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# On the Choice of Batch or Fixed Bed Adsorption Processes for Wastewater Treatment

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**ABSTRACT:** Newly emerged nanomaterials, such as graphene or carbon nanotubes, are of increasingly widespread importance in environmental remediation, especially in their ability to remove undesirable chemicals from hydrological systems. Despite recent advances, the high cost of these materials and the relative inability to regenerate them hinders their use at larger scales. Although it is commonly held that adsorption in fixed bed processes is more efficient than in batch processes, the definition of efficiency needs to be examined closely. In this paper, we show that there exists a critical effluent concentration above which batch processes are more efficient than fixed bed processes from this perspective. This work proposes a simple method to choose either batch or fixed bed processes when the goal is to minimize the quantity of adsorbent needed to remove contaminants to below a specified threshold level. It also provides a systematic set of self-consistency checks on experimental measurements that may be used for comparative studies of these methods.

## 1. INTRODUCTION

Fresh water is essential to human health and affects ancillary activities needed for survival. It also is a critical feedstock in the manufacture of pharmaceuticals and food, much of which depends on agriculture.[1] Although the demand for freshwater is constantly rising with the increase in world population, the available supplies are rapidly decreasing due to extended droughts and increasing groundwater and environmental pollution.[2] Human activities have contributed to the accumulation of a large variety of potentially hazardous substances in hydrological environments.[3] The most widespread contaminants range from organic dyes, pharmaceuticals, personal care products, nitrosamines, phenolic compounds, pesticides and herbicides to heavy metal ions.[4−6] Among these chemicals, most can have toxic, persistent, carcinogenic, mutagenic and detrimental effects that can harmfully affect the health, survival or activities of humans and other living organisms.[7]

Whereas numerous technologies including membrane filtration, reverse osmosis, and electrochemical methods have been applied worldwide to purify water, the development of an economic, effective and rapid water treatment at a large scale is still a challenging issue.[8−11] Adsorption technology is widely considered to be the most promising and robust method to purify aqueous solutions at low cost and with high-efficiency.[12] These techniques are attractive because they are easy to implement and are capable of removing contaminants with exceedingly low concentrations, a regime where most other separation techniques are challenged due to the small concentration gradients involved.[13] The ability to treat dilute solutions is even more valuable, as the price of solutes is inversely correlated with the concentration of the various products.[13] Moreover, adsorption is a versatile method that can remove or minimize a wide variety of organic and inorganic compounds, hence producing highly pure effluents for point-of-use water applications. Adsorption comprises the transfer of undesirable chemicals from a fluid phase (either gas or liquid) to the surface of a solid adsorbent in a transient process. Adsorption processes are limited in their ability to remove

pollutants by the capacity of the adsorbent itself. Once saturated, contaminants can no longer be removed from a solution.

Activated carbon (AC) in different forms (granular, powder, fiber or cloth) is the most common adsorbent used to treat wastewater effluents due to its high specific surface area, practical applicability and good adsorptive properties.[14−16] However, its high cost and its poor regeneration capability restrict its use.[17,18] The replacement of AC by low cost adsorbents derived from natural materials, industrial wastes, and agricultural byproducts has thus been examined.[19−21] However, the adsorption capacity of these alternative low cost adsorbents is typically less than that of AC.[22,23] Recent advances in nanoscale science and technology have enabled the development of innovative materials with enhanced adsorption properties.[24−26] Newly emerged nanostructures such as graphene, carbon nanotubes (CNTs), and their derivatives have shown great potential to remove various contaminants from aqueous systems.[27−29] Graphene and CNTs typically exhibit increased adsorption capacities than AC for both organic[28−35] and inorganic[36−40] compounds; this increase is attributed to their high specific surface area, large delocalized $\pi$ electrons and hydrophobic surfaces. The vast number of chirality configurations and functionalization possibilities of these nanostructures enables selective interactions with targeted chemicals.[41] Moreover, high regeneration efficiencies have been achieved, although the requisite processes are often energy intensive and environmentally taxing.[42−46] Commercialization of purified nanomaterials and their use in continuous flow systems is hence hindered by their cost and environmental impact.[47] To examine fully the potential of these nanostructures in adsorption processes, then, it is of paramount importance to

ensure that they are employed as efficiently as possible as new ones are developed.

