Analysis and Design of Adsorption Systems for the Combined Removal of Arsenic and Gallium from Wastewater

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ABSTRACT: *Adsorption is a suitable method for simultaneous removal of Ga and as ionic species from semiconductor fabrication wastewater. In this and other similar multicomponent processes, the adsorption of each component affects that of others through competition for surface sites, surface charge, and the effects of pH and ionic species in the liquid phase. Process models are developed to simulate the process kinetics and reactor configurations. The results show that the modeling and parametric study are powerful methods for the design of new systems as well as for the optimization of operation in existing systems. Comparisons of different reactor configurations shows that a two-stage fixed-bed reactor system, with an optimum pH for adsorption in each stage, is an effective system for the combined removal of Ga and as species as well as other vastly different ionic impurities.*
KEYWORDS: *adsorption, arsenic, gallium, multicomponent, semiconductor, wastewater*

I. INTRODUCTION

Development of robust and efficient methods for the on-site removal gallium and arsenic ions from wastewater in semiconductor fabrication plants (fabs) is considered a high-priority research area for the electronics industry. This is due to the expected increase in the application of gallium arsenide as the substrate in the state-of-the-art fast devices. These impurity compounds need to be removed from wastewater before its discharge or recovery/reuse. Therefore, there is a need for treatment methods and systems that would be suitable for on-site operation and handling of wastewater from processes that handle gallium and arsenic compounds.

The wastewaters from high technology manufacturing, such semiconductor fabs, are generally less complicated than most other forms of wastewater. For example, waste streams from wafer polishing processes are well characterized and contain on the average about 2000 mg/l dissolved arsenic [1], compared to typical industrial wastewaters that usually contain a wide verity of contaminants at much higher concentrations. This presents an opportunity to develop efficient systems that are tuned for selective removal of targeted impurities from fab wastewater. However, these systems need to be robust, small in footprints, and possibly transfer impurities froma highly dilute phase to a concentrated form that can be hauledaway to off-site facilities for large-scale treatment, recovery, and disposal.

Previous studies have shown that removal by adsorption is potentially a suitable method for removal of Ga and As from semiconductor wastewater; a variety of sorbents have been considered and evaluated for this application[2]. However, these studies haveprimarily focused on the adsorption kinetics, sorbent capacities, and optimum operating conditions for effective adsorption of a single compound (sorbate). The dynamic properties, the sorbent capacity, and the optimum operating conditions of multi-component adsorption are generally less understood and more complicated than those of single component adsorption due to differences in charge, size, and chemical properties of various ions. Forexample, the adsorption of one component could inhibit the adsorption of another or possibly even reverse thecapture of a compound by replacing what is already adsorbed on the surface. These issues present additional challenges in the choice of proper sorbent, the design of the system configuration, and the optimization of operating conditions for the adsorption vessels (called reactors in this study). More specifically, the combined removal of Ga and As is challenging due to the large differences in the properties of these two ions, including mass and charge.

Process modeling is proven an effective method for the analysis and design of reactors. However, in most previous studies of adsorption systems single-component isotherm models have been used to analyzemulti-component systems. For example, the extended Langmuir equation [3] is one such model, which has been widely employed for multi-component adsorption. This model assumes a constant energy of sorption, no interaction between components and equal competition between species for the sorption sites, which violate

the fundamental assumptions since sorbate interactions tend to occur in multi-component systems. Examples of mechanistic modeling of multi-component can be found in literature [4, 5]. However, in these studies only positively charged ions with limited competition on the sorbent surface were considered.

Choosing the suitable reactor type is an important aspect of development and design of an adsorption system. Once a sorbent is selected and the operating conditions are optimized at the laboratory scale, the challenge is in the scale-up to largerreactors for treating large volumes of wastewater in a cost-effective manner. Finding the optimum level of mixing in these systems is key to a successful process design,particularlywhen the complexities of adsorption are combined with the application of Continuous Stirred Tank Reactors (CSTRs) and Fixed-Bed Reactors (FBRs) systems [6, 7, 8].The purpose of this study has been tounderstand the dynamics of combined adsorption of Ga and As, determine the key kinetics and thermodynamic properties needed for process design, suggest a system configuration for this multi-component adsorption, and develop a generic model useful for evaluating the options on the system configuration and its operating conditions.

II. METHOD OF APPROACH

2.1 Process Kinetics Model

Although the mechanism of adsorption varies for different sorbents, the model developed for As and Ga removal will have general features applicable to other multi-component ionic adsorptionsystems. A key factor is the effect of pH and the role that it plays in the interaction among adsorbates. In general, pH affects the sorbent surface charge and influences the dynamics of the adsorption process. Inmulti-component systems, there are two ways that the presence of a component affects the dynamics of adsorption of another compound: the primary effect is the competition among compounds on occupying sorbent sites; the secondary and less significant effect is the potential change in the pH and the resulting surface charge when a new contaminant is introduced.

