Sorption Study of Water Vapor and a Dye on Chitosan-Based Framework Materials

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ABSTRACT: Two types of chitosan framework materials were functionalized with carboxyl groups via a supramolecular cross-linking process by citric acid (CA) and trimesic acid (TMA). The role of surface chemistry (i.e., functional groups) and textural properties (i.e., pore size and surface area) in adsorption properties of these chitosan frameworks toward water vapor and dye was investigated. Extensive characterizations using N₂ adsorption−desorption, contact angle measurements, differential scanning calorimetry, atomic force microscopy, and confocal microscopy were carried out to understand structure−property relationships of these framework materials. The dynamic vapor sorption analyzer measured water vapor sorption percentage (R %) values of 46.7, 43.9, and 41.5 for TMA1, CA1 framework materials, and chitosan, respectively. The calculated adsorption percentage values of dyes in aqueous solution were 69.7, 39.2, and 18.8 (R %) for TMA1, CA1, and chitosan, respectively.

INTRODUCTION

Evaluation of physiochemical properties of newly synthesized materials is indispensably critical for the fate of their applications. Understanding the role of water molecule interactions with other materials is essential before using them because of their pertinent effects on the swelling and hydration properties of materials. These interactions have been widely investigated in diverse types of materials such as cellulose, starch, fruit pills, woods, cork, biomass, and chitosan. Application of chitosan materials with high sorption capacity toward water is being developed for use in dehumidifiers and heat exchangers as adsorbents, whereas chitosan materials with low water affinities are being considered for use in food packaging.

Chitosan has high tendency to dissolve in water, which makes it an unsuitable candidate in many applications, particularly the aforementioned ones. Therefore, there is a need to modify the structural and chemical properties of chitosan to overcome this obstacle. In this regard, cross-linking is one of the most promising techniques and has been used in a few studies to obtain insoluble chitosan-based materials with tunable water uptake properties. A study by Kildee et al. described application of genipin as a cross-linker to originate packaging film and indicated that cross-linking has significant effect on reducing the water vapor sorption properties of the generated chitosan material. In another study, Acevedo-Fani et al. utilized ethyl(dimethylaminopropyl) carbodiimide/N-hydroxysuccinimide as a cross-linker to design film for packaging of food. The cross-linking process in these studies reduced water vapor sorption capacity by eliminating the porous structure of materials, which made them suitable for use as packaging film.

As mentioned earlier, applications of chitosan and its modified forms as adsorbents have been investigated in many studies for removal of different pollutants, which revealed the crucial role of hydration phenomena and swelling properties of these materials. A few studies showed that the presence of organic vapor pollutants from the atmosphere can be involved in competitive sorption of water vapor because of the displacement of water molecules with adsorbed organic species. This competition can serve to reduce the removal efficiency of adsorbents; therefore, assessment of water sorption properties is essential to understand the adsorption process. A water vapor sorption study can therefore be used as a valuable technique for characterization using measurement of sorption isotherms. The dynamic vapor sorption (DVS) technique has been introduced more recently for studying the sorption properties of materials, which offers high data reproducibility and short measurement time.

Depending on the type of the modification process, chitosan materials may adopt variable surface chemistry (e.g., amine, hydroxyl, and carboxyl) and textural properties (e.g., surface area and pore size). Enhancement in adsorption properties of chitosan-based adsorbents take place because of alteration in physicochemical characteristics (i.e., surface chemistry and...
textural properties) that finally affect interactions (e.g., hydrogen bonding and van der Waals) and hydrophile–lipophile balance (HLB) properties at the surface binding sites.

In a previous report, chitosan framework materials were synthesized using two types of cross-linkers [citric acid (CA) and trimesic acid (TMA)] using a one-pot method. Herein, this study reports systematic adsorption properties of chitosan framework materials toward water vapor and dye molecules. This study hypothesized that the application of CA and TMA as tripodal cross-linkers would potentially enhance the adsorptive capacity of chitosan-based materials because of their unique structures. Employment of such tripodal cross-linkers enables the generation of a three-dimensional network, specifically in the form of planar versus nonplanar could yield chitosan materials with tunable adsorptive properties.

