

Article

Isoniazid-Modified Silica for Hydrophilic Interaction Chromatography and as an Adsorbent for Dye Removal in Wastewater Samples

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ABSTRACT: The new isoniazid-derived material was synthesized with a surface-immobilizable functional group by a reaction between isoniazid and succinyl anhydride and grafted onto silica surfaces. The material was designed so that multiple functional groups could interact with the guest molecules. Initially, the silica surface was modified with 3-amipropyltrime-thoxysilane. Succinyl isoniazid (SID) was synthesized and then immobilized to 3-aminopropylsilica by an amide coupling reaction to obtain Sil-SID. The ATR-FTIR and ¹H NMR were used to characterize the SID before immobilization. After grafting, Sil-SID was confirmed by elemental analysis, ATR-FTIR, scanning electron microscopy, and thermogravimetric analysis (TGA). The same material was finally used as a stationary phase in hydrophilic interaction chromatography (HILIC) to separate nucleosides and nucleobases and as an adsorbent for wastewater treatment for the first



time. Due to the presence of multiple functional groups and a heteroaromatic ring in the phase, it exhibited excellent separation for polar analytes in HILIC and, at the same time, exceptionally high adsorption capacity and removal efficiencies for an anionic dye in wastewater. The maximum adsorption capacity reached 714.3 mg/g at pH 3. Here, a single material (Sil-SID) was used as a stationary phase and an adsorbent with excellent performance in both cases. This work is a good example of material development and its multiple applications. It will also reduce the design and production costs of novel materials for various applications. A single material can serve two or more purposes.

INTRODUCTION

Isoniazid is one of the most important drugs used in the treatment of tuberculosis. It is a heterocyclic aromatic compound with special properties. Isoniazid and its derivatives showed biological activities of antibacterial,¹ anti-inflammatory,^{2,3} antioxidant,⁴ and anticarcinogenic.⁵ Pyridine ring-containing phase has also been used in chromatography.⁶ Another important property is the formation of complexes with metals leading to improved antibacterial properties.⁷ On the other hand, mesoporous silica-based materials have been used in different fields of applications such as stationary phase for high-performance liquid chromatography,^{8–11} adsorbents for the treatment of contaminated water,^{12,13} solid-phase extraction,¹⁴ electronics,¹⁵ food sciences.²⁰ Therefore, due to the synergistic effect of isoniazid and mesoporous silica, materials developed from them are supposed to have the potential for multiple applications.

Hydrophilic interaction chromatography (HILIC) was first coined by Alpert in 1990 by using surface-modified silica with poly(2-sulfoethyl aspartamide).²¹ HILIC has been generally used as an advanced or updated method of separating basic and highly polar compounds, which is not suitable for

separation in most popular reversed-phase high-performance liquid chromatography with hydrophobized silica stationary phase. Hence, to accomplish the separation needs of polar and basic compounds, various HILIC stationary phases have been developed with mesoporous silica²² and their surface modification by amide,²³ ionic liquids,²⁴ amino,²⁵ diol,²⁶ zwitterionic groups,²⁷ triazole,²⁸ carbohydrates,²⁹ and hydrophilic polymers.³⁰ These stationary phases have been applied for the analysis of many important analytes such as nucleosides and nucleobases,³¹ carbohydrates,³² peptides,³³ proteins,³³ amino acids,³³ oligo saccharides,³⁴ and polar pharmaceuticals.³⁵

On the other hand, water pollution by various dyes from textile, leather, and other industries has become a crucial issue due to industrial growth in the 21st century.³⁶ Therefore, the treatment of industrial wastewater is becoming of prime

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importance to develop a sustainable society.³⁷ To treat this kind of wastewater, various kinds of methods are available like chemical oxidation, membrane separation, photocatalytic degradation, coagulation, and adsorption.^{38–42} However, among these methods, adsorption is the most common due to its simplicity, effectiveness, easy operation, high efficiency, and less secondary pollution.⁴³ Among the developed adsorbents for the removal of inorganic and organic pollutants, mesoporous silica has gained a lot of attention due to its high surface area, tunable structure, very good thermal stability, and large pore volume.^{44–46} Moreover, due to the existence of abundant silanol groups, silica surfaces can be modified with various functional organic molecules.