Usually, the adsorption of negatively charged species is favored at low pH values where the surface groups are protonated and the surface is rich in positively charged sites. On the contrary, positively charged species prefer higher pH conditions. The model developed in this research assumes that the sorbent has two types of sites, namely positively charged and negatively chargedsites. The total number of sites is a given property of the sorbent; however, the number of each type of site changes with pH.In this model, α is defined as the ratio of the available sites for adsorption of component 1, which is assumed to be a negatively charged impurity (such as As ionic species).Consequently, 1-α is the fraction of available sites that are negative and are available for adsorption for component 2 which is a positively charged species(such as gallium ion).Based on our study of algae as a biosorbent, α,as a function of pH,is represented by the following equation:

$$\alpha = 0.35 \log(pH + 1) \quad (1)$$

This equation allowsα varying between 0 and 1 in the pH range of 0 to 14. There are more available sites for component 1 at higher pH, which means that the adsorption of component 1 is favored by higher ph. The adsorption rates are as follows:

$$r_{a1} = k_{a1} C_1 (\alpha S_0 - C_{s1}) \quad (2)$$
$$r_{a2} = k_{a2} C_2 ((1 - \alpha) S_0 - C_{s2}) \quad (3)$$

where k_{a1} and k_{a2} (m^3/mol·s) are the adsorption rate coefficients for components 1 and 2, $C_1$and C_2(mol/m^3) are the concentrations of components 1 and 2 in the liquid phase at time t, C_{s1} and C_{s2} (mol/kg) are the amounts of components 1 and 2 adsorbed by the sorbent at time t, and S_0 (mol/kg) is the total available binding sites or the maximum adsorption capacity of sorbent.

The desorption rate for each species depends on its solid phase concentration as well as on the liquid phase concentration of the other component which attracts it back to the liquid phase through its opposite charge attraction. Therefore, the desorption rates for the two species can be expressed as:

$$r_{d1} = k_{d1} C_{s1} C_2 \quad (4)$$
$$r_{d2} = k_{d2} C_{s2} C_1 \quad (5)$$

where k_{d1} and k_{d2} (m^3/mol·s) are the desorption rate coefficients of components 1 and 2, respectively.

2.2 Fixed-Bed Reactor (FBR) Model

Assuming a homogeneous and isothermal system, the mass balance for the FBR system is expressed by:

$$\frac{\partial C_1}{\partial t} = D_z \frac{\partial^2 C_1}{\partial z^2} - u \frac{\partial C_1}{\partial z} - \frac{\rho(1-\varepsilon)}{\varepsilon} \frac{\partial C_{s1}}{\partial t} \quad (6)$$

$$\frac{\partial C_{s1}}{\partial t} = k_{a1} C_1 (\alpha S_0 - C_{s1}) - k_{d1} C_{s1} C_2 \quad (7)$$

$$\frac{\partial C_2}{\partial t} = D_z \frac{\partial^2 C_2}{\partial z^2} - u \frac{\partial C_2}{\partial z} - \frac{\rho(1-\varepsilon)}{\varepsilon} \frac{\partial C_{s2}}{\partial t} \quad (8)$$

$$\frac{\partial C_{s2}}{\partial t} = k_{a2} C_2 ((1 - \alpha) S_0 - C_{s2}) - k_{d2} C_{s2} C_1 \quad (9)$$

where t(s) is time, z (m) is the axial position, D_z (m^2/s) is the axial dispersion coefficient, ρ (kg/m^3) is the density of biomass,ε is the bed porosity, and u (m/s)is the interstitial velocity.The initial and boundary conditions are:

$t = 0, \quad z > 0, \quad C_1(t,z) = 0, C_{s1}(t,z) = 0, \quad C_2(t,z) = 0, C_{s2}(t,z) = 0 \quad (10)$

$t > 0, \quad z = 0, \quad u(C_{01} - C_1) = -D_z \frac{\partial C_1}{\partial z}, \quad u(C_{0,2} - C_2) = -D_z \frac{\partial C_2}{\partial z} \quad (11)$

$t > 0, z \to L, \quad \frac{\partial C_1(t,z)}{\partial z} = 0, \quad \frac{\partial C_2(t,z)}{\partial z} = 0 \quad (12)$

where C_{01} and C_{02} (mol/m^3) are the inlet concentrations of component 1 and 2, respectively, and L (m) is the length of the reactor.In case of two FBR in series with different pH, the entire system can be regarded as one FBR where a change in pH along the reactor length.

2.3 Continuously-Stirred Tank Reactor (CSTR) Model
Assuming perfect mixing and ignoring the heat produced by stirring, the mass balance for the CSTR system is expressed by:

$\frac{\partial C_1}{\partial t} = \frac{Q(C_{01} - C_1)}{\varepsilon V} - \frac{\rho(1-\varepsilon)}{\varepsilon} \frac{\partial C_{s1}}{\partial t} \quad (13)$

$\frac{\partial C_{s1}}{\partial t} = k_{a1} C_1 (\alpha S_0 - C_{s1}) - k_{d1} C_{s1} C_2 \quad (14)$

$\frac{\partial C_2}{\partial t} = \frac{Q(C_{02} - C_2)}{\varepsilon V} - \frac{\rho(1-\varepsilon)}{\varepsilon} \frac{\partial C_{s2}}{\partial t} \quad (15)$

$\frac{\partial C_{s2}}{\partial t} = k_{a2} C_2 ((1-\alpha) S_0 - C_{s2}) - k_{d2} C_{s2} C_1 \quad (16)$

where Q (m^3/s) is the feed rate, and V (m^3) is the volume of the reactor. The initial conditions are:

$t = 0, \quad C_1(t) = 0, C_{s1}(t) = 0, \quad C_2(t) = 0, C_{s2}(t) = 0 \quad (17)$

For two CSTR in series, four more equations are added for the second CSTR:

$\frac{\partial c_1^*}{\partial t} = \frac{Q(C_1 - c_1^*)}{\varepsilon V^*} - \frac{\rho(1-\varepsilon)}{\varepsilon} \frac{\partial c_{s1}^*}{\partial t} \quad (18)$

$\frac{\partial c_{s1}^*}{\partial t} = k_{a1}^* c_1^* (\alpha^* S_0 - c_{s1}^*) - k_{d1}^* c_{s1}^* c_2^* \quad (19)$