To support the water vapor sorption study results and gain a better insight into the structure–property relationship of chitosan framework materials, several complementary techniques such as N₂ adsorption–desorption, differential scanning calorimetry (DSC), contact angle measurement, confocal microscopy, and atomic force microscopy (AFM) were employed alongside a methylene blue (MB) adsorption study in aqueous solution. MB is a commonly used cationic dye in the diving industry because of its high water-solubility property. MB is hazardous, especially if ingested. In many studies, adsorptive removal of MB with cross-linked chitosan is reported effective owing to its high adsorptive capacity, high surface area (SA), and presence of variable functional groups (e.g., OH and NH₂). To address the need for development of renewable biomaterial-based adsorbents with improved dye adsorption capacities, synthesized chitosan framework materials mentioned in this study could represent a versatile new class of adsorbents.

The results of this study will contribute to development of chitosan framework materials with application as adsorbents, dehumidifiers, and packaging films owing to their tunable properties in terms of interaction with water molecules.

RESULTS AND DISCUSSION

Because of the complexity of the chitosan structure and its modified forms and presence of various functionalities, evaluating the polarity and its effect on the adsorptive behavior can provide a useful means for understanding the adsorption process. Water contact angle measurement is a useful technique, which enables evaluation of polarity and HLB properties of the surface. A new technique based on the Young–Laplace equation was designed to measure the water contact angles. In this approach, a first-order perturbation method assists to analytically solve the Young–Laplace equation according to photographic images of drops. Figure 1 represents the water contact angle measurements on chitosan materials. Noticeably, all chitosan materials in this study could be considered generally hydrophilic because the measured values of contact angles are less than 90°; however, the greater hydrophilic character of the CA1 framework can arise from existence of a greater number of functional groups (e.g., COOH, NH₂, and OH) on its structure. Although TMA1 has same functionalities on its structure, the presence of aromatic rings in the structure and their orientations makes it less hydrophilic. Interestingly, resistance of chitosan toward water diffusion after 15 s (cf. Figure 1iii) may be the result of the lack of channels, while existing channels inside the TMA1 and CA1 framework materials may serve as diffusion ports for transferring the water molecules.

The obtained results from the N₂ adsorption–desorption isotherm for Chi, and TMA1, and CA1 samples are given in Figure S1. According to the IUPAC classification, shapes of the isotherms for the TMA1 and CA1 materials corresponds to type IV and V systems, respectively, where these IUPAC categories describe adsorption for mesoporous materials (pore diameter for CA1 and TMA1 is 7.8 and 6.6 nm, respectively). TMA1 framework with type IV isotherm has a stage at the beginning of the sorption process in which monolayer coverage is complete and multilayer adsorption begins, whereas CA1 has only one step with multilayer sorption. The specific SA calculated using the Brunauer–Emmett–Teller (BET) method for Chi (0.29 m²/g), CA1 (0.43 m²/g), and TMA2 (33.35 m²/g) indicated that the type and ratio of cross-linking can alter the textural modification magnificently. The large SA value for the TMA1...
framework materials are shown in Figure 2a. The successive for isotherm of these materials in Figure 2b. Completed. This observation agrees with the observed hysteresis TMA1 and pristine chitosan takes a longer time to be sample is almost equal, desorption of water vapor molecules on completion of the adsorption/desorption processes of the CA1 indicates that rate of adsorption is faster for cross-linked sorption of all chitosan samples are close while it increases with saturation point. Nevertheless, the running time for water vapor sorption process. Disappearance of mesopores from the structure of the CA1 framework material during water vapor sorption can be explained on the basis of its structure. Variable cross-linkers (TMA vs CA) have diverse effects on properties of the final cross-linked products. Where cross-linking the chitosan by the TM molecule with a planar shape results in layered and rigid structure, CA offers more flexibility to the chitosan structure because of its nonplanar structure.

The obtained isotherms from water vapor sorption using the DVS instrument for variable chitosan materials are given in Figure 2b. The success of sorption mass uptake curves become apparent in response to the steps in the external water content. Kinetic curves approach an equilibrium point at each step and subsequently reach the saturation point. Nevertheless, the running time for water vapor sorption of all chitosan samples are close while it increases with the following trend; CA1 < TMA1 < chitosan. This trend indicates that rate of adsorption is faster for cross-linked samples. In addition, while the running time required for completion of the adsorption/desorption processes of the CA1 sample is almost equal, desorption of water vapor molecules on TMA1 and pristine chitosan takes a longer time to be completed. This observation agrees with the observed hysteresis for isotherm of these materials in Figure 2b.

