PERSPECTIVE

Best Practices for Evaluating New Materials as Adsorbents for Water Treatment

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ABSTRACT: Water pollution is becoming a major concern, because of the increasing numbers and concentrations of persistent, bioaccumulative, and toxic anthropogenic pollutants in fresh water resources. Many recent studies have considered new adsorbents to remove these emerging contaminants from water resources, including metal−organic frameworks (MOFs), covalent-organic frameworks (COFs), porous organic polymers (POPs), porous aromatic frameworks (PAFs), porous cyclo-dextrin-based polymers, and many others. These materials systems incorporate elements of molecular design to target specific pollutants, and many have porosity and high surface areas that provide rapid uptake and high capacity. Although they represent timely and important advances in materials design and synthesis, the characterization of their adsorption performance is sometimes not relevant for water treatment, insufficient, or implemented in ways that prevent comparison to the state-of-the-art materials. This Perspective scrutinizes common practices in the recent literature and provides guidance for designing conclusive and effective adsorption experiments with novel adsorbents. Efforts to adhere to these best practices will allow researchers to evaluate novel adsorbents effectively and will facilitate the emergence of general design criteria for the removal of emerging contaminants from water. Proper experimental design can give crucial insights for understanding adsorption mechanisms, as well as enabling comparisons among different studies, which will better contribute to solving current and future water quality problems.
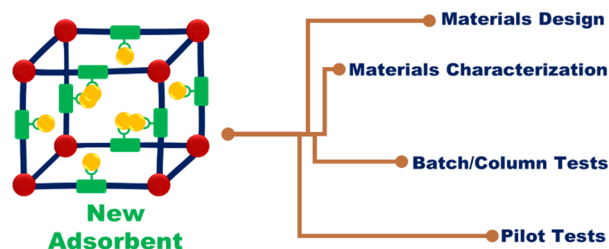
Water security is threatened by continued economic development and the steady increase in global population. Emerging contaminants, or contaminants of emerging concern, are trace compounds (mostly organic) that occur in water resources, including pharmaceuticals, personal care, or household cleaning products, pesticides, and perfluoroalkyl substances.[1,2] The presence of these contaminants, even at trace levels, can disturb the aquatic ecosystem and has been linked to a variety of negative health effects.[3−5] Among the available techniques for removing emerging contaminants from water, adsorption has proven to be efficient and cost-effective. Conventional adsorbents, such as activated carbon and commercial ion-exchange resins, have been used in treatment plants and/or point-of-use systems.[6] However, the removal efficiency of emerging contaminants using conventional adsorbents can be unsatisfactory, because of their nonselective nature and irregular pore structure.[7] Therefore, the quest for effective, simple, selective, and long-lasting solutions for the removal of emerging contaminants is of paramount importance. Over the past decade, several new classes of materials have shown promise as next-generation adsorbents, such as metal−organic frameworks (MOFs),[8,9]

covalent organic frameworks (COFs),[10,11] porous organic polymers (POPs),[12,13] porous aromatic frameworks (PAFs),[14] porous cyclodextrin-based polymers,[15,16] and several others (see Scheme 1).[17−21] These novel materials have been at the forefront of research as novel adsorbents, because of their modular design, tunable functionality, and, in some cases, tailorable porosity.[22,23]

Two types of interactions, namely, physical and chemical, are possible between an adsorbent and adsorbate. Physisorption is the result of attractive noncovalent interactions between sorbent and adsorbate molecules, whereas chemisorption involves forming ionic or covalent bonds between the adsorbent and adsorbate species.[24] Although this distinction is conceptually useful, the molecular mechanism of adsorption is sometimes

Scheme 1. Target-Specific Adsorbents Are Tailored To Have Precise Pore Structure and Functional Groups to Selectively Remove a Contaminant or Group of Contaminants
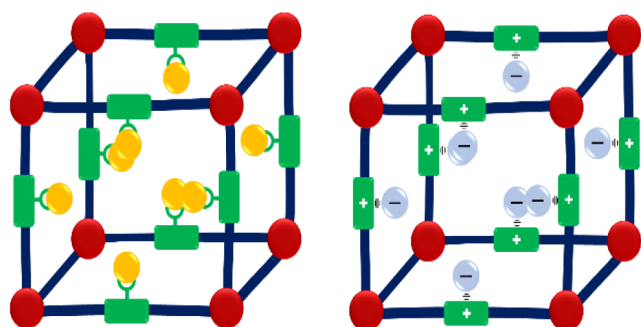
unknown, and the nature of the adsorbate−adsorbent interaction is often assigned by its strength.[25,26] A proper design and interpretation of adsorption experiments is critical for the overall understanding and improvement of adsorption mechanisms and effective design of engineered processes.[25,27,28] Yet, many studies, especially those reporting newly discovered materials, report proof-of-concept experiments not designed to provide relevant comparisons to existing materials.

For instance, despite the relative simplicity of batch experiments, some studies do not report adequate experimental design and operation protocols. These variations hinder or completely preclude comparisons of materials across different studies. Furthermore, testing new materials under ideal conditions (i.e., high adsorbate concentrations in pure water matrices) are suitable for initial screening purposes. However, new materials intended for real-world water treatment must later be evaluated under environmentally relevant concentrations and in the presence of natural water constituents. This Perspective is intended for researchers developing novel adsorbents and will outline standard protocols for experiments and data interpretation. It is based on our experience in developing cyclodextrin-based polymers for removing emerging contaminants from water and our increasingly rigorous characterization of their behavior as they continue to show promise. We are also motivated to provide these guidelines to help researchers make effective decisions in how to evaluate their materials at different stages of new materials development (Figure 1).

> Systematic adsorption experiments help to unlock removal mechanisms and reveal areas for further materials improvement.

■ MATERIALS CHARACTERIZATION TO PREDICT SORPTION BEHAVIOR

Surface Functionality and Charge of Adsorbents.

