Adsorptive Removal of Se(IV) by Citrus Peels: Effect of Adsorbent Entrapment in Calcium Alginate Beads

Subhabrata Dev, Aibyk Khamkhash, Tathagata Ghosh, and Srijan Aggarwal

1. INTRODUCTION

Selenium (Se) serves as a necessary nutrient for living organisms at trace concentrations because of its role as an important cofactor for several enzymes such as glutathione peroxidase, deiodinase, methionine sulfoxide reductase B1, and some forms of thioredoxin reductase.1 These enzymes protect the living cells from the toxic effect of oxide radicals.2 Se shows a toxic effect, however, when consumed in excess. Dietary intake of Se above 400 μg is reported to cause severe damage known as selenosis, which shows symptoms like fatigue, gastrointestinal disorder, hair loss, and neurological disorder.3 The permissible limit of Se proposed by the U.S. Environment Protection Agency, the European Union, and the World Health Organization (WHO) has been reported to be 40, 10, and 50 μg·L\(^{-1}\), respectively.4 The contamination of water bodies by Se arises from both natural and industrial activities. The contamination from natural processes includes volcanic explosion and weathering of Se-rich rocks.5 The industrial Se sources include combustion of coal, petroleum refining, mining, mineral processing, pesticide manufacturing, and agricultural irrigation.6 Se is present in an aqueous solution in two different forms namely selenate (SeO\(_4^{2-}\)) and selenium (SeO\(_3^{2-}\)), where the former is less toxic than the latter.7 The speciation of Se is governed primarily by pH and redox potential of the localized aqueous environment.8

Removal of Se from contaminated water can be achieved using precipitation, ion-exchange resins, coagulation, membrane processes, electrochemical process, floatation, evaporation, adsorption, and microbial processes.9 Most of these processes are cost-prohibitive and often inefficient in Se removal, especially for the water co-contaminated with other metals.10 The membrane processes suffer from fouling and need regular replacement of membranes,11 while microbial processes are slow and require an additional and ongoing supply of a carbon source.12 Biosorption techniques, however, have gained importance for the treatment of Se contaminated waters especially due to their low-cost and waste resource recovery potential, making them alternative sustainable options.13−20 Se has been removed from contaminated water using different biosorbents such as peanut shell,21 crustacean shell,22 wheat, maize, and rice bran,23 dry yeast biomass,24 and seaweed.25

The citrus peels have been recently used as non-conventional biosorbents to remove various inorganic aquatic contaminants such as Pb(II),26 U(VI),27 Ni(II),28 and Cr(VI).29 Characteristics of citrus peels like nontoxicity,
biodegradability, water solubility, and presence of cellulose connected by β 1→4 bonds make it an efficient biosorbent.\(^\text{26}\) Another adsorbent, calcium alginate beads, have also been frequently used to remove several inorganic contaminants from water\(^\text{29}\)\(^\text{−}\)\(^\text{31}\) with and without embedded adsorbents. Calcium alginate beads are composed of 1,4-β-D-mannurionate and α-L-guluronate; the presence of −OH and −COOH groups in Ca-alginate beads provides them efficient sorption capacity through chelation and ion-exchange mechanism.\(^\text{32}\) Several studies have shown that the porous structure of ionotropic metal alginates contributes a crucial role in the biosorption of toxic metals from wastewater.\(^\text{33}\)\(^\text{−}\)\(^\text{35}\) The bare citrus peels are reported to get disintegrated and cause clogging when used as an adsorbent media inside packed-bed reactors.\(^\text{36}\) Entrapment of bare citrus peels in Ca-alginate would increase the structural stability and reusability of citrus peels. The Ca-alginate entrapped citrus peel beads would have enhanced biosorption capacity for other metallic ions in addition to Se\(^{\text{25}\text{−}\text{26}}\) and Se\(^{\text{4+}}\)\(^\text{27}\text{−}\)\(^\text{28}\) because of the presence of a high number of −OH and −COOH functional groups from alginate beads.\(^\text{37}\) To our knowledge, biosorption of Se using bare citrus peels, Ca-alginate, and Ca-alginate entrapped citrus peels (Ca-alginate@citrus) has not been explored previously; in this research, we report a detailed investigation of Se biosorption with citrus peels, Ca-alginate, and Ca-alginate@citrus.

The objective of this study is to evaluate the biosorption potential of citrus peels, Ca-alginate beads, and Ca-alginate@citrus for the removal of Se from aqueous solutions. Several factors that might influence the biosorption of Se, such as pH, Se concentration, and biosorbent dose, were tested in controlled batch experiments to investigate their influence on Se biosorption. Setting up simultaneous batch experiments, we also evaluated kinetics and isotherm behavior of Se biosorption for these three biosorbents. Kinetics and isotherm data were fit with established analytical models to get a mechanistic understanding of Se adsorption on the sorbents. Overall, this study presents insights on a novel and sustainable method for the removal of Se, a contaminant of increasing concern, using low-cost waste-derived biosorbents.