The observed hysteresis for water vapor sorption in TMA1 can be explained by the collapse of mesopores and structural deformation similar to the N2 adsorption isotherm. In addition, another reason for occurrence of the hysteresis phenomenon is because of swelling properties that can take place during the dehydration process. The adsorption process undergoes two stages; (i) in the first stage, water adsorbs on the surface, where it can form clusters around the hydrophilic functional groups (e.g., COOH, OH, NH2), and (ii) in the second stage, water diffuses into the polymer network.

The chitosan materials were tested using DSC right after the water swelling test to evaluate the hydration in adsorbents. DSC results showed an endothermic peak ca. 100 °C, which is attributed to the elimination of adsorbed water (cf. Figure S2). Lower observed intensities of this thermal event for chitosan and CA1 adsorbents compared to TMA1 is related to a reduced amount of water bound to the surface because of their smaller SA. In turn, a wide temperature transition of the CA1 sample infers greater stabilization of water in the interior part of the polymer matrix versus surface bound environments.

The presence of various active sites and channels in the framework materials proved by the water vapor sorption experiment motivated us to explore the sorption abilities of these chitosan frameworks toward a cationic dye, MB, in aqueous solution. Organic dyes are widely employed in many industries, which can cause serious environmental pollution because of their toxicity and carcinogenic effects in humans and animals. Dye removal is therefore an essential step for treatment.
of the factory effluents. Chitosan materials as adsorbents are promising candidates for uptake of these pollutants. Herein, adsorption of MB using the chitosan framework materials was studied by investigating the effects of parameters such as contact time, pH, and concentration. In Table S1, the calculated monolayer adsorption capacity (Q_m) from the Sips isotherm model (Figure 3a) provides a measure for uptake of MB along with the best-fit results. A comparison of the Q_m values for the

Figure 3. (a) Adsorption isotherms, (b) kinetic uptake profile vs time, (c) single-point sorption at variable pH, and (d) adsorption–desorption cycle of MB at 293 K. Chi (yellow circle solid); CA1 (green circle solid); and TMA1 (blue circle solid).

Figure 4. Confocal microscopy images of chitosan materials with RH (1 mM) at variable exposure times with 10 Å image magnification: (i) 2, (ii) 10, and (iii) 30 min.
chitosan framework materials indicates that TMA1 displays the highest uptake, which implies its higher SA and polarity. Apparently, the strong bonding affinity of MB with TMA1 relates to possible π−π stacking between the aromatic rings of MB and TMA of the cross-linked chitosan framework.

MB sorption kinetic results indicated that saturation of the active adsorption sites of the chitosan materials with MB occurs within ca. 30 min (Figure 3b). The PFO kinetic models were used to analyze the kinetic results, and estimates of $q_e$ and $k_1$ were obtained by plotting the $Q_e$ against time (cf. Figure 3b). A comparison of the kinetic uptake results for various chitosan materials are given in Table S1, which indicates that cross-linking contributes to greater sorption capacity as follows: TMA1 > CA1 > Chi, in agreement with the isotherm study. The goodness-of-fit factors ($R^2$ and $\chi^2$) revealed that the PFO model provides a good description for the experimental results that infers a reversible exchange between the solid phase of the adsorbent and the aqueous phase.

The single-point adsorption test for MB at variable pH (cf. Figure 3c) shows a strong dependence on the surface charge of chitosan materials. Favorable binding between MB and the chitosan material surface occurs because of the existence of electrostatic interactions and hydration phenomena. Carboxyl groups are inferred as the active sites for MB adsorption on modified chitosan framework materials; therefore, an increase in the pH increases the negative charge of the surface and accounts for the favorable observed MB adsorption, which is in accordance with the results of zeta-potential measurements. The uptake properties of all materials show a sudden drop-off, as evidenced by decreased sorption capacity at pH values above 8 because of precipitation of MB.