The performance of an adsorbent depends not only on its intrinsic equilibrium isotherm that relates the quantity adsorbed to bulk concentration but also on the process in which adsorption is implemented. In a fixed bed process, contaminated fluid is fed continuously through a packed column of adsorbent, which ultimately becomes fully loaded with contaminants (i.e., adsorbate) when the adsorbent achieves equilibrium with the feed concentration. Mass transfer limitations and axial dispersion in actuality limit the degree of adsorbent utilization, but a large fraction of the column is in fact in equilibrium with the feed. By contrast, in a batch process, where the adsorbent is dumped into a constant volume of contaminated fluid and adsorption then ensues, the adsorbent is ultimately in equilibrium with the residual concentration in the bulk. Material balances on the solution dictate that this latter concentration is significantly lower than that of the feed. Because typical isotherms that govern equilibrium (e.g., Langmuir or Freundlich) are very steep at low concentrations, small changes in bulk concentration can lead to large changes in adsorbed contaminants. Accordingly, for low solution concentrations in the steep part of an equilibrium isotherm, the uptake of a given adsorbent can be substantially higher per unit mass in fixed bed operations than in batch processes. This can translate into a significant decrease in the amount of adsorbent material needed to remove contaminants from a given volume of wastewater effluent. Such an example is provided by Cussler[13] for the case of a linear isotherm. However, for a nonlinear isotherm (such as the Langmuir isotherm), this benefit is lost at higher bulk solution concentrations, where the amount of contaminant adsorbed is insensitive to bulk concentration. Fixed bed processes do have the benefit that all fluid exiting the column is free from contaminants up to a certain time. Although it is not possible to achieve complete removal of pollutant in a well-mixed batch process, the threshold concentration of most chemicals is greater than zero.[48] In such cases where complete removal is not required, it is possible to minimize the mass of adsorbent required to achieve a given separation by choosing either batch or fixed bed adsorption. Although continuous flow adsorption in fixed bed columns has wide application in different areas of the petroleum refining and chemical industry, cyclic-batch processes may be preferred in some cases because of the complexity of design and difficulties in controlling the continuous processes. Examples of industrial cyclic-batch adsorption applications include methanol recovery and oxygenate removal processes.[49] These considerations motivate a comparative study of the performance of batch and fixed bed adsorption.

In this paper, we examine literature that comparatively examines batch and fixed bed processes for a wide range of adsorbent/solute systems. From the perspective of adsorbent capacity, results reveal that batch processes are superior to fixed bed processes in many cases, but in other cases fixed bed processes are better. To understand these mixed results, we have examined the literature in the context of a simple model that allows one to determine the process that minimizes adsorbent utilization. Data collected from prior literature are used to validate the model. Although the present study is limited to aqueous phase adsorption, the results may be easily extended to adsorption of all types of solutions and gases. Our approach provides a practical framework by which adsorption

processes may be selected and future comparisons between fixed bed and batch processes catalogued.

## 2. METHODOLOGY

The adsorption capacities of different batch and fixed bed processes for the removal of a wide range of chemicals on various adsorbents have been examined using data extracted from the literature over the past five years. In what follows, the adsorption capacity achieved during a batch process, $q_b$, is defined as the amount of solute adsorbed on the surface of the solid at equilibrium per mass of adsorbent. Alternatively, the adsorption capacity achieved in fixed bed techniques, $q_{fb}$, corresponds to the mass of chemicals retained in the column when exhaustion is reached per mass of adsorbent. For comparison purposes, the values of $q_b$ and $q_{fb}$ have been extracted from prior literature data for similar conditions (e.g., initial concentration, temperature, solution pH) for given adsorbent/solute systems. In most cases, note that these values are lower than the maximum adsorption capacity of the solid based on the equilibrium isotherm, since achieving this maximum adsorption depends on the bulk concentration when equilibrium is achieved in the process. Therefore, a natural expression that may be used to quantify the relative efficacy of batch and fixed bed processes is given by the following ratio:

$$r = \frac{q_b}{q_{fb}} \tag{1}$$

In practice, mass transfer limitations and axial dispersion reduce the ability of the system to adsorb material in fixed bed adsorption, since the contaminant concentration front moves downstream before a given axial location in the column is fully loaded. In batch processes, there is no such loss of efficiency. Thus, although the quantity $q_b$ is a true equilibrium quantity, $q_{fb}$ is not.