$\frac{\partial c_2^*}{\partial t} = \frac{Q(C_2 - c_2^*)}{\varepsilon V^*} - \frac{\rho(1-\varepsilon)}{\varepsilon} \frac{\partial c_{s2}^*}{\partial t} \quad (20)$

$\frac{\partial c_{s2}^*}{\partial t} = k_{a2}^* c_2^* ((1-\alpha^*) S_0 - c_{s2}^*) - k_{d2}^* c_{s2}^* c_1^* \quad (21)$

where the symbols with " * " represent the properties of the second CSTR. The liquid concentration at the outlet of the first CSTR is the same as the inlet concentration of the second one. The initial conditions for the second CSTR are:

$t = 0, \quad c_1^*(t) = 0, c_{s1}^*(t) = 0, \quad c_2^*(t) = 0, c_{s2}^* = 0 \quad (22)$

2.4 Multi-Stage Reactors Model
An option explored in this study for the adsorption treatment of complex multi-component wastes is a two-stage configurationwhere the stages of the system are operated at two different pH conditions (Fig. 1). Stage 1 would be at a relatively high pH, suitable for removal of positively charged contaminants such as gallium and most metallic ions. The second stage, operated at relatively low pH, would be primarily for the removal of negatively charged impurities such as arsenic species. Adsorption in two stages while controlling pH, would allow foroptimization of the adsorption process for each class of impurities. The optimum values and the range of pH in the two stages would depend on the type and the composition of the ions to be removed.

Fig. 1 Treatment of multi-component wastewater by staged adsorption
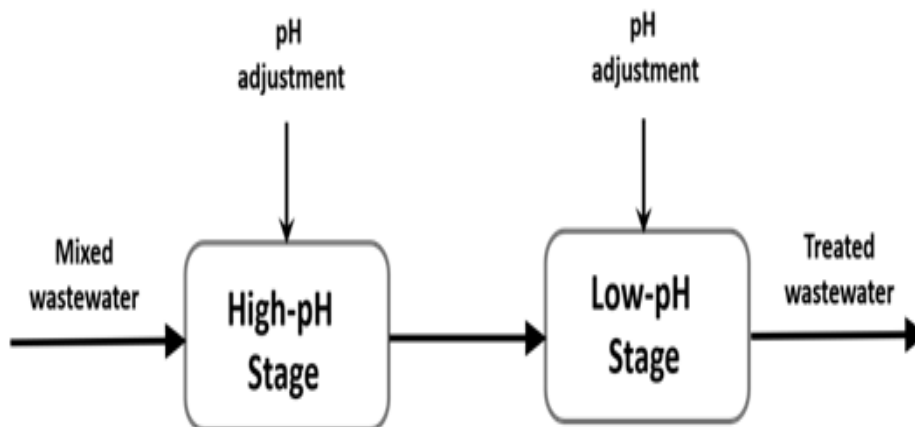
Selection of suitable reactor type and its design parameters are often a key aspect for developing and optimizing chemical process system. In this study, two types of reactor systems, FBRs and CSTRs are compared

for their adsorption performances. The choice of reactor type and their conditions are discussed through case studies.

2.5 Model Parameters

A number of case studies were conducted to illustrate the application of the process modeling for studying and designing optimum systems for multi-component adsorption forwastewater treatment andpurification. This study included comparison of FBR and CSTR systems, using models developed in the previous section.Inparticular, the cases considered removal of two impurities with vastly different adsorption properties. The use of both single reactor as well as staged dual-reactor systems were investigated.Thesystem parameters used in this study are for illustration purposes and may not correspond exactly to the operation of a particular fabrication plant.However, the parameters are close to properties of arsenic and gallium in wastewater from GaAs semiconductor processing [1, 9]. The assumed parameters to illustrate the model application are listed in TABLEs 1 and 2.In comparing systems, the total system size, feed properties, and operating conditions were kept the same. Instaged-reactor systems, the two reactors in series were equal in volume at two different pH values; each pH value favoring the adsorption of one of the two impurities.

TABLE 1 Parameters for single reactor system.

Parameter	Value	Parameter	Value
S_0 (mol/kg)	1	D_z (m²/s)	1.2E-7
C_{01} (mol/ m³)	1.5	pH	8.5
C_{02} (mol/ m³)	1.5	L (m)	1
k_{a1} (m³/mol·s)	3.5E-6	d (m)	0.2
k_{d1} (m³/mol·s)	8E-8	ε	0.96
k_{a2} (m³/mol·s)	2.2E-5	Q (m³/s)	1.67E-7
k_{d2} (m³/mol·s)	8.5E-7		

TABLE 2 Parameters for staged reactor system.

Parameter	Value	Parameter	Value
S_0 (mol/kg)	1	pH_1	8.5
C_{01} (mol/ m³)	1.5	pH_2	2.3
C_{02} (mol/ m³)	1.5	L_1(m)	0.5
k_{a1} (m³/mol·s)	3.5E-6	L_2(m)	0.5
k_{d1} (m³/mol·s)	8E-8	d (m)	0.2
k_{a2} (m³/mol·s)	2.2E-5	ε	0.96
k_{d2} (m³/mol·s)	8.5E-7	Q (m³/s)	1.67E-7
D_z(m²/s)	1.2E-7		

III.   RESULTS AND DISCUSSION

There are twoprimary measures of performance, when comparing the configuration and operation of different reactor systems:

a) The rate and the extent of purification, given a specific feed flow rate and impuritiesconcentrations. This is best shown by comparing the temporal profiles of the impurities concentrations in the system outlet.

b) The lifetime for the system, defined as the length of time during which the system is able to provide the required purification before the sorbent useful life is expired. The required purification in this study is selected to beat least 80%of the incoming concentration for each impurity (C_1/C_{01} and C_2/C_{02} less than 0.2 in the system outlet). Once this lifetime is reached, the system operation will no longer continue to meet the purification specification and the sorbent needs to be regenerated or replaced.