The elution process using NaCl (aq) was utilized for the removal of adsorbed MB in several cycles and offered a low-cost and facile method for the regeneration. The concentration of bound MB for the TMA1 system is shown in Figure 3d for several adsorption−desorption cycles. The adsorption of MB reaches an equilibrium within approximately 1 h, whereas 90% of the bound dyes are desorbed within the first 30 min after washing. The TMA1 was reset by using water and subjected to additional cycles of adsorption−desorption of MB. This process was repeated for four cycles in which the uptake capacity of MB dropped significantly for the first cycle and stayed constant for the rest of the cycles. This observation can be explained based on the variable types of adsorption in the TMA1/MB system. It can be assumed that adsorption of MB onto these frameworks is primarily physical, so the application of a monovalent salt with an elevated level could saturate the binding sites and may result in desorption of the adsorbed dyes; however, the result of regeneration study on TMA1 infers that chemisorption may play a role in the process.

To further study the sorption kinetics and map the morphology of different chitosan materials, confocal microscopy was employed and rhodamine B (RH) was used as a dye probe because of its chemical structure similarity to MB (cf. Figure S4). Figure 4 illustrates several representative confocal images for the Chi, CA1, and TMA1 in the presence of RH at certain exposure intervals (2, 10, and 30 min). The variable fluorescence emission profile shows the extent of dye diffusion into the structure of various chitosan materials. By keeping the laser beam intensity and RH concentration ($C_{RH} = 1 \mu M$) constant, the progression of dye diffusion from the bulk solution to the interior adsorption sites is achieved (cf. Figure 4). The continual movement of RH over these intervals indicates that cross-linking not only prevents dye diffusion but also improves it by providing hydrophobic channels. These channels can be created during the cross-linking reaction because of pillaring effects. Furthermore, comparison of brightness in the confocal images of RB dyes illustrates that the TMA1 (cf. Figure 4i−iii) framework materials with intense brightness of green have a greater affinity toward RB, probably because of the presence of π−π stacking between the aromatic rings, in agreement with the results of the MB adsorption study.

**CONCLUSIONS**

Two chitosan framework materials containing carboxyl functional groups were synthesized using CA and TMA cross-linkers. The presence of aromatic rings in the structure of TMA1 leads to the formation of channel structures, which form a water port for transferring the water molecules inside the chitosan polymeric network. The channels of the network are occupied by water molecules via hydrogen bonding at low pressure. The chitosan framework materials exhibited variable adsorption affinity toward MB dye molecules from aqueous solutions because of the presence of variable polar functional groups. The existing of π−π stacking interactions between layers of the chitosan matrix in the TMA1 framework resulted in the greater MB uptake, which is further substantiated by intense fluorescence light using confocal microscopy. The observed differences for water vapor and dye uptake capacities of chitosan framework materials in this study come from differences in the surface chemistry and textural properties of each chitosan system. These results are in...
accordance with the variable HLB properties of the chitosan frameworks, consonant with the type of the cross-linker (CA and TMA).

**EXPERIMENTAL SECTION**

**Materials.** CA, TMA, dimethyl sulfoxide (DMSO), low-molecular weight chitosan (75–85% deacetylation with a molecular weight in the range: 50,000–190,000 kDa), and MB were purchased from Sigma-Aldrich, Canada (Oakville, ON), and used without further treatment unless specified otherwise.

**Synthesis of Chitosan Aerogel Materials.** Figure 5 illustrates the material design of the synthesized chitosan framework materials using two types of cross-linkers. In brief, cross-linked chitosan frameworks were prepared by means of sonication in an ultrasonic bath. A total of 17 g of CA or TMA was dissolved in 100 mL of DMSO at 295 K with stirring at 300 rpm for 2 h for the variable composition and sample ID of materials. This solution was transferred to the ultrasonic bath, and 10 g of chitosan powder was added gradually into the solution and progressively heated up to 60 °C for 200 min. The resulting organogels were transferred first to 1000 mL of 2% glacial acetic acid solution to remove the unreacted chitosan powder and then placed in a Soxhlet apparatus with high-performance liquid chromatography grade methanol to remove soluble impurities. After drying, samples were grinded into a powder form for further studies. The pristine chitosan was denoted as Chi, and the samples cross-linked with CA and TMA were denoted as CA1 and TMA1, respectively.