Functional Groups. Incorporating various functional groups into a novel sorbent is one of the most common strategies to modulate its interactions with adsorbates and other physical properties. For instance, acidic and/or protic functional groups—such as carboxyl, phenolic hydroxyl, lactone and quinone groups—increase the hydrophilicity of the adsorbent and can affect the surface area and pore structure.[29] Basic and neutral surface functional groups can also be introduced.
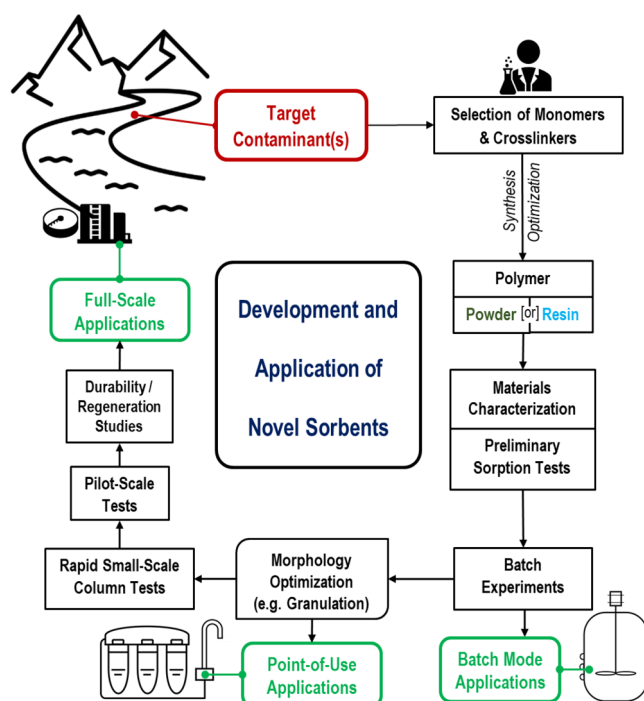

Figure 1. A roadmap for the development and application of new adsorbents for water treatment applications.

Previous studies have shown that the chemical nature of the adsorbent determined by the amount and nature of the surface complexes generally could have more influence than the surface area and the porosity in the case of the adsorption of inorganic and some organic compounds from aqueous solutions.[30,31] Thus, characterization of functional groups, such as through solid-state nuclear magnetic resonance (ssNMR) and/or Fourier-transform infrared (FTIR) spectroscopies, on a target adsorbent is routine. It is also important to understand structural information of a polymer network (e.g., crosslinking density).[11] Elemental analysis determines the amount of C, H, N, S, and O atoms present in a sample, which can offer very useful information on a new adsorbent's structure and composition. Monomers or crosslinkers are designed in such a way that provide one or multiple functional groups. Thus, the performance of the adsorbent will be sensitive to the micro-environment created from crosslinking density and loading of each functional moiety.

Surface Charge. The point of zero charge (pH_{PZC}) is the pH at which the surface of an adsorbent is globally neutral (i.e., it contains as much positively charged surface functions as negatively charged surface functions). Since electrostatic interactions also play a major role in many adsorption processes, the determination of surface charge can be beneficial to predict the sorption behaviors of materials. For nanomaterials, zeta potential is a measure of the effective electric charge on the nanoparticle's surface. When a nanoparticle has a net surface charge, the charge is screened by the concentration of ions of opposite charge near the nanoparticle surface (Figure 2A). However, zeta potential measurements require samples to be highly stable suspensions, which limit its applications to many materials (e.g., adsorbents >300 nm in size, because they aggregate and settle).[32] These technical challenges largely impact the accuracy and reproducibility of pH_{PZC} values acquired using a Zetasizer. Thus, the pH drift method can be
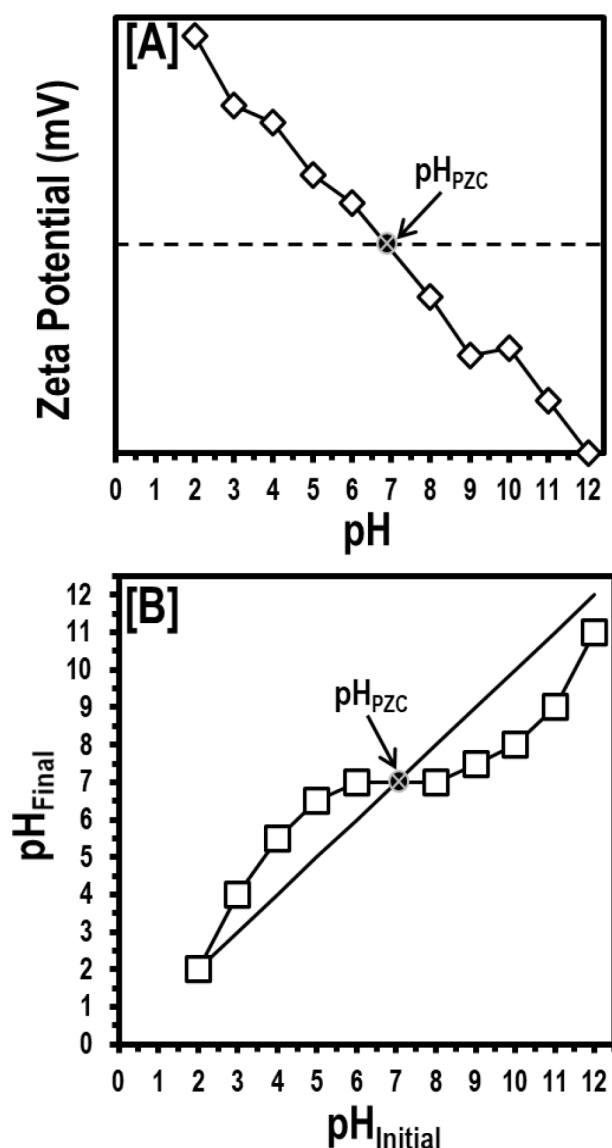
[A]

[B]

Figure 2. Determining pH of point of zero charge (PZC) using [A] zeta potential measurements and [B] the pH drift method.

used as a simple alternative for determining pH_{PZC}. The method, originally developed for activated carbon, provides quick yet reliable values of pH_{PZC}.[33,34]

> The pH drift method may overcome the technical limitations of zeta potential measurements to determine pH_{PZC}.

The pH drift method has been shown to be both simple and reproducible. A solution of 0.01 M NaCl is boiled and purged with nitrogen gas to remove dissolved CO_2 and then cooled to room temperature. A series of 0.01 M NaCl solutions is then adjusted to different pH values from 2 to 12, using diluted HCl or NaOH solutions. pH solutions are added to vials containing known amounts of adsorbents to generate an adsorbent concentration of 2−3 g/L. Vials without adsorbents are also prepared as blanks. Samples and blanks are shaken at 200 rpm for 48 h at room temperature, and then left for 6 h to settle. The

pH_{PZC} can be determined by plotting initial pH values versus final pH values for all samples, as shown in Figure 2B.