Figs. 2-5 show the time profiles for components1 and 2 in FBR and CSTR configurations. Figs.2-3 are for the single-stage reactor systems and Figs.4-5are for two-stage reactor systems. The operation lifetimes for the removal of each component (t_{f1} and t_{f2}) are also shown on these graphs. The system lifetime (t_{fs}) is the smaller of the $t_{f1}$and t_{f2} values, indicating the first time the purification of one of the impurities fails to meet the overall system specification. The lifetime corresponding to these results are also shown on Figs. 2-5.
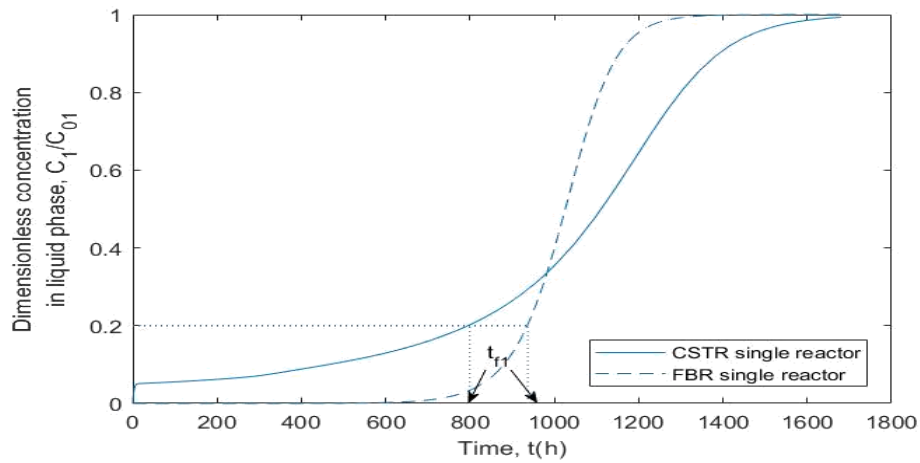
Fig. 2Concentration profiles of impurity 1 (negatively charged)in the outlet of the single CSTR and FBR systems
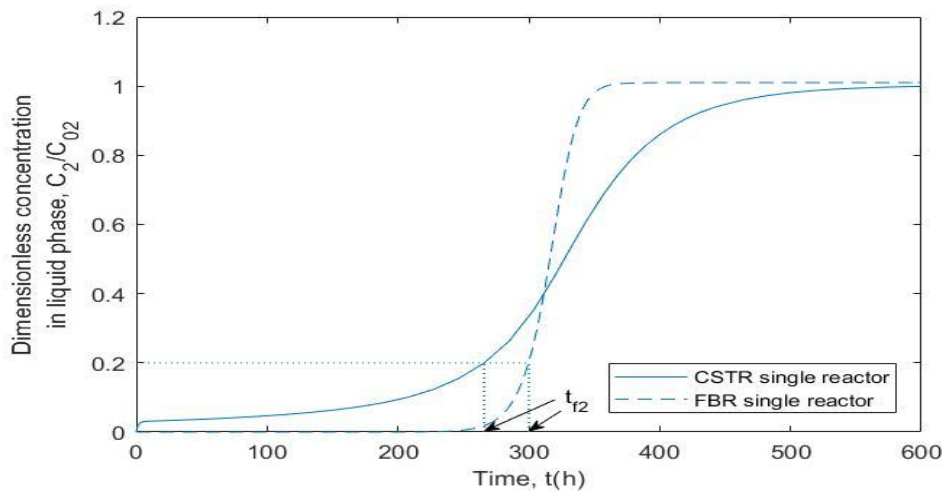

Fig. 3Concentration profiles of impurity 2(positively charged) in the outlet of the single CSTR and FBR systems
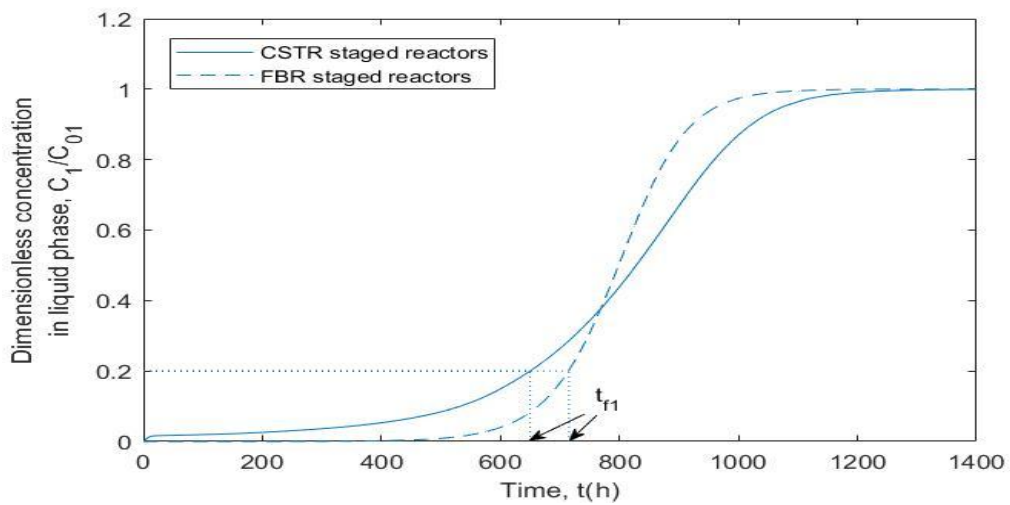