**Characterization.** The water contact angle (θ) measurements of samples were obtained using a PGX contact angle analyzer and modified ImageJ software for data acquisition. A film of each sample was prepared and placed under the instrument, and Millipore water was added dropwise on the film surface using a droplet volume of 1 μL.

The BET SA and pore characteristics of materials were calculated from the adsorption isotherm of nitrogen gas. The N2 gas adsorption isotherms were obtained using a Micromeritics ASAP 2020 (Norcross, GA) to assess the SA and pore structure. Approximately, a 1.0 g powdered sample was degassed at 100 °C and evacuation rate of 5 mmHg s⁻¹ in the sample chamber until the outgas rate became stabilized (<10⁻⁵ mmHg min⁻¹). An alumina standard (Micromeritics) was used for calibration of the instrumental parameters.

The study of water vapor sorption properties was performed using the Hiden Isochema IGA-002 sorption analyzer (UK). The sorption analyzer is an intelligent gravimetric analyzer, which uses the gravimetric technique to measure the magnitude of water vapor sorption of materials with the aid of the HIsorp software program accurately. Each adsorption–desorption experiment took ca. 4 days during which the running time, target relative pressure, sorption, and sample mass were recorded. The mass of samples used was ca. 10 mg. Degassing of the samples took place in the water bath at 70 °C. The adsorption–desorption measurements were performed at 25 °C.

A TA Q20 thermal analyzer DSC was used to evaluate the characteristics of water loss by heating up the water-swelled samples from 40 to 200 °C. Samples were sealed in hermetic pans, the lid of which was punctured to avoid explosion. The scan rate was set to 5 °C/min, and dry nitrogen gas provided purging and temperature regulation of the sample compartment.

AFM imaging of dried samples was obtained using a Multimode Nanoscope III (Digital Instruments, Santa Barbara, CA) equipped with a piezoelectric tube scanner E with a 10 Å ~ 10 μm scan size in the XY direction and a 2.5 μm in vertical range. For imaging of water-swelled samples with high resolution and better signal-to-noise in a liquid environment, the magnetic AC mode (MAC mode) was used. Tapping mode cantilevers for imaging had a tip with a radius less than 10 nm. The tip height was in the 10–20 μm range, and the spring constants ranged from 5.5 to 22.5 N/m and tuned to the 290 Hz resonant frequency. The height variation of the resulting topographic maps was illustrated by a color scale, where bright and dark colors represent higher and lower topographies, respectively.

Dye adsorption study was performed using the batch method by weighing the fixed amounts (~10 mg) of the sample and mixing with 10 mL of MB at variable concentrations (10–200 μM). The equilibration of the samples was obtained using a horizontal shaker table (SICLOGEX model SK-O330-Pro) at 295 K for 24 h and 200 rpm. The concentration of the dye was determined before adsorption (C₀) and after adsorption (Cₑ) in triplicate at variable pH using a Varian Cary-100 Scan UV–vis spectrophotometer at λmax = 405 nm. By considering the volume of solution (V) and mass of adsorbents (m), the difference between initial (C₀) and residual (Cₑ) concentrations of MB was used for determination of the relative uptake capacity of the samples using eq 1

$$Qₑ = \frac{(C₀ - Cₑ)}{m} \times V$$  \hspace{1cm} (1)

The equilibrium uptake of MB by the framework systems was analyzed by the Sips isotherm model, which can be defined by eq 2

$$Qₑ = \frac{Qₘ \times (KₛCₑ)^n}{1 + (KₛCₑ)^n}$$  \hspace{1cm} (2)

where Kₛ is the adsorption constant, nₛ is the heterogeneity parameter of the sorbent surface, Cₑ represents the residual adsorbate concentration, and Qₑ represents the monolayer adsorption capacity of the sorbent surface.

Kinetic study of MB was conducted using the one-pot method by in-situ tracking of the bound adsorbate concentration at pH 7 at 25 °C using a Varian Cary-100 Scan UV–vis spectrophotometer at λmax = 405 nm. At first, fixed amounts (~50 mg) of chitosan materials were mixed with a 200 mL aqueous solution containing MB (200 μM). This setup enabled time-dependent adsorption studies with continuous pipetting of aliquots (2 mL) over a 60 min time interval.