Keeping in mind the mentioned advantages and applications of isoniazid and mesoporous silica, in this work, we designed and prepared a material derived from isoniazid and mesoporous silica, as shown in Figure 1. Usually, after the



Figure 1. Synthesis of the isoniazid-derived succinyl isoniazid (SID)grafted silica (Sil-SID) organic phase.

column packing, the extra materials remain. To utilize this excess material as well as its further application in different fields for broadening the application of a single material and design of a new material, this work was carried out. The same material was applied as a stationary phase in HILIC for the separation of polar analytes and as adsorbents for the removal of an anionic dye (Congo Red) from wastewater for the first time. As expected, the new material (Sil-SID) shows excellent performance as a stationary phase in HILIC mode separation as well as an adsorbent for the removal of Congo Red from aqueous solutions.

EXPERIMENTAL SECTION

Materials and Reagents. Isoniazid, succinic anhydride, 3aminopropyltrimethoxysilane (APS), diethylphosphorocyanidate (DEPC), and triethylamine (TEA), were purchased from Sigma-Aldrich (Darmstadt, Germany). Numerous solvents such as chloroform, tetrahydrofuran, methanol, diethyl ether, and ethanol were obtained from the VWR (Darmstadt, Germany). The Tanaka test probes (Table S1), nucleosides, and nucleobases were obtained from Sigma-Aldrich (St. Louis, MO, USA). The anionic dye (Congo Red, CR), hydrochloric acid, and sodium hydroxide were purchased from TCI (Tokyo, Japan). The silica particles were obtained from AppliChrom Silica HR1003 (Germany) with a surface area of 331 m²/g, a pore size of 10 nm, and a diameter of 3 μ m.

Initially, the silica particles were modified with 3-aminopropyltrimethoxysilane (APS) to obtain Sil-APS. Succinyl isoniazid (SID) was prepared from the reaction between succinic anhydride and isoniazid and then immobilized on silica to obtain Sil-SID (Figure 1). The prepared isoniazidderived mesoporous silica material (Sil-SID) was characterized and applied as a stationary phase in HILIC and the adsorbent. To be used as a stationary phase, the material was packed into narrow-bore stainless steel columns of 150×2.1 mm i.d. The column packing was carried out with the slurry method by the company Dr. Maisch GmbH, Germany. The reference zwitterionic column was purchased from Merck, Germany. Other HILIC reference columns such as Luna-NH2 and Luna-Diol were obtained from Phenomenex, USA. To understand the performance of the new material Sil-SID, a comparative table of physical properties with the reference column materials is given in Table S2, and the experimental details are also presented in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Characterization. Mesoporous silica materials have been functionalized with various ligands to be used as the HILIC stationary phase.⁴⁷ At the same time, different functional groups were incorporated onto silica to be applied as adsorbents for wastewater treatment.^{13,48} Here, we chose an isoniazid-derived ligand with triple amide and pyridyl ring groups (Figure 1) to be used as the HILIC stationary phase for the separation of polar compounds and as an adsorbent for the removal of dye with the same material for the first time to increase applicability of a single material and reduce the preparation cost. The isoniazid-derived new mesoporous silica material (Sil-SID) was characterized by different techniques like elemental analysis, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). Half of the prepared material was packed into a stainless-steel column ($150 \times 2.1 \text{ mm i.d.}$) for HILIC mode chromatographic separation, and the remaining half was used as adsorbent for the removal of dye from aqueous solutions.

The surface coverage of the silica material by the APS and SID was calculated from the elemental analysis results using the following equation to 4.34 and 0.82 μ mol/m², respectively (Table S3).⁴⁹

$$N(\mu \text{mol/m}^2) = 10^6$$
. $P_c/1200n_c - P_c(M-1) \times 1/S$

where, N = surface coverage, $S = \text{specific surface area } (m^2/g)$, $P_c = \text{measured carbon } \%$, M = molecular weight of bonded molecule, $n_c = \text{number of carbon atoms in the bonded silane}$ molecule, and the factor $P_c(M-1)$ corrects for the weight increase of the silica.