A simple model is proposed to assess whether batch or fixed bed processes is better to minimize the quantity of adsorbent needed to remove contaminants to below a specified threshold level. To begin, it is assumed that the equilibrium adsorption isotherm is known for the given fluid–solid system in the form of $q$ vs $C$, where $q$ is the adsorbent capacity per unit mass (mass of contaminant adsorbed/mass of adsorbent) and $C$ is the bulk concentration. It is assumed that the system obeys the Langmuir isotherm:[50]

$$q = \frac{q_m K_L C}{1 + K_L C} \tag{2}$$

where $q_m$ and $K_L$ are temperature-dependent constants, with $q_m$ indicating the maximum monolayer adsorption capacity of the solid; $K_L$ is often referred to as the Langmuir constant. Note that the entire analysis to follow can easily be recast with a different isothermal model (i.e., Freundlich, Temkin, etc.), but the form in eq 2 has been chosen for definiteness, as it is the most commonly used isotherm in adsorption studies and provides a good fit to the data in Tables 1 and 2.

First, a batch system having fluid volume $V$ with initial bulk contaminant concentration, $C_0$, in contact with adsorbent mass used in the batch process, $M_b$, is considered. Once equilibrium is achieved in this system at a later time, the bulk contaminant concentration is reduced to a value $C_f$. A mass balance on the fluid that reflects the solute transfer process from the initial time to equilibrium can be expressed as
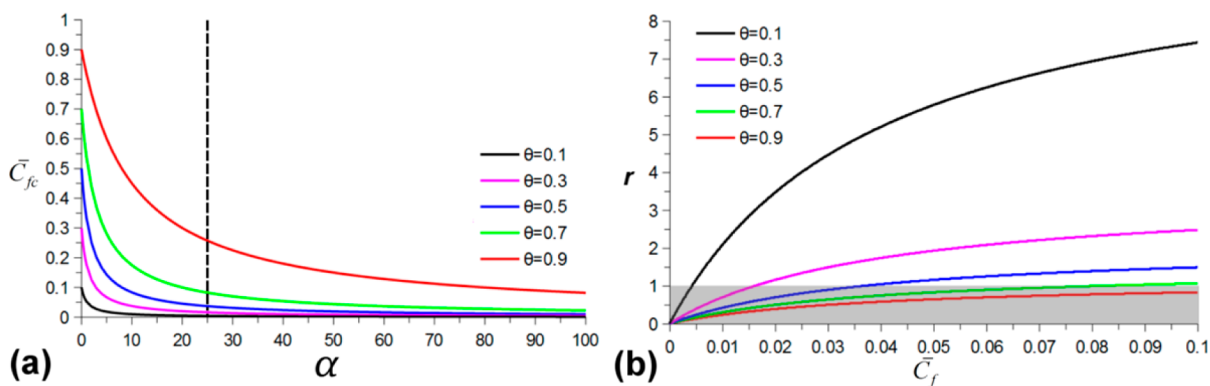
**Figure 1.** (a) Plot showing the dependence $\overline{C}_{fc}$ as a function of $\alpha$ for given values of $\theta$. (b) Graph of the ratio, $r$, as a function of $\overline{C}_{fc}$ for $\alpha = 25$ and different values of $\theta$. The shaded area represents the regime where fixed bed adsorption exhibits higher uptakes of pollutant per unit mass of adsorbent. In panel b, the value of $\alpha = 25$ was chosen as it lies within the range of fixed bed conditions based on prior literature; this value is indicated in panel a by a vertical dashed line.

$$V(C_0 - C_f) = M_b q_{C_f} \tag{3}$$

In eq 3, it has been assumed that the volume of the liquid is unaffected by the mass transfer process, which is an excellent assumption for the dilute contaminant systems usually encountered in adsorption processes. The notation $q_{C_f}$ indicates that the quantity $q$ in eq 2 is evaluated at the final concentration $C_f$. Alternatively, for a fixed bed process, the same fluid volume $V$ can be treated with adsorbent mass $M_{fb}$ in a given time interval, and a mass balance on the fluid in this case is written as

$$V(C_0 - C_f) = \theta M_{fb} q_{C_0} \tag{4}$$

In eq 4, the quantity $q_{C_0}$ is the isotherm (eq 2) evaluated at the feed concentration, $C_0$, and $\theta$ is the fraction of the fixed bed that is actually loaded when the process is terminated. Note that mass transfer resistances and axial dispersion will yield values of $\theta$ less than 1. Its value, which strongly depends on the experimental conditions (i.e., flow rate, column length and diameter, adsorbent packing, etc.), can be deduced from an analysis of breakthrough curves as described elsewhere.[13] The eqs 3 and 4 are divided and rearranged to yield:

$$\frac{M_{fb}}{M_b} = \frac{q_{C_f}}{\theta q_{C_0}} \tag{5}$$

The relation in eq 5 provides an expression for the relative adsorbent masses required to achieve the same final concentration $C_f$ for the same fluid volume $V$. It is further noted that the right-hand side of eq 5 is directly related to experimental results reported in the literature. In particular, the following expressions must hold based on the relationship between the experimentally observed adsorption capacities and reported equilibrium isotherms:

$$q_{fb} = \theta q_{C_0}, \qquad q_b = q_{C_f} \tag{6a}$$

Combining eqs 1, 5 and 6a, the ratio $r$ can be expressed in the following equivalent ways as

$$r = \frac{q_b}{q_{fb}} = \frac{q_{C_f}}{\theta q_{C_0}} = \frac{M_{fb}}{M_b} \tag{6b}$$

It is thus observed that the relative amounts of adsorbent material is directly related to the quantity, $r$, with batch processes favored (less adsorbent usage for batch compared

with fixed bed under similar conditions) when $r > 1$. Equation 6b explicitly shows that higher adsorbent capacities translate into less adsorbent material that is needed to accomplish a desired separation.

The relations in eqs 6a and 6b are general for any isotherm, but it is now written specifically for the Langmuir Isotherm. By evaluating the Langmuir isotherm (eq 2) at the concentrations $C_f$ and $C_0$ (i.e., $q_{C_f}$ and $q_{C_0}$) and substituting these expressions into eqs 6a and 6b, the following convenient form is obtained that may be directly compared with experiment:

$$r = \frac{\overline{C}_f(1 + \alpha)}{\theta(1 + \alpha \overline{C}_f)}, \qquad \overline{C}_f = \frac{C_f}{C_0}, \qquad \alpha = K_L C_0 \tag{7a}$$

Of particular interest is the final desired bulk concentration at which the required mass of the fixed bed and batch process adsorbents are equal. This critical concentration, denoted as $C_{fc}$, is obtained by setting $r = 1$ in eq 7a and rearranging to yield:

$$\overline{C}_{fc} = \frac{\theta}{1 + \alpha(1 - \theta)}, \qquad \overline{C}_{fc} = \frac{C_{fc}}{C_0} \tag{7b}$$

The interpretation of (eq 7b) is as follows:

$$r > 1 \text{ for } \overline{C}_f > \overline{C}_{fc} \tag{7c}$$

$$r < 1 \text{ for } \overline{C}_f < \overline{C}_{fc} \tag{7d}$$

The above conditions (eqs 7c and 7d) indicate the utility of the critical concentration, $C_{fc}$, as it allows one to determine whether batch or fixed bed adsorption processes will require more adsorbent to achieve a desired final concentration.

## 3. RESULTS AND DISCUSSION

**3.1. General Implications of the Model.** Figure 1a exhibits a plot of the dependence of $\overline{C}_{fc}$ on $\alpha$ for given values of $\theta$ governed by eq 7b. This plot allows one to choose the process for which a given mass of adsorbent will hold the highest capacity of solute. For each value of $\theta$, desired final concentrations that fall above the $\overline{C}_{fc}$ curve may be achieved with less adsorbent in a batch process compared with a fixed bed. Alternatively, the concentrations that fall below the curve will require less adsorbent in a fixed bed process to reach the desired separation. Because $\alpha$ is by definition only depends on the initial concentration of the effluent for a given adsorbent at a specific temperature, Figure 1a shows that batch processes

**Table 1. Comparison of the Adsorption Capacity in Batch and Fixed Bed Processes for the Removal of Organic and Inorganic Compounds on Different Types of Adsorbents**