Morphology of Adsorbents. *Particle Size.* Physical characteristics of adsorbents significantly influence their removal rate and capacity, as well as dictate how adsorbents can be applied for treatment. For instance, reducing the particle size of activated carbon from 53 μm to 7 μm resulted in dropping adsorption equilibrium time of trichlorophenol from >200 min to <20 min.[35] Although reporting the particle size distribution can simply be determined using a Zetasizer for nanomaterials or by sieves for bigger adsorbents, details on particle sizes are commonly missing in literature studies.[36] Granular adsorbents have particles in the range of a few millimeters in size, whereas powdered adsorbents have typical particle sizes of tens to hundreds of micrometers. While small adsorbents in the form of fine powder exhibit a tendency to have faster removal kinetics and are favorable for suspended-mode applications, flow-through applications require granular adsorbents with relatively larger particles or a uniform particle size distribution, to avoid back-pressure limitations. Therefore, reporting the particle size distribution would be highly beneficial when deciding the application mode. For instance, a packed column with adsorbents with a wide range of particle sizes is more prone to pore blockage than columns containing adsorbents with similar particle sizes. Besides, measuring the particle size distribution will be required when developing agglomeration methods to form granules. It should also be highlighted that more efforts are needed in developing agglomeration methods for newly discovered adsorbents. For example, binders are components which are added prior to or during agglomeration to increase the strength of the agglomerated product under otherwise unchanged processing conditions. The development of these binders cannot be generally treated, since they must be compatible with the materials to be agglomerated and the proposed uses of final products. Thus, innovative research is needed to study application of different agglomeration methods on the different classes of novel adsorbents.

> Adsorbent morphology helps predict removal kinetics and capacity and dictates the application mode of adsorbents for treatment.

Surface Area and Porosity. Porous materials generally have high surface areas, which provide more active adsorption sites than nonporous materials. Specifically, materials possessing mesopores (pore size of 2−50 nm) are desirable when rapid diffusion of molecules into the internal surface of porous adsorbents is required. Thus, next-generation adsorbents with precise pore engineering that fit the target contaminant will give superior advantages over conventional adsorbents. Fine particle analysis is commonly used to determine a material's surface area, total pore volume, average pore volume, average micropore volume, and pore size distribution by a gas adsorption experiment.

Physical adsorption results from relatively weak van der Waals forces between the adsorbate gas molecules (typically nitrogen or argon) and the adsorbent's surface area. Nitrogen adsorption is often performed at 77.4 K by cooling using liquid nitrogen. The analysis is done using a physisorption gas analyzer with a

degassing unit [e.g., accelerated surface area and porosity (ASAP) analyzers]. For pore structure analysis, the gas adsorption—desorption isotherms should be determined over the widest possible range of relative pressure, while allowing for slow equilibration at very low pressures.[37] Samples should be dried before starting the measurements. Depending on how the samples are processed during isolation and solvent removal, some retain their porous structure or collapse into less-porous or nonporous structures during analysis. Thus, sample activation should be performed by heating under vacuum (for robust samples) or by supercritical CO_2 washing (for highly sensitive ones).[38] Samples with a total surface area of at least 5—10 m^2 (under a nitrogen atmosphere) or 1.25 m^2 (under an argon atmosphere) are activated by vacuum and/or heat, such that they off gas at a rate of >2 mm Hg/min. More comprehensive articles have been recently published on the activation of new classes of adsorbents.[39,40]

The measurements of surface area and porosity are mostly automated. Users measure and record the mass of the materials accurately for surface area calculations, using different models in the instrument's software to fit the adsorption—desorption isotherm data (e.g., Figure 3A) and estimate the surface area and pore volume of the sample.[41] Surface areas of an adsorbent are typically calculated by applying the Brunauer—Emmett—Teller (BET) equation to a gas adsorption isotherm. This method relies on adsorption of a gas on the adsorbent's surface and the specific surface area of a sample is determined by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. The total pore volume is determined by the amount of gas adsorbed when the material is saturated with a gas slightly below atmospheric pressure. Although there are many ways to determine the average pore volume, micropore volume, and pore size distribution (e.g., t-plots, alpha-S, the Kevin equation, Barrett—Joyner—Halenda (BJH)), the International Standard Organization (ISO) recommends using Non-Local-ized Density Functional Theory (NLDFT).[42] NLDFT works by fitting experimental isotherms to a kernel of a calculated model isotherm of increasing pore size and fixed geometry.[43] Note that these measurements indicate the gas-accessible surface area in the dry state, which does not necessarily mean that these sorption sites will be equally accessible during the adsorption of pollutants in the aqueous phase.

In cases where a physisorption unit is not available, determining an adsorbent's iodine number offers a simple and rapid alternative assessment of its surface area. This analysis is widely used for the characterization of activated carbons and is defined as the milligrams of iodine adsorbed on one gram of material when the iodine residual concentration of the filtrate is 0.02 N (0.01 M). This parameter is determined using a three-point isotherm, according to American Society for Testing and Materials (ASTM) Standard ASTM D4607.[44] The iodine number does not necessarily provide a measure of the material's ability to adsorb other species. However, it can give an estimate of the material's surface area and porosity,[45] if its overall stability to the test is confirmed.

The detailed methods and calculations were reported by the ASTM.[44] Briefly, the sample is treated with 10 mL of 5% (v/v) HCl. The mixture is boiled for 30 s and then cooled at room temperature. A solution of iodine in water (100 mL of 0.1 N) is immediately added to the mixture and stirred for 30 s. The solution is then filtered and 50 mL of the filtrate is titrated with 0.1 N (0.05 M) sodium thiosulfate solution. The amount of iodine adsorbed per gram of adsorbent is plotted against the residual iodine concentration using logarithmic axes. If the residual iodine concentration is not within the range (0.008—0.04 N), the procedure is repeated using different adsorbent masses for each isotherm point. A regression analysis is applied to the three points and the iodine number is calculated as the amount adsorbed at a residual iodine concentration of 0.02 N (Figure 3B).

BATCH-MODE ADSORPTION EXPERIMENTS

Batch studies rely on the adsorption phenomenon at the solid/liquid interface that leads to a change in the concentration of the solution. Generally, adsorption data, including kinetic and equilibrium studies, are performed using standard procedures consisting of mixing a fixed volume of target adsorbate solution with a known amount of adsorbent in controlled conditions of contact time, agitation rate, temperature, and pH. At predetermined times, the residual concentration of the adsorbate is measured and the adsorption capacity or the adsorption uptake rate is then calculated and is usually expressed in terms of mass (mg) of adsorbate adsorbed per dry mass (g) of the adsorbent (see eq 1).
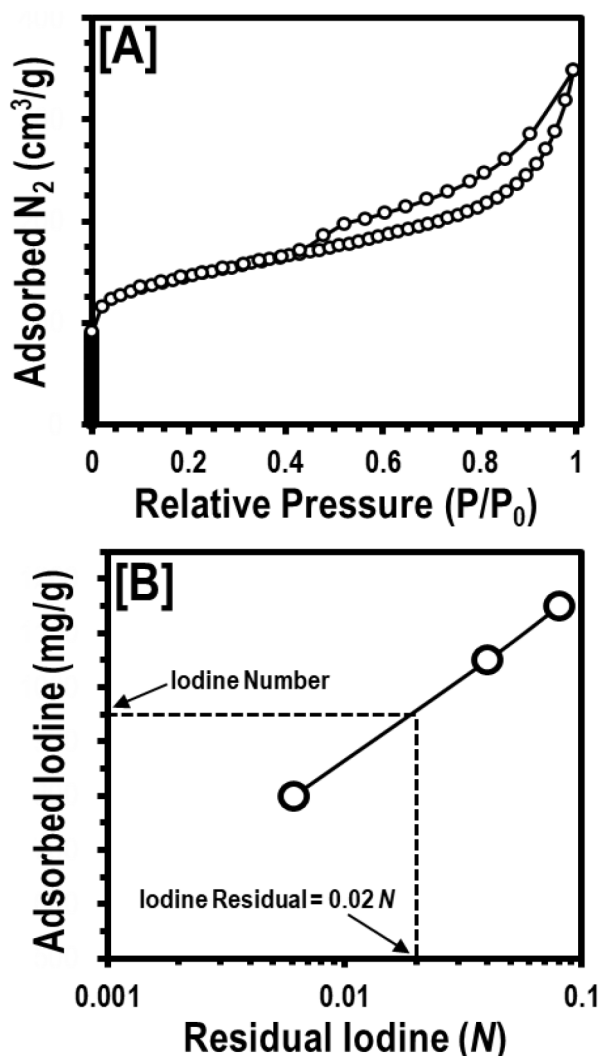