The SEM was measured for the silica particles before and after grafting to observe the particle size and whether the silica broke during stirring, which is detrimental to use as a stationary phase for LC (Figure S2). Moreover, the grafting of APS and SID was also confirmed by TGA (Figure 2 and Table S3). Furthermore, the immobilization of the APS and SID onto silica was determined by the ATR-FTIR analyses.

For example, a broad band at 3321 cm^{-1} is attributed to N– H stretching. Slight bands at 2936 and 2855 cm⁻¹ indicate the C–H bond stretching of Sil-SID, and sharp bands at 1641 and 1548 cm⁻¹ clearly indicate amide bonds (Figure S3).¹¹

Chromatographic Evaluation. In HPLC, a column selection system (CSS) is very important to identify suitable



Figure 2. TGA curves of bare silica, Sil-APS, and Sil-SID.

columns for the separation of an analyte or a complex real sample.⁵⁰ Some test probes have been developed to characterize columns for applying the CSS. In HILIC, Tanaka test probes (Figure S4) were developed to evaluate a newly prepared column to understand its applicability.⁵¹ When the Tanaka test probes were used for the developed column (Sil-SID) in this work and compared with the common and commercial HILIC columns such as diol (Luna-Diol), zwitterionic (ZIC-HILIC), and amine (Luna- NH_2), very comparative results were obtained (Figure 3 and Table S4).

Therefore, the developed material used in the Sil-SID column is very suitable for application in the HILIC mode separation. For further observation, the column with Sil-SID was used for the separation of 14 nucleosides and nucleobases, whereby the best results were obtained with this column compared to the commercial columns (Figure 4). While the Luna-NH₂ has separation problems with the peak pairs 2/3, 6/7, and 8/9, the ZIC-HILIC with 2/3, 7/8, and 11/12, only the peak pair 2/3 is not separated with the Sil-SID. The theoretical plate count and peak asymmetry data are given in the Supporting Information (Table S5). Here, the chromatographic conditions were optimized for Sil-SID and reference columns. For the reference column, ACN-ammonium acetate buffer (20 mM in the aqueous portion, pH 4.7) (95:5, v/v) mobile phase gave high retention of the analytes. On the other hand, (90:10) presented very low retention, and therefore, to compare the chromatograms, (95:5) was selected for the Sil-SID column and lowered the buffer concentration to 10 mM to avoid salt precipitation.

It is possible to explain the reasons for the outstanding separation abilities of Sil-SID in HILIC. In HILIC, the separation mechanism is still under investigation.^{47,52,53} The initial mechanism was proposed by Alpert,²¹ who invented the HILIC mode separation. According to this assumption, analytes are partitioned between the standing-water-rich layer



Figure 3. Separation of Tanaka test probes (a-d) on Sil-SID and reference columns. Mobile phase: ACN-ammonium acetate buffer (20 mM in the aqueous portion, pH 4.7) (90:10, v/v). Column temperature: 30 °C. Flow rate: 0.2 mL/min. UV detection: 254 nm. For Sil-SID, ACN-ammonium acetate buffer (10 mM in the aqueous portion, pH 4.7) (95:5, v/v).



Figure 4. Separation of 14 nucleosides and nucleobases on Sil-SID and reference columns. Mobile phase: ACN-ammonium acetate buffer (20 mM in the aqueous portion, pH 4.7) (90:10, v/v). Column temperature: 30 °C. Flow rate: 0.2 mL/min. UV detection: 254 nm. For Sil-SID, ACN-ammonium acetate buffer (10 mM in the aqueous portion, pH 4.7) (95:5, v/v).



Figure 5. Effect of (a) pH, (b) adsorbent dosage, (c) initial concentration, and (d) contact time on the adsorption of Congo Red using Sil-SID.