| type of adsorbent | type of adsorbate | $C_0$ (mg/L) | $q_b$ (mg/g) | $q_{fb}$ (mg/g) | $r^a$ | ref |
|---|---|---|---|---|---|---|
| oil palm frond AC | 2,4-dichlorophenoxyacetic acid | 50 | 28.7 | 15.1 | 1.9 | 53 |
| | | 100 | 56.8 | 40.3 | 1.4 | |
| | | 150 | 84.1 | 45 | 1.9 | |
| boron waste | phosphate | 100 | 52.5 | 90.4 | 0.6 | 54 |
| | nitrate | | 63.2 | 94.1 | 0.7 | |
| chitosan−clay composite | Methylene blue | 100 | 79.8 | 125.5 | 0.6 | 55 |
| | | 200 | 135.7 | 142.3 | 0.9 | |
| graphene−sand composite | Rhodamine 6G | 1 | 55 | 26.6 | 2.1 | 56 |
| AC−chitosan composite | Methylene blue | 50 | 148.4 | 127.9 | 1.2 | 57 |
| | Acid blue 29 | | 166.4 | 334.9 | 0.5 | |
| chitosan−Fe(III) | Reactive red 120 | 100 | 290.7 | 250 | 1.2 | 58 |
| raw peanut husk | Drimarine black CL-B | 50 | 38.6 | 10.3 | 3.7 | 59 |
| | | 75 | 41.2 | 14.5 | 2.8 | |
| | | 100 | 44.3 | 15.2 | 2.9 | |
| jackfruit leaf | Crystal violet | 50 | 43.4 | 68.6 | 0.6 | 60 |
| peanut husk | Indosol yellow BG | 50 | 42.8 | 20.2 | 2.1 | 61 |
| | | 75 | 60.2 | 23.8 | 2.5 | |
| | | 100 | 72.1 | 25.9 | 2.8 | |
| montmorillonite | Methylene blue | 40 | 322.6 | 253.1 | 1.3 | 62 |
| CEC-HDTMA-clay | | | 227.3 | 43.5 | 5.2 | |
| CEC-TDMA-clay | | | 178.6 | 32.1 | 5.6 | |
| bamboo charcoal | tetracycline | 50 | 22.7 | 21.3 | 1.1 | 63 |
| granular AC | 2-phenylethanol | 200 | 20.6 | 182.2 | 0.1 | 64 |
| biomass AC | Paracetamol | 7 | 59.8 | 88.4 | 0.7 | 65 |
| sugarcane bagasse | Direct yellow 50 | 50 | 17.7 | 10.4 | 1.7 | 66 |
| volvariella volvacea | Rhodamine B | 50 | 24.2 | 8.1 | 2.9 | 67 |
| | | 100 | 33.5 | 16.2 | 2.1 | |
| | | 150 | 38.2 | 11.8 | 3.2 | |

$^a$From eq 1.

will eventually have adsorption capacities higher than those for fixed bed operations since $C_{fc}$ approaches zero when $C_0$ increases.

For given adsorbents and effluent concentrations (i.e., cases when $\alpha$ is known), eq 7a provides a quantitative comparison of the adsorbent capacities in batch and fixed bed processes. Figure 1b shows the evolution of the ratio, $r$, as a function of the desired final concentration, $\overline{C}_{fc}$, for different fixed bed column efficiencies, $\theta$, at a given value of $\alpha$. This plot can be used to determine the relative amounts of adsorbent needed in batch and fixed bed processes to accomplish a desired separation. From a practical perspective, if there were an economic reason where the use of batch and fixed bed processes were being considered, the information in Figure 1b could be used to determine the cost implications associated with the amount of adsorbent required to achieve a targeted separation. From both Figure 1a,b, it can be observed that the fixed bed efficiency, $\theta$, has a strong influence on the results. This emphasizes the importance of determining this quantity in fixed bed operations, as it not only determines the amount of adsorbent that should be added to compensate for inefficiency-induced losses, but it also may affect the selection of the type of adsorption process that may be implemented if adsorbent usage is the primary economic consideration. The efficiency of fixed bed adsorption systems is strongly dependent on the process parameters.[51] Almost all previous studies have investigated the effect of individual process parameters, such as solution pH, initial concentration, flow rate, temperature, etc. This approach not only is time-consuming but also does not account for the combined effects of all process parameters. Statistical experimental designs such as the response surface methodology or the Taguchi experimental method allow for the optimization of all the process parameters collectively based on empirical model development.[52] Such statistical tools can also be employed to evaluate the relative significance of different process parameters even in the presence of complex interactions.

**3.2. Comparison between Batch and Fixed Bed Adsorption Processes.** There is a relative lack of comparative studies between fixed bed and batch processes in prior literature, as compared with studies of each process separately. A summary of the reported adsorption capacities of batch and fixed bed processes for the uptake of a large variety of organic and inorganic solutes (adsorbates) on different types of adsorbents is reported in Tables 1 and 2, respectively. Whereas it is commonly stated that fixed bed adsorption is a more efficient method for water purification, data in these tables reveals that the capacity of the adsorbent in batch processes often exceeds that for fixed bed processes (this corresponds to cases where $r > 1$ in eqs 7a−7d).[53,56,58,59,61−63,66,67,69,71,72,74,76,77,79] From this perspective, batch processes can be seen to outperform their fixed bed counterparts under similar conditions (i.e., initial concentration, adsorbent type, temperature, solution pH, etc.). On the other hand, there also are cases where the alternative is true ($r < 1$ in eqs 7a−7d).[54,55,57,60,64,65,68,70,73,75,78] Fixed bed processes are often chosen for their continuous flow adsorption design and their ability to completely remove contaminants from an

effluent up to a certain time set by a threshold effluent concentration. However, mixed results reported in Tables 1 and 2 demonstrate that the efficiency of an adsorption process in