Figure 3. Determination of adsorbent's surface area using [A] fine particle analysis and [B] iodine number.
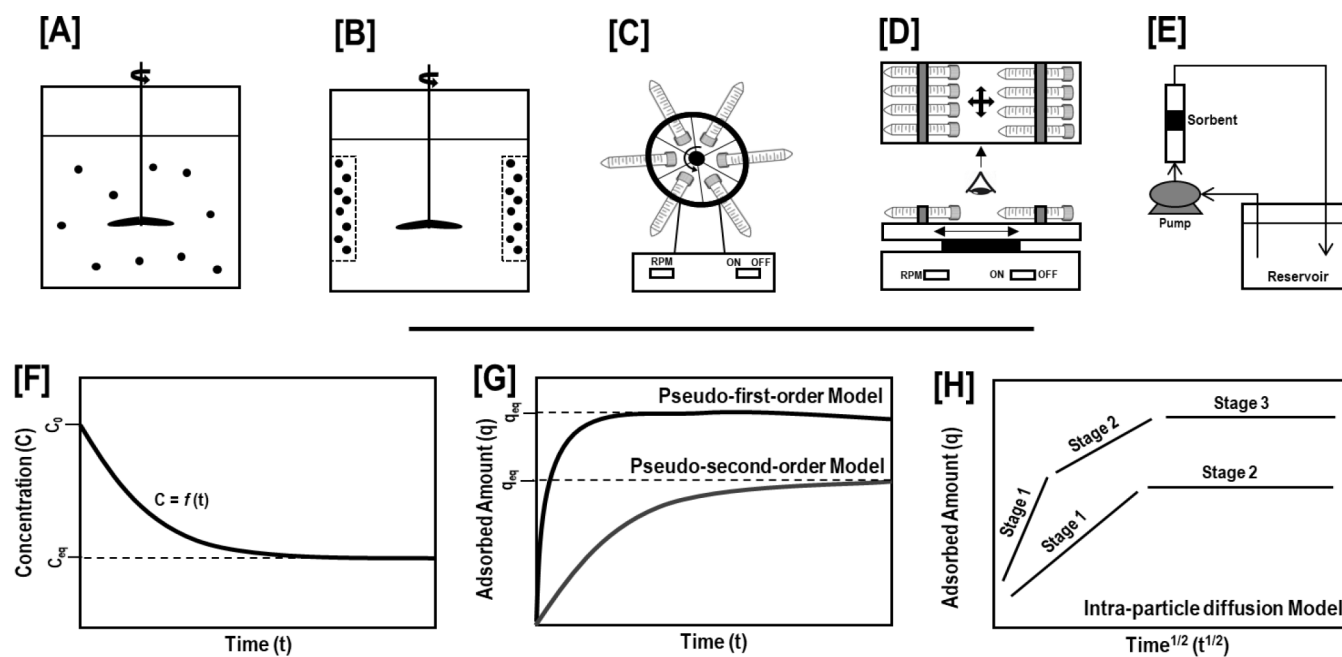
Figure 4. Kinetic experiments can be run in different batch configurations, including [A] slurry batch reactor, [B] slurry batch reactor with basket, [C] tumblers, [D] orbital shakers, and [E] differential column batch reactors. Also shown are typical curves for [F] the relationship between pollutant concentration and time during kinetic experiments, [G] pseudo-first-order and pseudo-second-order kinetic models, and [H] the intraparticle diffusion model.

$$q = \frac{(C_0 - C)V}{m} \tag{1}$$

where q (mg/g) is the adsorption density after a predetermined contact time, C_0 the initial concentration of adsorbate in the bulk liquid (mg/L), C the concentration of adsorbate in the bulk liquid at time t (mg/L), V the volume of the bulk solution (L), and m the the dry mass of the adsorbent (g).

In this regard, two common shortcomings can be found in many batch studies that widen the gap between the development of new materials and downstream applications. First, the use of high adsorbent loadings (up to several grams per liter) during the material's evaluation, whereas actual water treatment applications using conventional adsorbents mandate loadings on the order of single-digit milligrams per liter. Second, some studies use percentage removal (%) to report their results with removal efficiencies that surpass the limit of analytical detection. Such experiments do not give sufficient insights about the system performance, which should be evaluated under adsorption−desorption equilibrium conditions. To overcome these limitations, we describe practices to design effective batch experiments in the following sections.

Kinetic Experiments. Kinetics experiments are sometimes used to merely complement the adsorbent evaluation by fitting experimental data to pseudo-first-order or pseudo-second-order models. However, study of the kinetics is a very important step to understand the adsorption mechanism and to design columns on laboratory, pilot, and full scales.[46] Depending on the potential target application, different experimental procedures for determining the kinetics are described below.

Slurry Batch Reactor. This type of reactor is used typically for the determination of equilibrium data; however, it can be also used to run kinetic tests. Slurry batch reactors are suitable for evaluation of ion exchange resins and other adsorbents with relatively large particle size (> 1 mm). In order to minimize the effect of film diffusion on the kinetic results, a higher stirrer

speed should be used. Slurry batch reactors simply consist of a tank with an electrical mixer (Figure 4A). If adsorbents are susceptible to destruction by mixers, a basket reactor should be used (Figure 4B).[47]

Procedures:

(1) Run a preliminary experiment to determine and set a proper range for the contact time, which will help to determine the number and the frequency of the sample intervals, as well as the adsorption equilibrium time;

(2) Prepare a stock solution of target adsorbate in an appropriate solvent;

(3) Prepare a working aqueous solution at a known concentration of the adsorbate and place in the reactor;

(4) Add a known amount of the adsorbent and start mixing;

(5) Stop the mixer and collect samples at predetermined time intervals then filter samples (Note: use a centrifuge if interference by filter media is a concern);

(6) Analyze the concentration of pollutant in the supernatant; and

(7) Determine the equilibrium concentration (C_e) and time needed to reach equilibrium (Figure 4E).[48]

> Kinetics experiments can be designed using different reactor configurations depending on an adsorbent's particle size and intended final application.