Fig. 4Concentration profiles of impurity 1 (negatively charged)in the outlet of the staged CSTR and FBR systems
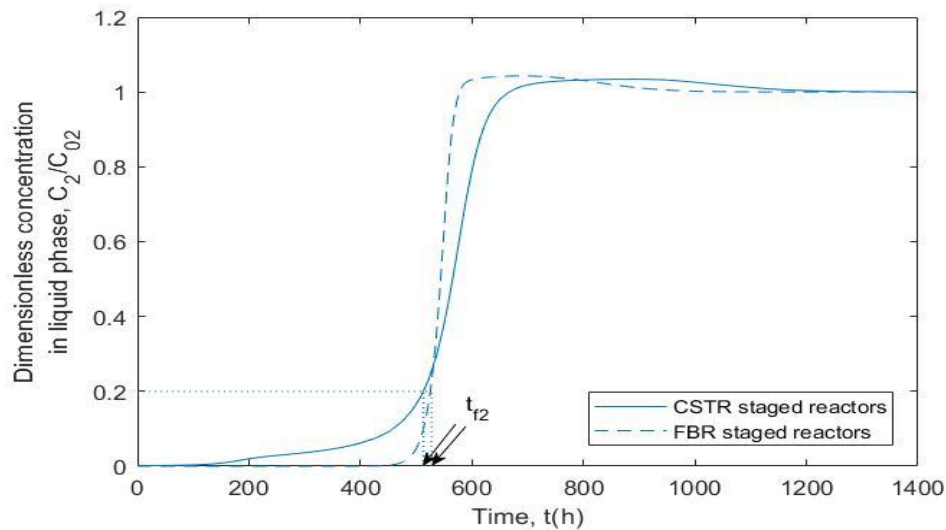
Fig. 5Concentration profiles of impurity 2 (positively charged)in the outlet of the staged CSTR and FBR systems

The above results show that FBR delivers a significantly lower concentration of both components in the outlet; this means better purification quality and dynamics. The cross over and the reversal of the position of the profiles in these figures are in the range past the acceptable lifetime duration and therefore are not of practical significance and do not change this general conclusion. TheFBR system shows a generally larger t_{f1}, t_{f2}, and the systems lifetime, t_{fs}, compared to the CSTR system.

Regarding the benefits of staging the system, the staged systems show much better performance compared tothe single reactor systems in purification quality and dynamics. However, comparison of the lifetime in single reactors with that in the staged reactors does not follow ageneraltrend.This is because in a staged system two opposing factors affect the overall system lifetime. One factor is the enhancement of the adsorption rate due to staging of the pH for higher removal of each component. However, in a constant volume system, staging reduces the volume of each stage; this means that only a portion of the bed (not the entire reactor) is used forthis enhanced adsorption in each stage.The net effect of these two opposing factors dependson various operating conditions.

Another set of results, which shows the fundamental difference between the two reactortypes, is the concentrationspatial profile of adsorbed impurities on the sorbent in the reactor.Figs.6-9aretypical profiles of the adsorbed concentrations in the single and staged CSTR and FBR systems during the operation. As expected, the CSTR has a uniform adsorbed concentration profile.However, the FBR shows a high concentration zone, which progresses from inlet to outlet as time goes on. This means the loading of the sorbent in the CSTR builds up uniformly at all locations inside the reactor where the loading in FBR is by saturating the upstream and a gradual drift of the adsorption front towards the outlet. These trends are observed for both impurities in both single and staged systems.

While the adsorbed loading distribution profiles in FBRs are very different from those in CSTRs, the total integrated amount (or average loadings on the sorbent) are not very different for these two reactor configurations, as shown in Figs. 10 and 11. This is because in an FBR, adsorption is heavy on the reactor upstream side and light on the downstream side; in a CSTR approximately the same loading is uniformly distributed. This aspect of the waste treatment was beyond the scope of the present study but will be addressed in future.
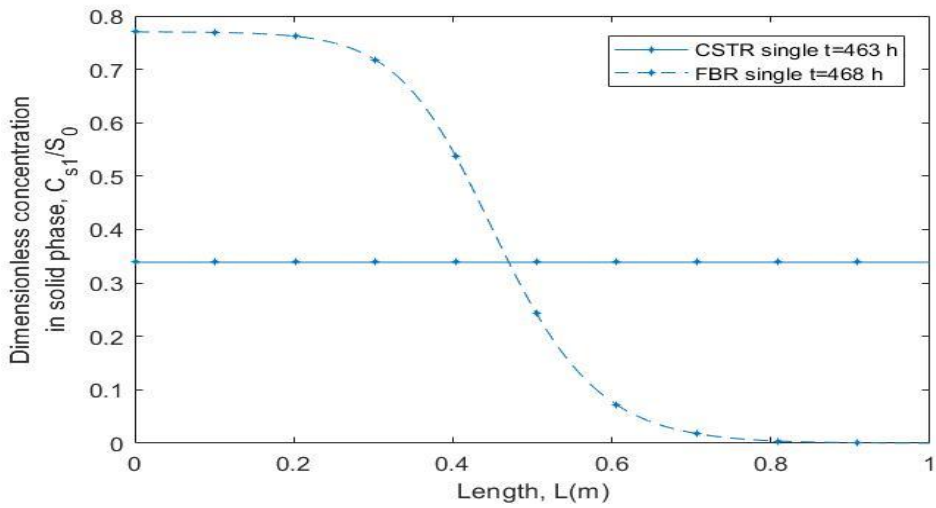
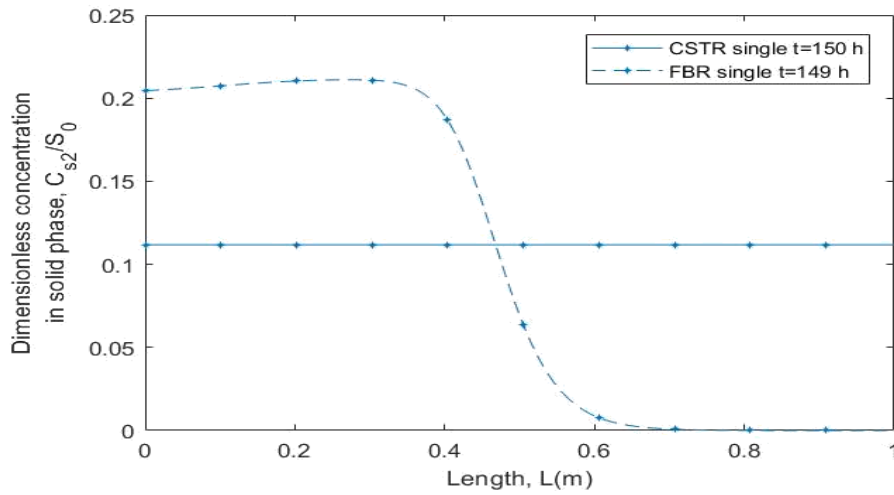**Fig. 6 Concentration profiles of impurity 1 along the single CSTR and FBR systems**