**Table 2. Comparison of the Adsorption Capacity in Batch and Fixed Bed Processes for the Removal of Inorganic Chemicals on Different Types of Adsorbents**

| type of adsorbent | type of adsorbate | $C_0$ (mg/L) | $q_b$ (mg/g) | $q_{fb}$ (mg/g) | $r$ | ref |
|---|---|---|---|---|---|---|
| natural hemp fibers | Co(II) | 25 | 3.3 | 12.5 | 0.3 | 68 |
| | | 50 | 5.8 | 15.4 | 0.4 | |
| boron waste | Cd(II) | 150 | 122.2 | 106.5 | 1.2 | 69 |
| | Zn(II) | | 107.7 | 97.9 | 1.1 | |
| seeweeds | Co(II) | 100 | 20.6 | 50.7 | 0.4 | 70 |
| | Ni(II) | | 18.6 | 39.7 | 0.5 | |
| zeolite rocks | Cs+ | 473.6 | 140.6 | 64.6 | 2.2 | 71 |
| | | | 104.3 | 46.8 | 2.2 | |
| zeolite A | Cs+ | 50 | 37.3 | 32.5 | 1.1 | 72 |
| | | 150 | 95.6 | 33.8 | 2.8 | |
| | Sr(II) | 50 | 44.8 | 44.5 | 1.0 | |
| | | 150 | 131.2 | 53.5 | 2.5 | |
| wheat straw | Cd(II) | 100 | 14.1 | 16.9 | 0.8 | 73 |
| functionalized mesoporous silica | Pb(II) | 50 | 52.3 | 27.6 | 1.9 | 74 |
| | | 100 | 92.2 | 16.1 | 5.7 | |
| | Cu(II) | 50 | 52.5 | 22.2 | 2.4 | |
| | | 100 | 92 | 12.3 | 7.5 | |
| | Cd(II) | 50 | 51.3 | 20.7 | 2.5 | |
| | | 100 | 75.2 | 9.3 | 8.1 | |
| polypyrole–graphene oxide | Cr(VI) | 25 | 138 | 576 | 0.2 | 75 |
| | | 50 | 157 | 585 | 0.3 | |
| protonated raw peels | Cd(II) | 10 | 31 | 13 | 2.4 | 76 |
| protonated alginate peels | | 10 | 43 | 28 | 1.5 | |
| waste pomace of olive oil factory | Cr(VI) | 50 | 6.1 | 1 | 6.1 | 77 |
| | | 100 | 10.3 | 3.3 | 3.1 | |
| | | 200 | 12.2 | 1.5 | 8.1 | |
| $Fe_3O_4$–graphene oxide | Sb(III) | 20 | 2 | 3.6 | 0.6 | 78 |
| iron-coated zeolite | Pb(II) | 5 | 5.1 | 2.3 | 2.2 | 79 |
| | Cu(II) | | 4.9 | 1.9 | 2.6 | |
| | Cd(II) | | 4.6 | 1.7 | 2.7 | |
| | Zn(II) | | 4.0 | 1.7 | 2.3 | |
| | Cr(VI) | | 3.6 | 1.2 | 3.0 | |

[a]From eq1.

term of uptake capacity per unit mass of adsorbent is not always higher in a continuous flow operation than in a batch process. In practical applications, the selection of the type of adsorption treatment can be based on the complexity of design, the difficulty of controlling the process and the minimization of the adsorbent mass to achieve a targeted separation. If adsorbent usage is the primary economic consideration in achieving a given separation, the model provided in Section 2 may be used to make this assessment.

**3.3. Assessment of Literature Data Based on the Model.** An explanation is needed for the observed mixed results in the relative adsorption capacities for fixed bed and batch processes summarized in Tables 1 and 2; in some data, batch processes has a higher capacity,[53,56,58,59,61–63,66,67,69,71,72,74,76,77,79] and in some data a

lower one.[54,55,57,60,64,65,68,70,73,75,78] The eqs 7a–7d may be used to explain these mixed results, and can serve as figures of merit to qualitatively and quantitatively determine the best adsorption method (i.e., fixed bed or batch) to reduce the bulk concentration of a known contaminated effluent to a targeted value. To this aim, the model presented in Section 2 has been employed to examine the literature survey data reported in Tables 1 and 2. This comparison demonstrates the utility of the model, but also recasts the experiments in a useful way. Additionally, it is found that the method of data analysis presented here may be used to establish self-consistency of experimental results, and highlights the measurements that should be conducted to do so. The methodology used for data extraction is first detailed before discussing the results and implications of the model.