2. MATERIALS AND METHODS

2.1. Chemicals. This study used analytical grade reagents such as anhydrous calcium chloride (CaCl\(_2\)), sodium selenate (Na\(_2\)SeO\(_4\)), sodium selenite (Na\(_2\)SeO\(_3\)), sodium alginate powder (C\(_6\)H\(_7\)NaO\(_6\))\(_n\), nitric acid (HNO\(_3\)), and sodium hydroxide (NaOH); all were purchased from Fisher Scientific (Massachusetts, USA).

2.2. Preparation of Sorbents. The citrus peels originating from oranges were collected, washed, and air-dried. The dried peels were crushed, grounded, and sieved to 1−4 mm size. The dried peels were added to 0.1 (N) HNO\(_3\) at 0.02% (w/v) followed by continuous stirring at 125 RPM for 3 h and 25 °C temperature for saturating the cation binding sites of citrus peels with H\(^+\). The excess acid was washed off the peels by continuously rinsing them with deionized water until the wash effluent pH increased to 4. Calcium alginate beads were prepared by taking 2% (w/v) sodium alginate into a disposable syringe and dispersing it as small droplets into a 3% (w/v) CaCl\(_2\) solution, followed by incubation at room temperature for 1 h to solidify the beads within the solution. The beads were subsequently collected and dried inside hot air oven at 37 °C for 48 h. The Ca-alginate@citrus was prepared by adding crushed citrus peels to 2% (w/v) sodium alginate solution at 0.02% (w/v) and stirred continuously to form a uniform mixture. The mixture formed the composite beads by its dropwise addition to 3% (w/v) CaCl\(_2\) solution followed by incubation at 25 °C for 1 h. The composite beads of Ca-alginate@citrus were dried by filtering it from the solution and incubating at 37 °C for 48 h.

2.3. Batch Biosorption Experiment. The batch biosorption study was performed in triplicate to evaluate the biosorption of Se(IV) by bare citrus peels, Ca-alginate beads, and Ca-alginate@citrus at 25 °C temperature. To prepare the Se(IV) concentration ranging from 2 to 100 mg L\(^{-1}\), Na\(_2\)SeO\(_3\) was added to deionized water followed by adjusting pH to 6.5 using 0.1 N HNO\(_3\) or NaOH solution. The batch biosorption experiments were performed in 50 mL vials containing 0.5 g of adsorbents and 25 mL of Se(IV) solutions, agitating them at 120 RPM using an orbital shaker, and sampling at 30 min intervals up to 5 h, followed by measurement of residual Se concentration. The biosorption efficiency, and biosorption capacity at different times (\(q_t\)) and at equilibrium (\(q_e\)) were measured using eqs 1−3.

\[
\text{biosorption efficiency (\%)} = \frac{c_i - c_f}{c_i} \times 100 \quad (1)
\]

\[
\text{biosorption capacity at time } t (q_t) = \frac{c_i - c_f}{M} \times V \quad (2)
\]

\[
\text{equilibrium biosorption capacity (} q_e \text{) in mg/g} = \frac{c_i - c_e}{M} \times V \quad (3)
\]

\(c_i\) indicates the Se concentration at equilibrium.

2.4. Optimization of Parameters. Biosorption of Se(IV) by citrus peels, Ca-alginate beads, and Ca-alginate@citrus was evaluated by optimizing parameters including pH, initial Se(IV) concentration, and biosorbent dosing. To perform the pH optimization, 0.05 g of biosorbents and 25 mL of Se(IV) solution having 50 mg L\(^{-1}\) concentration were taken in 50 mL vials and incubated at 25 °C for 240 h at a pH ranging from 2 to 12 with 2-unit intervals. Similarly, the initial Se(IV) concentration and biosorbent dosing were optimized by varying Se(IV) concentration from 10 to 100 mg L\(^{-1}\) and biosorbents dosing concentration from 0.5 to 15 g L\(^{-1}\), at pH 6.5. All of the batch experiments were conducted in triplicate, and comparative analysis of equilibrium biosorption capacity (\(q_e\)) was performed to identify the optimized Se(IV) biosorption.

2.5. Biosorption Modeling. Investigation of Se(IV) adsorption kinetics, adsorption isotherms, and sorption mechanisms was performed by modeling the biosorption data. Model equations and relationships are briefly described below.