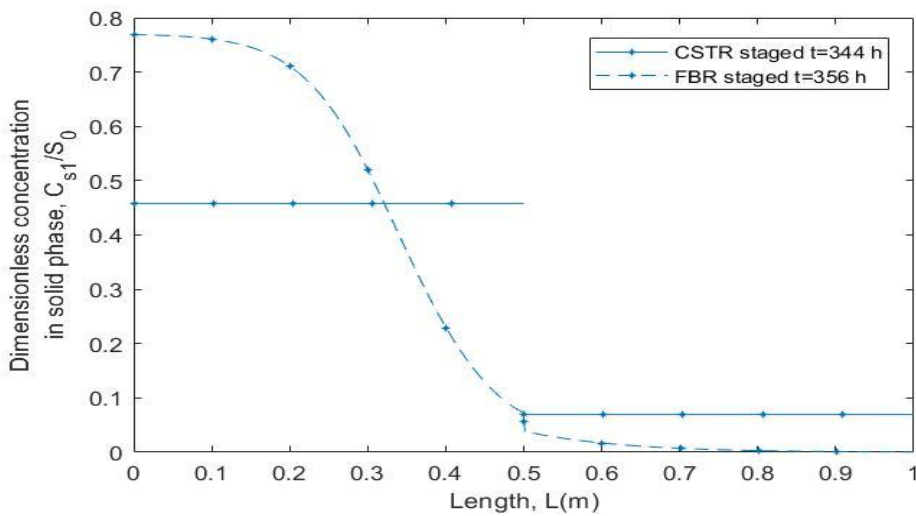**Fig. 7 Concentration profiles of impurity 2 along the single CSTR and FBR systems**

Fig. 8 Concentration profiles of impurity 1 along the staged CSTR and FBR systems
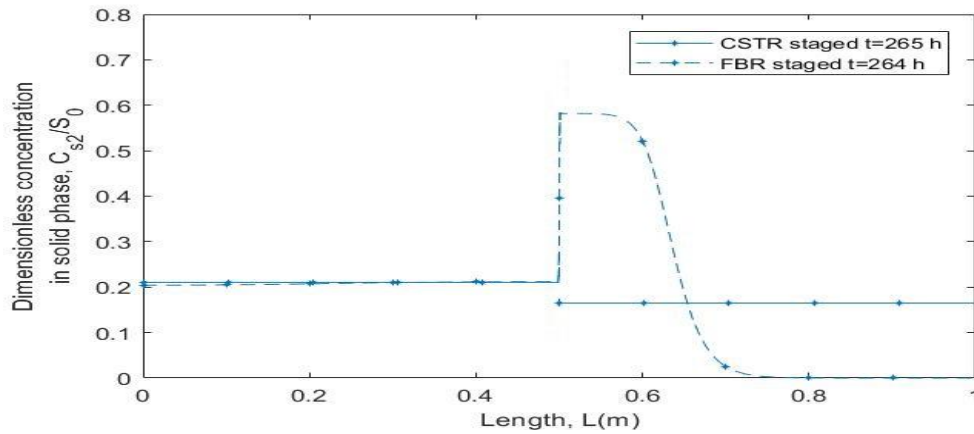
Fig. 9 Concentration profiles of impurity 2 along the staged CSTR and FBR systems
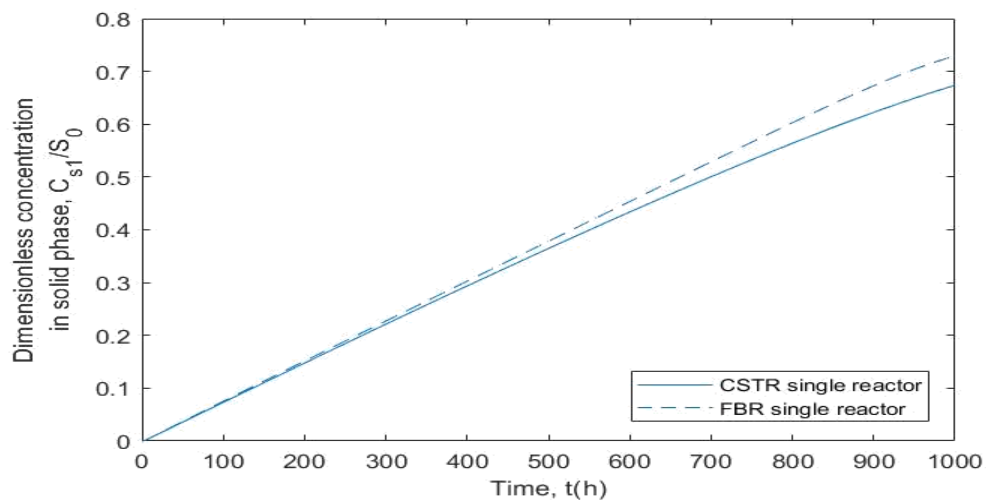