Data listed in Tables 1 and 2 were examined in the context of the model in Section 2, and a representative subset of those data is presented below—not all data in the table could be used reliably as there were inconsistencies that precluded their use. Data analyzed needed to satisfy the following criteria: (i) The reported values of $q_b$ and $q_{fb}$ could not be larger than the reported value of $q_m$ used in the adsorption isotherm (see eq 2). (ii) Experimental breakthrough curves needed to be provided. (iii) The values of $\theta$ extracted from the reported breakthrough curves needed to be in good agreement with the values of $\theta$ calculated directly from eq 6a. Note that because $q_{fb}$ is reported in Tables 1 and 2, the reported isotherm parameters allow for the determination of $q_{C_0}$ in accordance with eq 2, and the value of $\theta$ may be extracted independently from that determined based on the analysis of the breakthrough curve. (iv) In some data extracted from the literature survey, it was stated that linear regression was used to determine the reported best-fit isotherm parameters. However, the transformation of a nonlinear model into a linearized form tends to alter the error distribution, which may induce distortion in the parameters.[80–82] To avoid these limitations, we only utilized studies that utilized nonlinear methods to analyze the experimental data.

A representative subset of the data listed in Tables 1 and 2 that satisfied the above criteria (i−iv) are provided in Table 3. Note that Table 3 shows data for different organic and inorganic solutes over a wide range of initial concentrations and parameter values. These values provide necessary inputs for the models provided in Section 2.

The key data listed in Table 3 are summarized in Figure 2. This plot provides a comparison of theory, $r_{th}$ from eqs 7a–7d, with the corresponding experimental value, $r_{exp}$ calculated from eq 1. Agreement of the model with experiment is demonstrated by the scatter of the data around the diagonal line in the figure. Also superimposed on the figure is the delineation provided by eqs 7c and 7d, where the role of the critical concentration, $C_{fc}$, is shown explicitly. Although only a subset of the data satisfying the constraints (i−iv) are shown in Figure 2 for purposes of clarity, we can report that all data in Tables 1 and 2 satisfying these constraints exhibit similar agreement. Thus, it the model proposed in Section 2 is validated.

From another perspective, the method of analysis demonstrated in this study may be used as a check on data generated and/or extracted from adsorption studies. In particular, it has been shown that when fixed bed and batch processes are compared with regards to adsorbent capacity, eqs 7a−7d should be satisfied when necessary parameters are measured with

**Table 3. Adsorption Parameters Extracted from a Subset of Experiments Reported in Tables 1 and 2**[a]

| type of adsorbate | $q_m$ (mg/g) | $q_{fb}$ (mg/g) | $q_b$ (mg/g) | $\theta$ | $\theta_{BT}$ | $K_L$ (L/mg) | $C_0$ (mg/L) | $r_{exp}$ | $r_{th}$ | ref |
|---|---|---|---|---|---|---|---|---|---|---|
| inorganic | 625 | 576 | 138 | 0.92 | 0.94 | 2 | 25 | 0.24 | 0.27 | 75 |
|  | 625 | 585 | 157 | 0.94 | 0.97 | 2 | 50 | 0.27 | 0.31 |  |
|  | 270.3 | 64.6 | 140.6 | 0.27 | 0.29 | 0.16 | 473.6 | 2.18 | 2.11 | 71 |
|  | 170.4 | 46.8 | 104.3 | 0.27 | 0.29 | 0.18 | 473.6 | 2.23 | 2.33 |  |
|  | 38 | 13 | 31 | 0.34 | 0.38 | 0.04 | 10 | 2.38 | 2.57 | 76 |
|  | 54 | 28 | 43 | 0.52 | 0.57 | 0.04 | 10 | 1.54 | 1.69 |  |
| organic | 107.2 | 90.4 | 52.5 | 0.84 | 0.91 | 0.11 | 100 | 0.58 | 0.81 | 54 |
|  | 122.4 | 94.1 | 63.2 | 0.78 | 0.83 | 0.13 | 100 | 0.67 | 0.99 |  |
|  | 48.5 | 10.3 | 38.6 | 0.21 | 0.25 | 0.18 | 50 | 3.75 | 3.98 | 59 |
|  | 48.5 | 14.5 | 41.2 | 0.3 | 0.33 | 0.18 | 75 | 2.84 | 3.03 |  |
|  | 48.5 | 15.2 | 44.3 | 0.31 | 0.34 | 0.18 | 100 | 2.91 | 2.94 |  |