Figure 6. Langmuir adsorption isotherm (a) and Freundlich adsorption isotherm (b) for the adsorption of CR on Sil-SID.

around the stationary phase surface and the organic-rich moving layer. However, over time, many other interactions have been suggested that may work together or individually depending on the structure of the stationary phases and properties of the analytes such as hydrogen bonding, adsorption, dipole–dipole interaction, ion exchange, $\pi-\pi$, carbonyl- π , and $n-\pi$.^{47,54–56} In Sil-SID, the pyridyl ring, lone pair electron of nitrogen, and multiple amide bonds are supposed to take part in multiple interactions, as well as partition mechanisms. Additionally, the free amine groups on the silica surface may have taken part in the interaction mechanism, as all the amine groups did not react with the SID.

Adsorption Study. To observe the broad applicability of the developed material, it was used as an adsorbent for wastewater treatment. As an example, an anionic dye (CR) was selected as a probe to observe the removal performance from aqueous solutions, and various adsorption parameters were studied.

Effect of pH on Dye Adsorption. Using a 0.01 g Sil-SID adsorbent and an initial dye concentration of 400 mg L^{-1} in a 30 mL solution, the effect of pH on the equilibrium adsorption of CR was analyzed in the pH ranges 3 to 12. This experiment was initially conducted without an adsorbent to determine whether the dye solutions were affected in any way by varying pH levels. There were slight spectrum shifts brought on by variations in dye ionization, but no significant decolorization or degradation happened during the experiment. The most adsorption of CR by Sil-SID was observed at pH 3 and then decreased with increasing pH up to 6. At pH 7, the adsorption of CR increases significantly and then starts to decrease in basic conditions up to pH 12, as indicated in Figure 5a, indicating that the adsorbent is ideal under acidic conditions, possibly because it contains positively charged sites. The adsorption capacity was enhanced at pH 7, which may be due to an ion exchange interaction between CR anionic groups and the aminopropyl moieties on the surface of the silica. Detailed expected interaction mechanism is described in the possible interaction mechanism part.

Effect of Adsorbent Dosages. At pH 7 and room temperature, the impact of the adsorbent concentration on the adsorption capacity (Q_e) was examined using different adsorbent dosages of 10–20 mg per 30 mL with an initial dye concentration of 400 ppm. As demonstrated in Figure 5b, it is simple to conclude that when the dosage was increased from 0.01 to 0.02 g, CR dye removal rose from 73.84% to

95.06%. The adsorbent increase means an increased surface area, and it is likely to increase the removal percentage.

Conversely, for the CR, the Q_e showed a declining trend from 886.1 to 570.3 mg/g, accompanied by an increase in the adsorbent dosages. The observed pattern could be explained by a reduction in the total adsorption area per unit mass of the adsorbent because of adsorption sites aggregating or overlapping.⁵⁷

Effect of Initial Dye Concentration. Figure 5c illustrates the variation in CR adsorption capability on Sil-SID with regard to the initial concentration. At room temperature and pH 7, the effects of varying initial dye concentrations (100, 200, 300, 400, and 500 mg/L) on the adsorption of CR on Sil-SID were investigated in a 30 mL solution utilizing a 0.02 g Sil-SID adsorbent. The findings demonstrated that increasing the initial CR dye concentration (C_o) from 100 to 500 mg/L enhanced the adsorption capacity from 145.0 to 712.6 mg/g.

Effect of Contact Time. About the contact time, Figure 5d depicts the variation in CR adsorption capacity on Sil-SID. In a 30 mL solution containing 0.02 g of Sil-SID adsorbent, the effects of contact time on the adsorption of CR on Sil-SID were investigated at initial dye concentrations of 300 mg/L at pH 7 and room temperature. The first 5 min showed a quick uptake of the dye, which dropped down and eventually reached equilibrium after 60 min, at which point there was very little dye that had been adsorbed. The abundance of dye molecules on the surface of the Sil-SID and the progressive adsorption could be the cause of the dye's initial fast adsorption.