Fig. 10 Average adsorbed concentration of impurity 1 in the staged CSTR and FBR systems
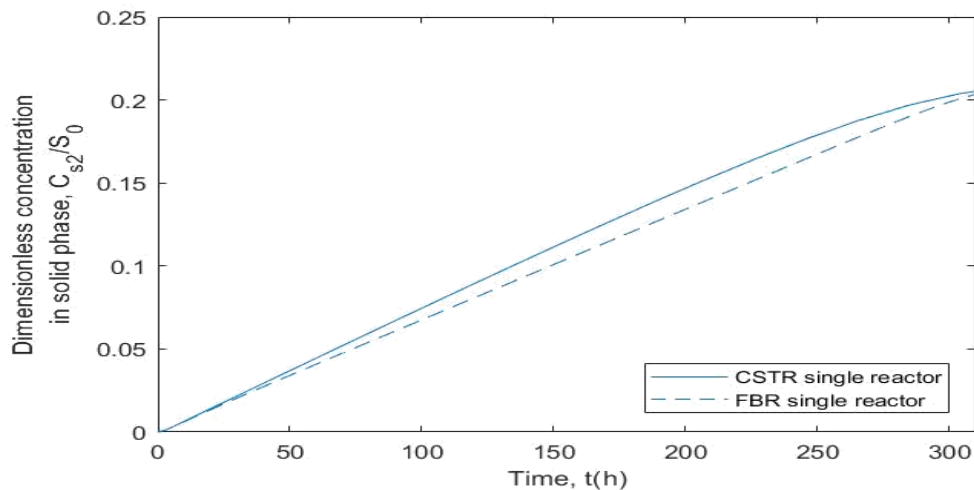

Fig. 11 Average adsorbed concentration of impurity 2 in the staged CSTR and FBR systems

The model developed in this study is potentially a powerful tool for design and optimization of adsorption processes for wastewater treatment. Typically, its application would involve a systematic parametric study to understand the effect of various design parameters on the performance of the system and its parts. Parametric studies are also useful to investigate the cause and safeguard against the unintended process disturbances and variations in a system during its routine operation. As an example of this parametric study, the

effect of key parameters on the lifetime of the staged reactors, which have been presented as a base case in this work, is summarized in TABLE3.Since flow rate is a key parameter, which is often subject to variations, the effect of change in the flow rate on the dynamics of purification and the process lifetime for each component is given in more details in Figs. 12-13.

TABLE 3 Operational Lifetime of CSTR and FBR Systems

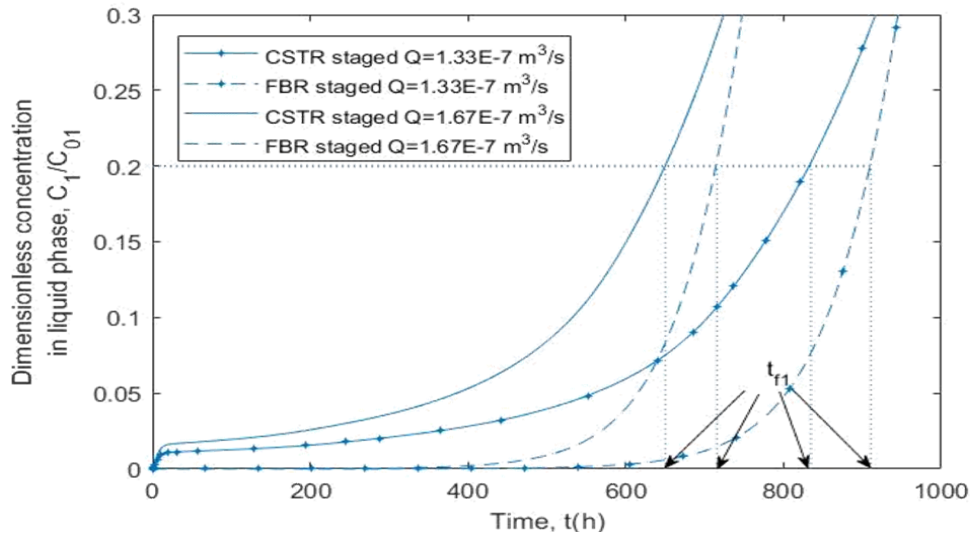| Parameter	Base value	% change in base value	% change in t_{f1}		% change in t_{f2}		% change in f_{ts}	
			CSTR	FBR	CSTR	FBR	CSTR	FBR
Q	1.67E-7 m^3/s	+30%	-31%	-25%	-24%	-24%	-24%	-24%
C_{01}, C_{02}	1.5 mol/m^3	+30%	-22%	-21%	-22%	-21%	-22%	-21%
ε	0.96	-3%	+74%	+71%	+68%	+64%	+68%	+64%
d	0.2 m	+30%	+78%	+75%	+72%	+70%	+72%	+70%
L_1, L_2	0.5 m	+30%	+34%	+33%	+31%	+31%	+31%	+31%
S_0	1 mol/kg	+30%	+32%	+31%	+29%	+28%	+31%	+28%
k_{a1}	3.5E-6 m^3/mol·s	+30%	+4%	+3%	+<1%	0	+<1%	0
k_{d1}	8E-8 m^3/mol·s	+30%	-1%	-<1%	-<1%	0	- <1%	0
k_{a2}	2.2E-5 m^3/mol·s	+30%	0	0	+1%	+<1%	0	0
k_{d2}	8.5E-7 m^3/mol·s	+30%	0	0	- <1%	- <1%	0	0