Single-Point Batch Reactor. This experimental setup gives a high level of flexibility in deciding solution volume and adsorbent amount, which is ideal for new materials with limited available quantity. The mobility of these reactors on tumblers (Figure 4C) or orbital shakers (Figure 4D) also make them

suitable for experiments where controlled temperature is required. In addition, single-point batch reactors are desirable for tests under headspace-free conditions, where the effect of the air/water interface is minimized. It is also advisable to use sample vials from materials that are compatible with the target adsorbate (i.e., adsorption of adsorbate to the vials themselves must be avoided).[47]

Procedures:

(1) Run a preliminary experiment to determine and set a proper range for the contact time, which will help in determining the number and the frequency of samples' intervals, as well as the adsorption equilibrium time;

(2) Prepare a stock solution of the target adsorbate in an appropriate solvent;

(3) Prepare a working aqueous solution at a known concentration of the adsorbate and add the known volume to each reaction vial (note: if controlled solution temperature is required, samples should be placed in a water bath or a temperature-controlled chamber before adding adsorbents);

(4) Add a known amount of the adsorbent and start mixing (note: Some fine powdered adsorbents are difficult to test in these reactor configurations. They can be added first, then the working solution can be added or some adsorbents can be prepared as a slurry that can be spiked into the solution);

(5) At predetermined time intervals, open a reaction vial and filter the sample (note: use a centrifuge if interference by filter media is a concern);

(6) Analyze the concentration of pollutant in the supernatant; and

(7) Determine the equilibrium concentration (C_e) and time needed to reach equilibrium (Figure 4F).[48]

Differential Column Batch Reactor. In this setup, solutions flow under high flow velocity conditions through a fixed bed of adsorbent with a small height (Figure 4E). A differential column batch reactor allows the solution to run in a circulation mode. By placing the particles in a fixed bed, they are shielded from destruction. Adsorbents should be small in size and packed properly in the column to avoid channeling, in which liquids flow through macroscopic cracks in the separation media.[47]

Procedures:

(1) Pack the adsorbents carefully using a uniform particle size by preparing a slurry of the adsorbent and letting it settle, using gravity, in the column on a supporting layer of glass wool;

(2) Prepare a working aqueous solution at a known concentration of the adsorbate and place in the reservoir;

(3) Run the pump and collect samples from the reservoir at predetermined time intervals;

(4) To avoid the effect of film diffusion, a minimum flow velocity is selected after trying a range of velocities until the shape of the kinetic curve remains constant; and

(5) Determine the equilibrium concentration (C_e) and time needed to reach equilibrium.[48]

Kinetic Modeling. Pseudo-first-order (eq 2) and pseudo-second-order (eq 3) models are the two most commonly used empirical models in liquid adsorption studies (see Figure 4G). However, in most cases, pseudo-first-order analysis fits adsorption data less well than a pseudo-second-order model, as determined by a least-square discrimination procedure. The calculated q_e using the pseudo-second-order model is often less

than, but close to, the experimental value.[24] Note that the wide applicability of the pseudo-second-order model does not necessarily stem from a physical basis, but a mathematical basis.[49]

$$q = q_e(1 - e^{-k_1 t}) \tag{2}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q is the adsorption density after a predetermined contact time (mg/g), t is time (min), and k_1 is the pseudo-first-order rate constant (1/min) and can be determined by plotting $\ln((q_e - q)/q_e)$ vs t to obtain a straight line that passes through the origin with a slope k_1 for systems that obey this model. k_2 is the pseudo-second-order rate constant (g/mg.min) and can be determined by plotting (t/q) vs t to obtain a straight line for systems that obey this model. The slope is $(1/q_e)$ and the intercept is $(1/k_2 q_e^2)$.

Many other models of varied complexity have been developed to predict the uptake rate of the adsorptive into the adsorbent. Understanding adsorption kinetics is largely limited by the theoretical complexity of adsorption mechanisms. Here, we introduce the use of an intraparticle diffusion model based on the theory proposed by Weber and Morris (eq 4).[50] This gives further insights on the removal mechanisms by newly developed materials, in addition to pseudo-first-order and pseudo-second-order models.

$$q_t = k_{id} t^{1/2} + I \tag{4}$$

where q_t (mg/g) is the adsorption density after a predetermined contact time t (min) and k_{id} (mg/(g min$^{1/2}$)) is the intraparticle rate constant. I (mg/g) is the intercept, and it represents an external resistance for mass transfer from the bulk solution across the boundary layer to the adsorbent surface. A larger I value implies a greater boundary layer effect. The adsorption can follow a two-stage or three-stage scenario (Figure 4H). Stage 1 (rapid adsorption) is film diffusion, which is attributed to the diffusion of the adsorbate through the liquid film surrounding the adsorbent surface. Stage 2 (gradual adsorption) corresponds to the intraparticle diffusion of the adsorbate molecules through the pores of the adsorbent. Stage 3 is the equilibrium stage.

Despite the relative ease in applying these empirical models, caution must be taken, because of their sensitivity toward at least two factors. First, experimental conditions (e.g., temperature) and design (e.g., sample frequency and distribution over the curve) can by highly influential, especially if using a linear form of the model. Second, calculating the rate constant (i.e., the rate to reach equilibrium) for an adsorption system, where only a small percentage of the adsorbate is removed, may lead to unrealistic/misleading conclusions about the system. Thus, careful experimental designs and data interpretations will help in having a reproducible study with comparable results.

Isotherm Experiments. Adsorption equilibrium is established when a solution with an adsorbate has been contacted with the adsorbent for sufficient time with a dynamic balance between the adsorbate concentration in the bulk solution and on the adsorbent surface. The adsorption isotherm, which is a curve describing adsorption equilibrium at constant temperature and pH, is a major tool to describe and predict the retention (or release) of an adsorbate through an aqueous media to an adsorbent.[25] Although finding the ultimate capacity of newly developed materials is advantageous, it requires running

experiments under conditions of high adsorbate concentrations. In this regard, the major limitation in the current literature is the absence of materials evaluation in a range within environmentally relevant concentrations. These retention/release phenomena are sometimes strongly kinetically controlled, so that time dependence of the sorption isotherm must be specified.[51] For experiments that run for long equilibrium times (ideally for runs that take more than 24 h), working solutions should be filtered through 0.2 μm filters to suppress any biological activities.