Confocal imaging was used to make an estimate the kinetics of adsorption by employing RH diffusion into the chitosan framework materials. The microscope (Model ZEISS LSM 510 Confo2) was attached to a Nikon Diaphot equipped with a 15 mW krypton/argon laser and fluorescein isothiocyanate (excitation filter 470–490) filter sets. Individual samples were imaged by horizontal scanning (section scanning) and a 10×, 0.30 Plan Fluor objective at variable stages of dye uptake. The background fluorescence was avoided by careful washing of the samples, and a ZEISS LSM software (version 4.2) was used for analyzing the obtained images.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02910.

Results of N₂ adsorption–desorption measurement, Sips isotherm adsorption parameters for the MB, kinetic parameters of MB according to the PFO Model, DSC curve, AFM images, and chemical structure of MB and RH (PDF).

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REFERENCES

(1) Zografi, G.; Kontny, M. J.; Yang, A. Y. S.; Brenner, G. S. Surface Area and Water Vapor Sorption of Macrocrystalline Cellulose. Int. J. Pharm. 1984, 18, 99–116.
(2) Chirkova, J.; Andersons, B.; Andersons, I. Determination of Standard Isotherms of the Sorption of Some Vapors with Cellulose. J. Colloid Interface Sci. 2004, 276, 284–289.
(3) Mali, S.; Sakana, L. S.; Yamashita, F.; Grossmann, M. V. E. Water Sorption and Mechanical Properties of Cassava Starch Films and Their Relation to Plasticizing Effect. Carbohydr. Polym. 2005, 60, 283.
(4) Telis, V. R. N.; Garbas, A. L.; Menegalli, F. C.; Telis-Romero, J. Water Sorption Thermodynamic Properties Applied to Persimmon Skin and Pulp. Thermochim. Acta 2000, 343, 49–56.
(5) Chirkova, J.; Irbe, I.; Andersons, B.; Andersons, I. Study of the Structure of Biodegraded Wood Using the Water Vapor Sorption Method. Int. Biodeterior. Biodegrad. 2006, 58, 162–167.
(6) Lequin, S.; Chassagne, D.; Karbowiak, T.; Gougeon, R.; Brachais, L.; Bellat, J.-P. Adsorption Equilibria of Water Vapor on Cork. J. Agric. Food. Chem. 2010, 58, 3438–3445.
(7) Dhabhai, R.; Mahaninia, M.; Niu, C. H.; Dalai, A. K. Drying of Nonpolar Gas in Using a Pressure Swing Adsorption Process of Canola Meal Biosorbents. Asia Pac. J. Chem. Eng. 2018, 13, N0-2232.
(8) Nasution, T. L.; Balyan, M.; Nainggolan, I. New Application of Chitosan Film as a Water Vapor Cell. Key Eng. Mater. 2017, 744, 339.
(9) Remuñáñ-López, C.; Bodmeier, R. Mechanical, Water Uptake and Permeability Properties of Crosslinked Chitosan Glutamate and Alginate Films. J. Controlled Release 1997, 44, 215.
(10) Miteiuţ, A.; Tanase, E.; Popa, V.; Popa, M. Sustainable Alternative for Food Packaging: Chitosan Biopolymer - a Review. AgroLife Sci. J. 2015, 4, 52–61.
(11) Qin, C.; Li, H.; Xiao, Q.; Liu, Y.; Zhu, J.; Du, Y. Water-Solubility of Chitosan and Its Antimicrobial Activity. Carbohydr. Polym. 2006, 63, 367.
(12) Schiffman, J. D.; Schauer, C. L. Cross-Linking Chitosan Nanofibers. Biomacromolecules 2007, 8, 594.
(13) Kildeeva, N.; Chalykh, A.; Belokon, M.; Petrova, T.; Matveev, V.; Svidchenko, E.; Surin, N.; Nazhnev, N. Influence of Genipin Crosslinking on the Properties of Chitosan-Based Films. Polymers 2020, 12, 1086.