Fig. 12 Effect of change in flow rate on the dynamics of adsorption and process lifetime (component 1)
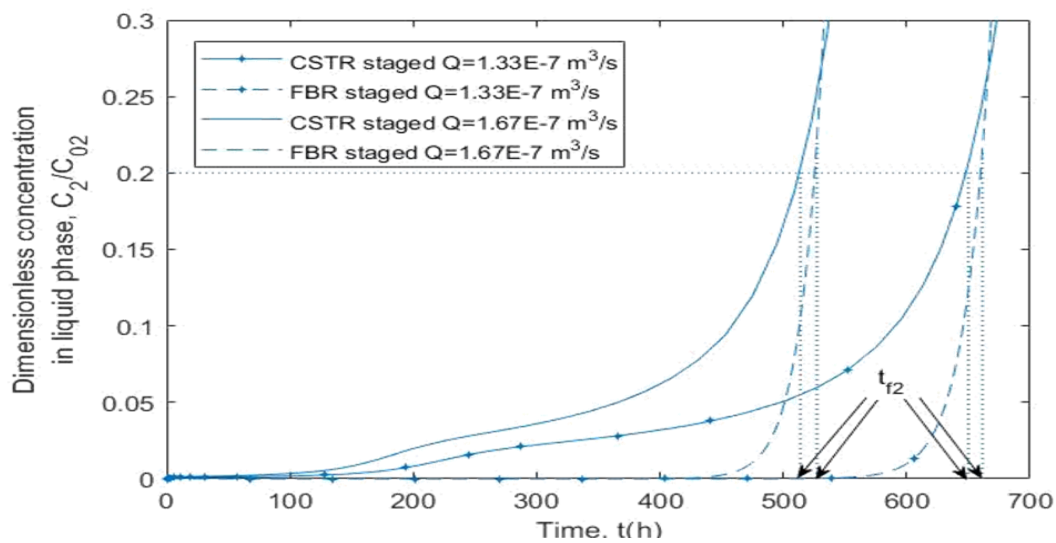

Fig. 13Effect of change in flow rate on the dynamics of adsorption and process lifetime (component 2)

IV. CONCLUSIONS

Multi-component models were developed to simulate the process kinetics and reactor configurations for the simultaneous removal by adsorption of arsenic and gallium from wastewater. Many aspects of these models are generic and can be applied to other similar multicomponent systems. The results show that for multicomponent ionic systems, the adsorption of each component affects that of others through competition for surface sites, surface charge effects, as well as the effect of charged ions and pH in the liquid phase. For vastly different ions, like arsenic and gallium, the optimum reactor configuration is a two-stage fixed-bed reactor system where each stage in series is operated at the optimum pH for adsorption of one type of impurity (for example, positively or negatively charged). This configuration gives superior performance in both the kinetics of adsorption, quality of treated water, and the sorbent system lifetime. The modeling and parametric study in this work present a method of approach that is applicable and useful for the design of new systems as well as for the optimization of operating conditions in an existing system.

ACKNOWLEDGMENT

V. NOMENCLATURE

C_1 concentrations of component 1 in the liquid phase at time t (mol/m^3)
C_2 concentrations of component 2 in the liquid phase at time t (mol/m^3)
C_{01} inlet concentrations of component 1 (mol/m^3)
C_{02} inlet concentrations of component 2 (mol/m^3)
C_{s1} amount of component 1 adsorbed by sorbent at time t (mol/kg)
C_{s2} amount of component 2 adsorbed by sorbent at time t (mol/kg)
d diameter of the reactor (m)
D_z axial dispersion coefficient (m^2/s)
k_{a1} adsorption rate coefficient of component 1 (m^3/mol·s)
k_{a2} adsorption rate coefficient of component 2 (m^3/mol·s)
k_{d1} desorption rate coefficient of component 1 (m^3/mol·s)
k_{d2} desorption rate coefficient of component 2 (m^3/mol·s)
L length of the whole reactor system (m)
L_1 length of the first reactor (m)
L_2 length of the second reactor (m)
Q feed rate(m^3/s)
r_{a1} adsorption rate of component 1 (m^3/mol·s)
r_{a2} adsorption rate of component 2 (m^3/mol·s)
r_{d1} desorption rate of component 1 (m^3/mol·s)
r_{d2} desorption rate of component 2 (m^3/mol·s)
S_0 total binding sites or maximum metal adsorption capacity of sorbent (mol/kg)
t time (s)
t_{f1} operation lifetime for the removal of component 1 (h)
t_{f2} operation lifetime for the removal of component 2 (h)
t_{fs} system lifetime (h)
u interstitial flow velocity (m/s)
V volume of the reactor (m^3)
z axial position (m)
α ratio of the binding sites for component 1 to the total binding sites
ε sorbent bed porosity
ρ density of sorbent (kg/m^3)

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