Adsorption lsotherms. At varying initial dye concentrations (100-500 mg/L), adsorption isotherm tests for CR onto Sil-SID were carried out. Eqs 1 and 3 were used to connect the measured equilibrium adsorption data to the Langmuir and Freundlich models, respectively. Below is the Langmuir equation in the linear form.

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{C_{\rm e}}{Q_{\rm max}} + \frac{1}{Q_{\rm max}K_{\rm L}}$$
(1)

where $K_{\rm L}$ = the ratio of adsorption to desorption rate (Langmuir isotherm constant), $C_{\rm e}$ = the equilibrium concentration of free CR dye molecules in the solution (mg/L), $Q_{\rm e}$ = the equilibrium adsorption capacity (the amount of CR dye adsorbed by 1 g of Silica-SID adsorbent) (mg/g), and $Q_{\rm max}$ = maximal specific adsorption of CR at equilibrium related to site saturation (monolayer coverage capacity) (mg/

g). The plot of C_e/Q_e vs $C_{e'}$ as indicated in Figure 6a, can be used to test the Langmuir model. C_e/Q_e and C_e at room temperature have a linear relationship, and the values of Q_{max} and K_L were determined from the slope and intercept, respectively. The dimensionless quantity known as R_L , or adsorption intensity, establishes the favorable nature of the Langmuir isotherm. The following formula (eq 2) displays the R_L equation.

$$R_{\rm L} = \frac{1}{1 + K_{\rm L}C_{\rm o}} \tag{2}$$

where C_{o} is the initial dye concentration that was applied to the adsorption tests.

The adsorption intensity of the adsorbent toward the dye molecule is ascertained using the Freundlich isotherm model (eq 3).

$$\log Q_{\rm e} = \log K_{\rm F} + \frac{1}{\rm n} \log C_{\rm e} \tag{3}$$

where C_e is the equilibrium concentration (mg/L), K_F is the Freundlich constant, and 1/n is the heterogeneity factor relating to the capacity and intensity of the adsorption. As seen in Figure 6b, the Freundlich model can be checked by charting log C_e vs log Q_e . The slope and intercept provided the values of K_F and 1/n, respectively.

The adsorption parameters from both isotherm models are shown in Table 1. The Langmuir model, which works well in monolayer adsorption processes, postulates that adsorption takes place at particular homogeneous spots on the adsorbent.

 Table 1. Adsorption Isotherm Parameter for Adsorption of

 CR on the Sil-SID

Langmuir isotherm				Freundlich isotherm		
Q _{max}	$K_{\rm L}$	R^2	R _L	n	$K_{\rm F}$	R^2
714.3 mg/g	0.7368	0.9693	0.0027	5.838	375.5 mg/g	0.9091
maximum sorption capacity:714.3 mg/g			maximum sorption capacity:375.5 mg/g			

The Langmuir model predicts a maximum monolayer adsorption (Q_{max}) of 714.3 mg/g for CR onto Sil-SID, which is extremely close to the experimental results (712.6 mg/g) obtained at an initial concentration of 500 mg/L in equilibrium dye adsorption tests. R_L provides a qualitative indicator of the favorable circumstances of the adsorption process in the Langmuir model. It designates the kind of adsorption as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The R_L values for 100, 200, 300, 400, and 500 mg/L in our investigation are 0.0134, 0.0067, 0.0045, 0.0034, and 0.0027, in that order. These points point to an extremely advantageous adsorption mechanism.

The adsorption is thought to get harder as n decreases in the Freundlich model. Based on the isotherm's order, 1/n can be categorized as irreversible (1/n = 0), favorable (0 < 1/n < 1), or unfavorable (1/n > 1). At room temperature, the value of 1/n in our investigation was computed to be 0.1713, indicating that the adsorption process will be advantageous. Significant adsorption occurs at low concentrations when the value of 1/n is less than unity and vice versa. At higher concentrations, the rise in quantity adsorbed with concentration is insignificant.⁵⁸