[a]Note that $\theta$ is the value extracted from each reference according to eq 6a, and $\theta_{BT}$ is that extracted from the reported breakthrough curve.
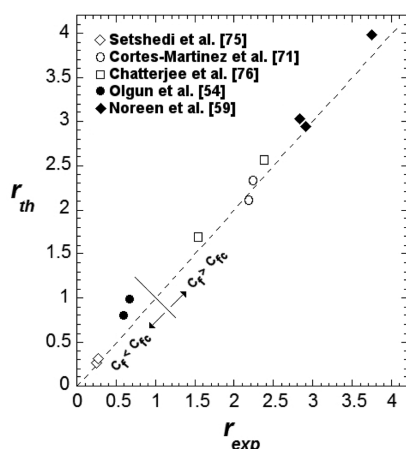


**Figure 2.** Plot showing the agreement between theoretical and experimental values of the ratio between $q_b$ and $q_{fb}$ for a representative range of studies from the literature. Ideally all data should lie along the diagonal dashed line. Note that the shaded symbols filled denote the adsorption of organic compounds, whereas the other symbols denote the adsorption of inorganic chemicals.

sufficient accuracy. Additionally, any bed efficiencies, $\theta$, can be checked by extracting its value based on the analysis of breakthrough curves and comparing with that calculated from eq 6a. This study has revealed a third check that may be made on experimental data based on eq 6b. However, such a check is not currently accessible as the mass of adsorbent is not reported in most literature examined in this study. If the mass of adsorbent is to be measured in future studies, it may be necessary to account for the differences in fluid volume used in batch and fixed bed processes, as eq 6b assumes that the same volume is treated via both methods. In such cases where different fluid volumes are treated, the ratio $r$ can be suitably adjusted as follows:

$$r = \frac{M_{fb}}{M_b} \frac{V_b}{V_{fb}} \tag{8}$$

where $V_b$ and $V_{fb}$ denote the respective fluid volumes for batch and fixed bed processes.

## 4. CONCLUSIONS

The present study has compared batch and fixed bed processes in their ability to remove contaminants from the perspective of adsorbent usage. A model has been proposed that allows one to choose either batch or fixed bed processes to minimize the amount of adsorbent needed to achieve a targeted separation. Results indicate that there is a critical effluent solution concentration that delineates concentration regimes where one process is more efficient than the other based on adsorbent usage. This critical concentration serves as figure of merit that allows one to identify the best process to use that minimizes adsorbent usage. The model has been validated by representative data from a prior literature for which comparisons are possible between fixed bed and batch process adsorption. This model also provides a systematic set of self-consistency checks on experimental measurements that may be used for comparative studies of batch and fixed bed methods, and thus provides a framework for future studies. In particular, self-consistency checks for experimental bed efficiency, relative adsorption capacities for fixed bed and batch processes, and relative amounts of adsorbent used in each treatment have been presented and discussed in this paper.

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## ■ NOMENCLATURE

**Symbol Unit Description**

$\alpha = K_L C_0$ (−)

$\theta$ = Fraction of the fixed bed that is loaded with solute at exhaustion (−)

$C_0$ = Initial bulk of solute concentration (mg/L)

$C_f$ = Bulk concentration of solute at equilibrium (mg/L)

$C_{fc}$ = Critical bulk concentration at equilibrium where the mass of adsorbents in the fixed bed and batch processes are equal for a given separation (mg/L)

$\overline{C}_{fc} = C_{fc}/C_0$ (−)

$\overline{C}_f = C_f/C_0$ (−)

$K_L$ = Langmuir constant (L/mg)

$M_b$ = Mass of adsorbent used in batch process (g)

$M_{fb}$ = Mass of adsorbent used in fixed bed process (g)

$q_b$ = Mass of solute adsorbed on the surface of the adsorbent at equilibrium per unit mass (mg/g)

$q_{fb}$ = Mass of solute retained in the column after exhaustion per unit mass of adsorbent (mg/g)

$q_m$ = Maximum monolayer adsorption capacity (mg/g)

$r$ = Relative efficacy of batch and fixed bed processes (−)

$V$ = Volume of solution (L)

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