 + S_2$); $\theta$ is the volumetric water content; $\rho$ is the solid concentration in resins; $R$ and $R_1$ are retardation parameters defined by ($1/R = 1 + K_p \rho / \theta$ and $1/R_1 = 1 + X_1 K_p \rho / \theta$); and $K_p$ is the equilibrium partition coefficient ($K_p = S/C$). Concentrations with superscript 0 denote values at some initial time $t_0$, taking into account the equilibrium of $C$ and $S_1$. The kinetic model of first-order equations used to describe adsorption rates for both the slowly desorbing fraction and the rapidly desorbing fraction are shown below.

$$\frac{q(t)}{q_0} = F_1 \exp \left[ -q_1 t \right] + F_2 \exp \left[ -q_2 t \right]$$

(41)

where $q(t)$ is the solid-phase sorbate concentration at a given time, $q_0$ is the initial solid-phase sorbate concentration, $F_1$ and $F_2$
are different compartments fractions, and \( q_1 \) and \( q_2 \) are apparent first-order rate constants for the rapidly and slowly adsorbing fractions, respectively.

\[
C \rightarrow S_1 \rightarrow S_2 \rightarrow S_3 \tag{42}
\]

When the process of adsorption was divided into three compartments which were rapidly, slowly and very slowly adsorbing, the first-order equation should be

\[
\frac{dC}{dt} = F_1 \exp(-q_1 t) + F_2 \exp(-q_2 t) + F_3 \exp(-q_3 t)
\]

where the \( q_i \) are constants for the very slowly adsorbing fractions. Correspondingly, that the first-order equation process of adsorption with \( n \) compartments could be deduced with the same method and it should be

\[
\frac{dC}{dt} = F_1 \exp(-q_1 t) + F_2 \exp(-q_2 t) + \cdots + F_n \exp(-q_n t)
\]

When we inquired about all kinetic models, we found that no attempt was made to characterize the extensional delivery parameter and a constant was used instead. The models that are short on delivery parameters for every compartment would not respond to the real relationships among the different courses. Thus, the new delivery parameter was included in this research through analyzing every delivery level.

\[
C \xrightarrow{k_1} S_1 \xrightarrow{k_2} S_2 \tag{45}
\]

in which \( k_1 \) and \( k_2 \) are the rate constants of every adsorption level and \( k_{1'} \) and \( k_{2'} \) are the rate constants of every desorption level, respectively.

When the adsorbate transfers to \( S_2 \), the concentration in \( S_1 \) can be approximated to be constant during the time interval studied because of the dynamic equilibrium. Thus, we approximated \( dS_1/dt \) by

\[
0 = \frac{dS_1}{dt} = k_1 C + k_2 S_2 - (k_{1'} + k_2) S_1
\]

Because the concentration in \( S_2 \) was much less than those in \( S_1 \) and \( C, S_2 \ll C \) and \( k_{2'} \ll k_{1'} \) could be obtained. This means that \( k_2 S_2 \approx 0 \), and eq 43 can be simplified to

\[
0 = k_1 C - (k_{1'} + k_2) S_1
\]

The total mass present in the system was described by

\[
M_t = C + S_1 + S_2
\]

The delivered mass reflected the change in mass in the adsorption process:

\[
\frac{dM_t}{dt} = \frac{dC}{dt} + \frac{dS_1}{dt} + \frac{dS_2}{dt} + \frac{dS_3}{dt}
\]

This approach was valid when the adsorption reached equilibrium

\[
\frac{M_t}{M_0} = e^{-k_{1'}(k_{1'} + k_2)t}
\]

in which \( M_0 \) is mass present at \( t = 0 \). Thus, the slope of a plot of \( \ln(M_t/M_0) \) with time is equal to \(-k_{1'}(k_{1'} + k_2)\). Upon biphasic adsorption, the adsorption curves were described by the sum of two equivalent exponential functions, assuming \( q_1 \gg q_2 \)

\[
\frac{M_t}{M_0} = F_1 e^{-k_{1'}(k_{1'} + k_2)t} + F_2 e^{-k_{1'}(k_{1'} + k_2)t} + F_3 e^{-k_2 k_3 (k_{1'} + k_2) t}
\]

Although adsorption is delivered to the third level, the equation should be deduced as the following:

\[
C \xrightarrow{k_{1'}} S_1 \xrightarrow{k_{2'}} S_2 \xrightarrow{k_{3'}} S_3 \tag{52}
\]