An approximate measure of the adsorption capacity is the anticipated K_F value (375.5 mg/g); the higher the K_F value, the

greater the adsorption capacity. The adsorption capacity calculated from the Langmuir model was shown to be nearer to the experimental value; also, the Langmuir model yielded a greater regression coefficient than the Freundlich model. The Langmuir isotherm uses the adsorbate's monolayer production to calculate the adsorbent's surface coverage. To support the idea of monolayer formation, we used the assumption in this study that Sil-SID (positive ion) and CR (negative ion) have an adsorption process through electrostatic attraction. On the contrary, the Freundlich model depicts the bond of attraction between them and presupposes that the adsorbate forms many layers. In this instance, there was no attraction between the molecules of the adsorbate (Congo Red). Because of this, the Freundlich model does not agree with the experimental results and represents only a subset of the adsorbed molecules.

Pseudo-First-Order and Pseudo-Second-Order Kinetic Model. The rate at which an adsorbate is adsorbed, which determines how long it takes for the adsorbate to adsorb to the solid—liquid surface, is described by adsorption kinetics. The most often used pseudo-first-order model by Lagergren has a linearized-integral version (eq. 4) that is

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{4}$$

It is possible to linearize the integral form of the pseudosecond-order model (eqs. 5 and 6) as follows.

$$\frac{t}{Q_{t}} = \frac{1}{k_{2}Q_{e}^{2}} + \frac{t}{Q_{e}}$$
(5)

$$\mathbf{h} = k_2 q_{\rm e}^2 \tag{6}$$

where the adsorption capacities in mg/g at equilibrium and time (min) are denoted by Q_e and Q_t , respectively. The rate constant for pseudo-first-order sorption is $k_1(\min^{-1})$, the rate constant for pseudo-second-order sorption is k_2 (g/mg-min), and the initial adsorption rate is represented by h (mg g⁻¹ min⁻¹). Should the kinetic data exhibit pseudo-first-order kinetics, a plot of $\ln(Q_e - Q_t)$ against t ought to yield a linear relationship, with the associated values of k_1 and Q_e derivable from the straight line's slope and intercept, respectively. The t/qt versus t linear plot verifies that the kinetic data conform to the pseudo-second-order kinetics. The values of Q_e and k_2 were obtained from the straight line's slope and intercept, respectively. Nonetheless, to assess the models' applicability, the error analysis function—that is, the Chi square test (X^2) formulas (eq. 7)—was also applied in addition to the R^2 value.

$$X^{2} = \Sigma \frac{(Q_{e} \exp - Q_{e} \text{model})2}{Q_{e} \text{model}}$$
(7)

The experimental and model values of the adsorption capacity are denoted by $Q_e \exp(mg/g)$ and $Q_e model(mg/g)$, respectively. A pseudo-first-order and a pseudo-second-order model's linearized form fitted to the experimental data are shown in Figure 7a,b.

A summary of correlation coefficients $(R_1^2; R_2^2)$, Chi square values $(X_1^2; X_2^2)$, and the kinetic parameters derived from the utilization of the two aforementioned kinetic models are presented in Table 2. From the table, it can be studied that R_1^2 and R_2^2 values in both models are high (around 0.99). On the other hand, the pseudo-second-order model showed that X_2^2 (0.4128) shows a very low value. As a result, it can be stated that the pseudo-second-order model describes the CR



Figure 7. Pseudo-first-order kinetic plot (a), pseudo-second-order kinetic plot (b), and intraparticle diffusion model (c) plot for the adsorption of CR on Sil-SID.

Table 2. Equation Parameters of Pseudo-First Order,Pseudo-Second Order Kinetic Models, and IntraparticleDiffusion Model Plot for the Adsorption of CR on Sil-SID

model	parameter	initial dye concentration (300 ppm)
pseudo first order	K_1	0.0645
	Q_{e1}	72.72
	R_1^{2}	0.9897
	X_1^{2}	1863.0
pseudo second order	K_2	0.0021
	Q_{e2}	454.5
	R_2^{2}	0.9998
	X_2^{2}	0.4128
intraparticle diffusion model	$K_{ m ipd}$	8.969
	С	375.8
	R^2	0.9610

adsorption kinetics on Sil-SID, supporting the idea that adsorption is a chemical process. $^{\rm 59}$