> Isotherm experiments should be performed both at high concentrations, to determine an adsorbent's capacity, and at low concentrations, to evaluate their efficiency under realistic conditions.

Procedures:

(1) Run kinetic experiments as described above to determine the equilibrium time;
(2) Prepare a stock solution of the target adsorbate in an appropriate solvent;
(3) Prepare a working aqueous solution at a known concentration of the adsorbate and add a known volume to each reaction vial;
(4) Add a known amount of the adsorbent and start mixing (note that some fine powdered adsorbents can be difficult to handle; they can be added first to the reaction vial, then a working solution can be added or some adsorbents can be prepared as a slurry that can be spiked into the solution);
(5) When the equilibrium time is reached, open the reaction vials and filter the samples (note: use a centrifuge if interference by filter media is a concern);
(6) Analyze the concentration of pollutant in the supernatant; and
(7) Determine the equilibrium concentration (C_e) and adsorbed amounts at equilibrium.[48]

Isotherm Modeling. *Traditional Isotherm Models.* The most commonly used isotherm models are the Langmuir (eq 5) and Freundlich (eq 6) models (see Figure 5A):

$$q_e = \frac{q_{max}}{1 + bC_e} \tag{5}$$

where q_e (mg/g) is the equilibrium adsorption density, C_e (mg/L) the equilibrium concentration, q_{max} (mg/g) the maximum adsorption density, and b the Langmuir constant. When C_e/q_e is plotted against C_e and the data are regressed linearly, q_{max} and b constants can be calculated from the slope and intercept.

$$q_e = K_F C_e^{1/n} \tag{6}$$

where q_e and C_e are defined in the same manner as in the Langmuir equation. The Freundlich constant (K_F) is related to the adsorption capacity of the materials, and $1/n$ is a constant related to surface heterogeneity. When log q_e is plotted against log C_e and the data are analyzed by linear regression, the $1/n$ and K_F constants are determined from the slope and intercept.

In the Langmuir isotherm, it is assumed that (i) adsorption occurs at specific homogeneous sites within the adsorbent, (ii)
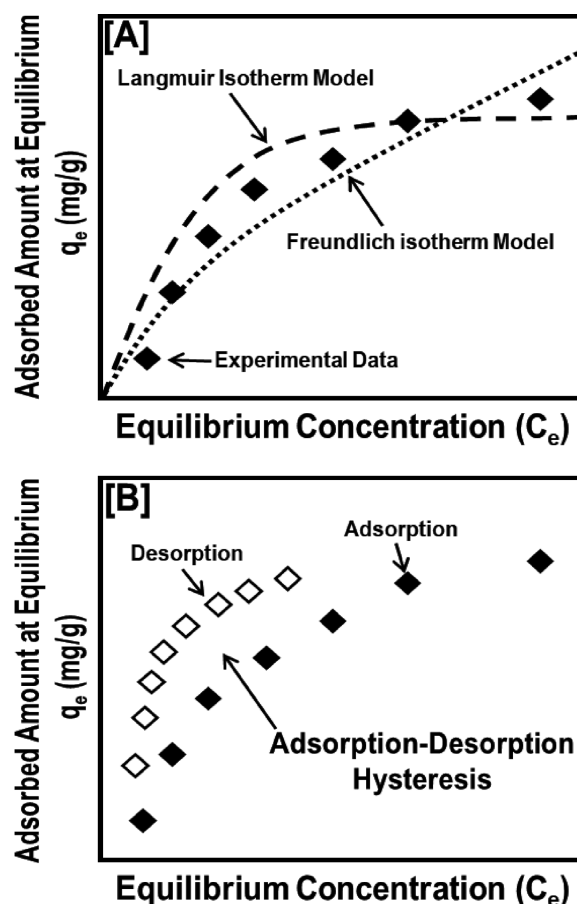

Figure 5. [A] Isotherm experimental data fitted to Langmuir and Freundlich models, and [B] Adsorption-desorption hysteresis.

no significant interaction occurs among the adsorbed species, and (iii) the adsorbent is saturated after one layer of adsorbent molecules forms on the adsorbent surface. The Freundlich isotherm is commonly used to describe the adsorption characteristics of multilayer adsorption and heterogeneous surfaces.[51]

It is again important to note that estimates of the above-mentioned isotherm parameters and coefficients can change when using the linearized form of these models with different adsorption densities and distributions of data over the isotherm curve. Thus, caution must be taken and nonlinear regression is preferred.

Distribution Coefficient (K_D). The estimation of distribution coefficients, K_D (L/g), is more relevant than traditional isotherms when evaluating emerging contaminants at environmentally relevant concentrations. K_D simply represents the slope of the linear region of any isotherm under conditions of infinite dilution (calculated as q_e/C_e at low adsorbate concentrations) and is often used to describe the affinity of an adsorbate to an adsorbent at infinite dilution.[52] To ensure that one is estimating K_D appropriately, one should estimate K_D under a range of conditions, to ensure that a constant value is obtained; the magnitude of K_D will decrease with increasing adsorbate concentration at higher adsorbate concentrations (i.e., outside of the linear region) if the isotherm is best modelled by a Langmuir or Freundlich model.

Adsorption–Desorption Hysteresis. Adsorption reversibility is an important factor when evaluating new adsorbents; however, it is widely overlooked in many studies of water

contaminants. It should be highlighted that it is different from regeneration of adsorbents by desorption, which will be discussed in a later section. Desorption hysteresis was widely reported for contaminants from many conventional adsorbents (e.g., soils, activated carbon)[53] and it can be attributed to an irreversible pore deformation of the adsorbent by the adsorbate and the formation of metastable states of the adsorbate in fixed mesopores (Figure 5B). Both rearrangement of aggregates and penetration of the adsorbate into closed interstitial spaces are responsible for desorption hysteresis. This mismatch between adsorption and desorption isotherms is called "pseudo-hysteresis". A more convenient term could be "apparent irreversibility", since the common term "irreversibility" can lead to the wrong conclusion that a part of the solute cannot be desorbed at all, rather than simply being slower than expected. Besides, two human errors while running experiments can cause artifact hysteresis. First, nonequilibrated adsorption is a typical artifact for desorption hysteresis, which can be fixed by running the experiments for prolonged contact time. Second, loss of adsorbate, such as degradation, evaporation, and particle loss during desorption, is another reason for artifact hysteresis.[53] Generally, true hysteresis should be repeatable through many cycles.[54]

Procedures:

(1) Run isotherm experiments as described above;
(2) When the equilibrium time is reached, open reaction vials and centrifuge the sample to recover adsorbents and collect the supernatant then measure adsorbate concentration in the supernatant;
(3) Replace the volume of the supernatant with distilled water, close the vials, and start mixing for prolonged contact time (note: preliminary desorption kinetic experiments can help decide the desorption equilibrium time);
(4) When the equilibrium time is reached, open reaction vials and filter the sample (note: use a centrifuge if interference by filter media is a concern and/or if desorption experiments are designed to run for multiple cycles);
(5) Analyze the concentration of pollutant in the supernatant;
(6) Determine the equilibrium concentration (C_e) and adsorbed amounts at equilibrium; and
(7) Use an appropriate organic solvent (e.g., methanol, ethanol) to desorb the adsorbate and analyze the concentration of pollutant on the adsorbent.