When the adsorbate transfers to \( S_3 \), the concentration in \( S_2 \) can be assumed to be constant during the time interval studied because of the dynamic equilibrium. Thus, we approximated \( dS_2/dt \) by

\[
0 = \frac{dS_2}{dt} = k_2 S_1 + k_3 S_3 - (k_{2'} + k_3) S_2
\]

Because the concentration in \( S_3 \) was much less than those in \( S_2, S_1 \), and \( C, S_3 \ll S_1 \) and \( k_{2'} \ll k_{1'} \) could be easily gained. This meant that \( k_2 S_2 \approx 0 \) and eq 53 could be simplified to

\[
0 = k_2 S_1 - (k_{2'} + k_3) S_2
\]

The total mass present in the system was described by

\[
M_t = C + S_1 + S_2
\]

The delivered mass reflects the change in mass in the adsorption process:

\[
\frac{dM_t}{dt} = \frac{dC}{dt} + \frac{dS_1}{dt} + \frac{dS_2}{dt} + \frac{dS_3}{dt}
\]

\[
= k_1 C - (k_{1'} + k_2) S_1 \tag{47}
\]

By introducing \( C \) into the equation above, \( dM_t/dt \) was obtained as

\[
\frac{dM_t}{dt} = -\frac{k_2 k_3}{k_{2'} + k_3} \frac{k_{1'}}{k_{1'} + k_2} = \frac{k_{1'} k_2 C}{(k_{1'} + k_2) (k_{1'} + k_2)} \tag{57}
\]

Thus, the equation of adsorption delivered to the third level should be

\[
\frac{M_t}{M_0} = F_1 e^{-k_{1'}(k_{1'} + k_2)t} + F_2 e^{-k_{1'}(k_{1'} + k_2)t} + F_3 e^{-k_2 k_3 (k_{1'} + k_2) t}
\]

Correspondingly, the adsorption delivered to the \( i \)th level can be deduced with the same method and can be
expressed as

\[
\frac{M_t}{M_0} = F_1 e^{-k_1/(k_2 + k_1) t} + F_2 e^{-k_1/k_2} + F_3 e^{-k_1/k_2} + \cdots + F_i e^{-k_1/k_i} + \cdots
\]

The equation denotes a general equation of adsorption delivered to the \(i\)th level. Thus, the transmission of the delivery process could be investigated from the adsorption equilibrium by Origin analysis of the homologous parameters, which were different from those in the classical models, we concluded that the forthcoming hypothesis of Wang and Karickhoff was unreasonable. The pattern in which the inductive effect passed to a higher level and the adsorption process contained more compartments was proposed. The real terminated layer and adsorption sections were investigated through a regression of the experimental information. The result showed that the new adsorption isotherm was better fitted than the classical models and that \(R^2 > 0.99\) when we assumed that the fourth inductive effect layer was involved. The

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<th>(K_1)</th>
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Table 7. Regression Result Based on the Adsorption Delivered Effect

Figure 8. Regression curves of the relationship between adsorption amount and time.

4. CONCLUSIONS

In this work, a series of macroporous adsorption resins with different functional groups and pore sizes were synthesized, and the adsorption features of the synthetic resins with respect to the purification effect were studied. The adsorption experimental data were not well fitted by classical models. Considering the restriction of existing models, a new adsorption isotherm model and a new adsorption kinetics model were created according to the multiparameter theory and Karickhoff’s theory. Through analysis of the homologous parameters, which were different from those in the classical models, we concluded that the forthcoming hypothesis of Wang and Karickhoff was unreasonable. The pattern in which the inductive effect passed to a higher level and the adsorption process contained more compartments was proposed. The real terminated layer and adsorption sections were investigated through a regression of the experimental information. The result showed that the new adsorption isotherm model was better fitted than the classical models and that \(R^2 > 0.99\) when we assumed that the fourth inductive effect layer was involved.
new adsorption kinetics model was also in good agreement with the experiment data, assuming that four compartments of an adsorption process was consistent with the current situation. Moreover, we found that the pore distribution of the resins and the temperature of the experiment would play important roles in the adsorption kinetic process.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +86-931-496-8248. Fax: +86-931-8277088. E-mail: didl@icp.cas.cn.

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