(14) Acevedo-Fani, A.; Salvia-Trujillo, L.; Soliva-Fortuny, R.; Martin-Bellosio, O. Layer-by-Layer Assembly of Food-Grade Alginate/Chitosan Nanolaminates: Formation and Physicochemical Characterization. Food Biophys. 2017, 12, 299.
(15) Zhu, H.-Y.; Jiang, R.; Xiao, L. Adsorption of an Anionic Azo Dye by Chitosan/Kaolin/γ-Fe₂O₃ Composites. Appl. Clay Sci. 2010, 48, 522.
(16) Kyzas, G. Z.; Siafaka, P. I.; Pavlidou, E. G.; Chrisafis, K. J.; Bikiais, D. N. Synthesis and Adsorption Application of Succinyl-Grafted Chitosan for the Simultaneous Removal of Zinc and Cationic Dye from Binary Hazardous Mixtures. Chem. Eng. J. 2015, 259, 438.
(17) Fan, L.; Luo, C.; Sun, M.; Qiu, H.; Li, X. Synthesis of Magnetic β-Cyclodextrin-Chitosan/Graphene Oxide as Nanoabsorbent and Its Application in Dye Adsorption and Removal. Colloids Surf. B Biointerfaces 2013, 103, 601.
(18) Annadurai, G.; Ling, L. Y.; Lee, J.-F. Adsorption of Reactive Dye from an Aqueous Solution by Chitosan: Isotherm, Kinetic and Thermodynamic Analysis. J. Hazard. Mater. 2008, 152, 337.
(19) Subramani, S. E.; Thinakaran, T. Isotherm, Kinetic and Thermodynamic Studies on the Adsorption Behaviour of Textile Dyes onto Chitosan. Process Saf. Environ. Prot. 2017, 106, 1.
(20) Crini, G.; Badot, P.-M. Application of Chitosan, a Natural Aminopolysaccharide, for Dye Removal from Aqueous Solutions by Adsorption Processes Using Batch Studies: A Review of Recent Literature. Prog. Polym. Sci. 2008, 33, 399.
(21) Dey, A.; Bairagi, D.; Biradha, K. MOFs with PUC Topology for the Inclusion of One-Dimensional Water Cages: Selective Sorption of Water Vapor, CO₂, and Dyes and Luminescence Properties. Cryst. Growth Des. 2017, 17, 3885–3892.
(22) Oliver, L.; Meinders, M. B. J. Dynamic Water Vapor Sorption in Gluten and Starch Films. J. Cereal. Sci. 2011, 54, 409–416.
(23) Hill, C. A. S.; Norton, A. J.; Newman, G. The Water Vapor Sorption Properties of Sitka Spruce Determined Using a Dynamic Vapour Sorption Apparatus. Wood Sci. Technol. 2010, 44, 497–514.
(24) Mahaninia, M. H. Chitosan-Based Absorbent Materials for Selective Adsorption of Dyes. Carbohydr. Polym. 2020.
(25) Bley, C. J.; Melchior, T.; Müller, M.; Sage, D.; Bla, T.; Unser, M. Low-Bond Asymmetric Drop Shape Analysis for Surface Tension and Contact Angle Measurements of Sessile Drops. Colloid. Surface. Physicochem. Eng. Aspect. 2010, 364, 72–81.
(26) Lowell, S.; Shields, J. E.; Thomas, M. A.; Thommes, M. Characterization of Porous Solids and Powders-Surface Area, Pore Size and Density. Part. Technol. Ser. 2004, 16, 157–188.
(27) Chang, X.; Chen, D.; Jiao, X. Chitosan-Based Aerogels with High Adsorption Performance. J. Phys. Chem. B 2008, 112, 7721–7725.
(28) Flores-Chaparro, C. E.; Castiñol, C. J.; Kulaots, I.; Hurt, R. H.; Rangel-Mendez, J. R. Pillared Graphene Oxide Composite as an Adsorbent of Soluble Hydrocarbons in Water: PH and Organic Matter Effects. J. Environ. Manage. 2020, 259, 110044.
(29) Fletcher, A. J.; Uygur, Y.; Thomas, K. M. Role of Surface Functional Groups in the Adsorption Kinetics of Water Vapor on Microporous Activated Carbons. J. Phys. Chem. C 2007, 111, 8349–8359.
(30) Rahimi; Ishnaturrahmi; Mustafa, I. Methylen Blue Removal from Water Using HZSO4 Crosslinked Magnetic Chitosan Nano-composite Beads. Microchem. J. 2019, 144, 397.
(31) Sips, R. On the Structure of a Catalyst Surface. II. J. Chem. Phys. 1950, 18, 1024–1026.