For volatile contaminants, hysteresis tests can be automated and performed using ASAP analyzers (see details above in the Morphology of Adsorbents section).

■ COLUMN-MODE EXPERIMENTS

A full-scale column can be scaled down to a Rapid Small-Scale Column Test (RSSCT) by using a smaller particle size of the adsorbent (the ratio between the particle sizes is the scaling factor). Using RSSCT breakthrough profiles, it can be feasible to estimate operational costs, adsorbent use rates, and bed life.[55,56] The basis for the RSSCT is the similitude between the dimensionless numbers of the dispersed-flow pore and surface diffusion model, which includes the mass transport mechanisms of advection, dispersion, film diffusion, and intraparticle diffusion.[57] Based on this dimensional analysis, simple scaling equations were developed relating the empty bed contact time (EBCT) and the hydraulic loading rate (HLR) to the mean particle diameters (d_p) of adsorbents, of the large column (L_C),

(i.e., pilot or full-scale), and small column (S_C), (i.e., RSSCT). Measuring and reporting these engineering parameters will significantly help readers to evaluate and compare the performance of new and conventional adsorbents. *Otherwise, the commonly adopted routine experiment of just pushing a solution through a new adsorbent on a filter using a syringe would not give a true evaluation for an adsorbent's performance in column setups.*

> Flow-through experiments should be designed following the principles of RSSCT while carefully considering the mechanism of a new adsorbent.

A mass transfer zone is formed in the column bed by passing contaminated water through it (see Figure 6). The depth of the
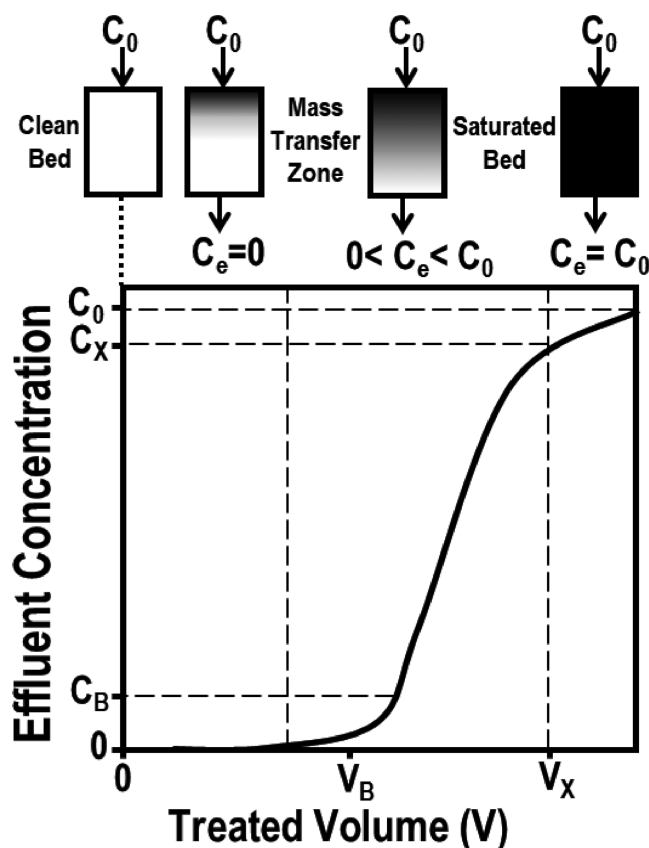

Figure 6. RSSCT breakthrough curve at different mass transfer zones.

mass transfer zone is a measure of the physical and chemical resistance to mass transfer and is controlled by the characteristics of the adsorbent, adsorbate, and other hydraulic factors. This zone moves down and reaches the bottom of the column, where pollutant concentrations in the effluent become equal to the influent concentrations and the breakthrough point of the column occurs. The contact time is dependent on the type of adsorbent and adsorbate and varies from 15 min to a few hours in both batch and column operations. However, an adsorption method with the minimum contact time interval is ultimately the best.[46]

The theory of RSSCTs was originally developed to study the adsorption of natural organic matter (NOM) on activated carbon. Thus, the governing assumptions and equations *might* translate to novel adsorbents, but it is unlikely that they will translate to novel adsorbents that are very different from activated carbon (i.e., pore size distribution and morphology). For example, the performance of a novel *mesoporous* adsorbent that is not limited by diffusion into *micropores* will scale differently than activated carbon. Ultimately, new adsorbents will need to be studied on a case-by-case basis, where researchers should interpret their new systems based on careful materials characterization and known or presumed adsorption mechanisms.

Sample Preparation: Adsorbents should be uniform in size to avoid any channeling. Affix a supporting medium (glass wool) at the lower end of the column by hydraulic filling. Packing of column is done by preparing a slurry of adsorbents in pure water and filling the column and stirring using a glass rod, then leaving undisturbed overnight to settle.

Procedures:

(1) Setup the glass column and pack it as described above;
(2) Cover the upper end of the column with a tube connection, to remove any air bubbles;
(3) Attach the upper end to a head tank, from which the flow of contaminated water is regulated;
(4) Calculate the amount of pollutant adsorbed on the adsorbent and determine the capacity of the column by drawing a breakthrough capacity curve (see Figure 6); and
(5) Design and fabricate pilot- and industrial-scale columns for treatment of contaminated water at a larger scale.

The proportional diffusivity (PD) design has been shown as a good approach.[58,59] The following relationships (eqs 7−9) are used between the parameters of large-scale columns and small-scale columns.

$$SF = \frac{d_{LC}}{d_{SC}} \tag{7}$$

$$EBCT_{SC} = \frac{EBCT_{LC}}{SF} \tag{8}$$

$$V_{SC} = \frac{Re_{SC} \times \nu_{SC} \times \varepsilon_{SC}}{d_{SC}} \tag{9}$$

where SF is a scaling factor, d the particle diameter, EBCT the empty bed contact time, V the hydraulic loading, *Re* the Reynolds number, ε the porosity of the adsorbent bed, and ν the kinematic viscosity of water (LC and SC denote the large columns and small columns, respectively).[48] Note here that scaling the system up will require more detailed analysis of the rate-limiting steps for adsorption, yet the proposed approach herein would allow for a consistent design among different studies.