Intraparticle Diffusion Model. The slowest phase in the multistep adsorption process determines the total rate. Adsorbate molecules are transported from the liquid phase to the solid adsorbent's surface and then diffuse into the interior pores. To determine the rate-limiting step, the intraparticle diffusion model was constructed using the adsorption kinetic experimental data. Weber and Morris

suggest the intraparticle diffusion model, whose linear mathematical form is expressed as eq 8

$$Q_{t} = K_{ipd}t^{1/2} + C \tag{8}$$

where the intraparticle diffusion rate constant is expressed as K_{ipd} (mg g⁻¹ min^{-0.5}), the adsorption capacity at time *t* is expressed as Q_t (mg/g), and constant *C* is proportional to the boundary layer thickness. Figure 7c displays the plots of the intraparticle diffusion model for CR on Sil-SID, and Table 2 lists the formula parameters. Characterizing the impact of intraparticle diffusion may be done by correlating the numerical value of the intraparticle diffusion rate (K_{ipd}), which is not the same as an actual reaction rate with system variables.⁶⁰ The maximum adsorption capacity of the Sil-SID material is extremely high (714.29 mg/g) compared to that of the other reported silica-based adsorbents (Table 3).

Mechanism for the ultrahigh adsorption capacity of the Sil-SID material to the CR dye is illustrated in Figure 8.

There are multiple interactions on Sil-SID as well as in the dye molecule. It showed very high adsorption capacity even at neutral pH indicating ion exchange, $\pi - \pi$, and carbonyl- π interactions (Figure 5a). The highest adsorption capacity was observed at pH 3 probably due to the ionization of free amine and pyridine nitrogen. Therefore, the new material Sil-SID has efficient applications in the field of HILIC and the adsorption of dyes. More applications such as the adsorption of carbon

Table 3. Adsorption Capacity of Silica-Based Adsorbents for the Removal of Congo Red

adsorbents	adsorption capacity, $Q_{\rm e} \ ({\rm mg/g})$	refs
graphene oxide-silica	333.3	61
xanthan gum–graft-poly(acrylamide) /SiO ₂ nanocomposite	202.4	62
aniline propyl silica xerogel	40.86	63
polyethyleneimine-functionalized lignin/SiO ₂	442.5	64
ZnO-modified SiO ₂	90.10	65
montmorillonite-silica nanocomposite	172.4	66
ZnFe ₂ O ₄ /SiO ₂ /tragacanth gum magnetic nanocomposite	128.2	67
polyamidoamine dendrimer-silica composite	16.04	68
Ni _{0.5} Cu _{0.5} Fe ₂ O ₄ /SiO ₂ nanocomposites	63.49	69
Co ₃ O ₄ @SiO ₂ core/shell–nylon-6 magnetic nanocomposite	138.9	70
Si-SID	714.3	in this work



Figure 8. Schematic illustration for the possible adsorption mechanism of CR dye on the Sil-SID surface.

dioxide onto Sil-SID are supposed to work (carbon capture) and will be studied in the future.

CONCLUSIONS

Herein, we have demonstrated the development of a novel single material to be used as a stationary phase for separating nucleosides and nucleobases and as an adsorbent for removing dyes from an aqueous solution. The material was evaluated with the separation of Tanaka test probes in HILIC as the stationary phase and the adsorption of anionic dye Congo Red as an adsorbent. The new material showed promising performance for the separation of 14 nucleosides and nucleobases compared with the common commercial HILIC columns. On the other hand, the maximum adsorption capacity was 714.3 mg/g, which is much higher than that of the developed silica-based adsorbents. It will open a door for the development of new single materials that can serve two or more purposes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c11535.

Synthesis of succinyl isoniazid and immobilization onto silica; proton NMR; SEM; FT-IR and elemental analysis; TGA; liquid chromatography; physical properties of tailor-made and reference columns; data analysis; adsorption study; and characterization of the new phases (PDF)

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Notes

The authors declare no competing financial interest.

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