■ EFFECT OF REAL WATER CONSTITUENTS

A very limited number of studies on new adsorbents have evaluated their materials under realistic conditions, which restrain their further development into real practice. The adsorption isotherm for a compound is defined under a given set of testing conditions: pH, temperature, initial concentration, range of equilibrium concentration, ionic strength, and composition of the test solution. However, the effects of

competitive adsorption further complicate predictions of the adsorbent's performance. Therefore, isotherm data reported for a compound in pure water or reference isotherms are not very useful when a mixture of contaminants are to be removed (e.g., contaminated groundwater, primary effluents, and landfill leachates). In addition, testing the effect of individual background constituents can give insights on the adsorption mechanisms and help in deciding potential regeneration methods. For instance, adsorbents that rely on electrostatic interactions for adsorption will be sensitive to the competition of ions carrying the same charge as the target contaminant. Inorganic ions can interfere with electrostatic interactions. Interferences are often attributed to compression of the double layer, direct-site competition with adsorbates of the same charge, and/or interactions between inorganic ions and the adsorbates with complementary charge.[60] In addition, NOM can interfere with hydrophobic interactions. Interferences are often attributed to pore blockage (where a large NOM molecule blocks access to a micropore) or direct-site competition.

> **Different water constituents may impact one or multiple adsorption mechanisms.**

Experimentally, the effect of NOM can be tested using standard humic substances (e.g. humic acid, fulvic acid). The effect of ions is tested using salts of different anions (e.g. Cl^-, NO_3^-, SO_4^{2-}) or cations (e.g., K^+, Na^+, Ca^{2+}, Mg^{2+}) of different valence. Ionic strength can be tested using NaCl or $CaCl_2$. Real water samples from rivers, lakes, groundwater, or wastewater effluent should be filtered (0.2 or 0.45 μm) and characterized for organics and ions prior to adsorption experiments.

■ REGENERATION EXPERIMENTS

The regeneration performance of newly developed adsorbents is one of the important considerations for practical applications.[61] Reuse by regeneration of adsorbents could prove desirable by recovering valuable resources, concentrating pollutants into reduced volumes, and minimizing costs associated with replacing as-prepared adsorbents. In this process, the main target of regeneration tests is to monitor the stability of adsorbents and their ability to recover their active sorption site. Since these experiments aim at saturating the adsorption sites, using a high dose of adsorbents and high concentrations of adsorbate can be acceptable. Depending on the adsorption mechanisms, different desorption solutions can be selected (e.g., water + salts, organic solvent, organic solvent + salts). For instance, the most efficient desorption solvents for adsorbents featuring relatively highly electrostatic segments included highly polar NaCl solutions in ethanol or water.[62,63] Meanwhile, acetone can be an efficient desorption solvent for adsorbents with more hydrophobic segments, for which the desorption solvent should better solvate the adsorbate, to disrupt its interactions with the sorbent.[64]

Procedures—Batch-mode:

(1) Run kinetic and isotherm experiments as described above to determine the equilibrium time and adsorption capacity of the material;
(2) Prepare a stock solution of the target adsorbate;

(3) Prepare a working solution at higher concentration than adsorbent's capacity and add a known volume to the reaction vial;

(4) When the equilibrium time is reached, open the reaction vials and centrifuge the sample to recover adsorbents and measure the adsorbate concentration in the supernatant;

(5) Replace the volume of the supernatant with the regeneration solution, close the vials, and start mixing for a prolonged contact time (note: preliminary desorption kinetic experiments can help in deciding the desorption equilibrium time);

(6) When the equilibrium time is reached, open the reaction vials and centrifuge the sample to recover adsorbents and measure adsorbate concentration in the supernatant; and

(7) Replace the volume of the supernatant with the working solution;

(8) Repeat Steps 4−7; and

(9) Monitor the change in the adsorption capacity.

Procedures—Column-mode:

(1) Setup column for RSSCT;

(2) Prepare a working solution of the target adsorbate at a known concentration;

(3) Run RSSCT column until the adsorbent bed is saturated (i.e., adsorbate concentrations in the influent and the effluent are equal);

(4) Quantify the adsorption capacity (mg/g);

(5) Replace the working solution with the regeneration solution and run the system again;

(6) Monitor the adsorbate concentration in the effluent until the adsorbent is clean;

(7) Replace the regeneration solution with the working solution;

(8) Repeat Steps 3−7; and

(9) Monitor the change in the adsorption capacity.

Moving forward, the great advances that have been accomplished in the development of novel adsorbents must be coupled with applying proper adsorption testing protocols. More research will be needed in tailoring next-generation adsorbents to fit into one or more application modes. These efforts will collectively result in a better understanding of adsorption mechanisms, which can support further developments in material designs and applications.

■ TOWARD COMPARABLE LITERATURE

To conclude, the limitations of conventional adsorbents in removing emerging contaminants from contaminated waters/wastewaters have motivated many researchers to develop novel selective adsorbents. These alternative materials are very promising; however, the path to using them in practical treatment processes is long. One major reason, as discussed above, is the big variation in testing methods and conditions among different studies in the literature. These variations limit the reproducibility of the work and widen the gap between a new finding in materials science and its potential target application in environmental engineering. Thus, the following recommendations summarize some tests and characterizations that should be included in any study to help researchers better evaluate and compare their novel adsorbents:

- **Materials characterization:** studies reporting on a novel adsorbent material should report as-synthesized particle size distribution and morphology, surface area, pore size distribution, and zeta potential or pH_{PZC}.

- **Batch-mode testing:** At least one kinetics experiment should be performed at environmentally relevant concentrations of the adsorbate (typically in the range of 1−1000 ng/L) and economically relevant concentrations of the adsorbent (typically on the order of 10 mg/L). Rate constants should be estimated from at least three independent experiments conducted at different concentrations. Distribution coefficients should be reported in lieu of adsorption isotherms when evaluating adsorption of a trace contaminant.

- **Column-mode testing:** Column experiments should be carefully designed as detailed in the previous discussion. New insights regarding RSSCT for novel adsorbents are expected to emerge when enough systematic studies are available in the literature.

- **Effect of water constituents:** New adsorbents will prove promising if they are evaluated under realistic challenging conditions. These conditions include testing the effect of NOM, anions, cations, pH, and ionic strength. Such tests will be important to elucidate the removal mechanisms, recognize the limitation of the technology, and identify the points that require further developments.

- **Regeneration experiments:** The application cost and the environmental impact of new adsorbents will be dependent on their feasibility to be regenerated and recycled. Thus, regeneration protocols should be developed and carefully reported.

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Notes

The authors declare the following competing financial interest(s): W.R.D. and D.E.H. own equity and/or stock options in Cyclopure, Inc., which is commercializing novel adsorbent materials.

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