2.5.1. Biosorption Kinetics. The Se(IV) biosorption kinetics was modeled via pseudo-first (eq 4) and pseudo-second-order (eq 5) relationships.

\[
\ln (q_e - q_t) = \ln q_e - k_f t \quad (4)
\]
\[
\frac{t}{q_t} = \frac{1}{k_f q_e^2} + \frac{t}{q_e}
\]  
(5)

where \(k_f\) (min\(^{-1}\)) and \(k_i\) (mg·g\(^{-1}\)·min\(^{-1}\)) denote the rate constants for the pseudo-first and pseudo-second-order equations, respectively.

2.5.2. Biosorption Isotherm. The Se(IV) biosorption isotherm was modeled using the Langmuir (eq 6) and Freundlich isotherms (eq 7).

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{1}{C_e}
\]  
(6)

where \(K_L\) (L·mg\(^{-1}\)) and \(q_{\text{max}}\) (mg·g\(^{-1}\)) denote the Langmuir adsorption constant and the maximum biosorption capacity, respectively.

\[
q_e = K_F q_e^{1/n}
\]  
(7)

where \(n\) and \(K_F\) ((mg·g\(^{-1}\)·(mg·L\(^{-1}\))\(^{-1/n}\)) denote the exponent and Freundlich isotherm constant, respectively.

2.5.3. Determination of Biosorption Mechanism. The biosorption mechanism of Se(IV) by the three absorbents was evaluated by employing the Morris–Weber intraparticle diffusion model (eq 8), and Boyd’s fixed-film diffusion model (eq 9).

\[
q_t = k_i t^{1/2} + c_i
\]  
(8)

where \(c_i\) (mg·g\(^{-1}\)) and \(k_i\) (mg·g\(^{-1}\)·min\(^{-1/2}\)) are constants relating to the boundary layer thickness and the intraparticle diffusion rate constant, respectively.

\[-\ln \left(1 - \frac{q_t}{q_e}\right) = k_i t\]
(9)

where \(k_i\) is a film diffusion constant.

2.6. Chemical Analysis and Characterization. A microwave plasma-atomic emission spectrophotometer (4200, Agilent Technologies, USA) was used for measuring the selenium (IV) concentration. The solution pH was measured using a pH electrode (H18424, Hanna Instrument). Biosorbents were observed under a scanning electron microscope (ESEM, FEI Quanta200, Thermo Fisher Scientific, USA) to determine their surface morphology before and after the biosorption of Se(IV). The samples were observed, without coating, in the ESEM mode using a 10 kV electron beam, and images were obtained at low (27×−64×) and high (875×) magnification.

3. RESULTS AND DISCUSSION

3.1. Biosorption Kinetics. Se(IV) biosorption by citrus peels, Ca-alginate, and Ca-alginate@citrus are presented in Figure 1A. The citrus peels, Ca-alginate, and Ca-alginate@citrus reduced the initial Se(IV) concentration from 50 mg·L\(^{-1}\) to 12.1, 6.1, and 17.4 mg·L\(^{-1}\), respectively, at a biosorbent dosing of 2 g·L\(^{-1}\). Biosorption reached equilibrium in 90 min for Ca-alginate and citrus peels; \(q_e\) was measured as 76.9 and 50.3 mg·g\(^{-1}\), respectively. The \(q_e\) for Ca-alginate@citrus was measured as 54.6 mg·g\(^{-1}\), and it reached equilibrium in 120 min. The kinetic parameters were determined by fitting experimental data to both of the adsorption kinetic models (Table 1). The plot of \(t/q_t\) versus \(t\) shows that the Se(IV) biosorption on the surface of all the three biosorbents closely matched with pseudo-second-order kinetics (Figure 1B). The coefficient of determination (\(R^2\)) for experimental versus modeled \(q_e\) was much higher (0.99) for pseudo-second-order than that for pseudo-first-order (0.44–0.85).

3.2. Biosorption Mechanism. The fitting parameters for experimental data with the Morris–Weber intraparticle diffusion model and Boyd’s fixed-film diffusion model are presented in Table 2. The nonlinearity for \(q_t\) versus \(t^{0.5}\) (plot not shown) and lower \(R^2\) values (0.74–0.81) indicate that the Se(IV) biosorption mechanism does not follow the Morris–
The Weber intraparticle diffusion model. The linearity between $-\log (1 - q_t/q_e)$ and $t$ and high $R^2$ (0.91−0.99) support the assertion that the Se(IV) biosorption mechanism follows Boyd’s fixed-film diffusion (Figure 1C). This also indicates that fixed-film diffusion is a rate-limiting step for Se(IV) biosorption on the surface of citrus peels, Ca-alginate, and Ca-alginate@citrus.

### 3.3. Biosorption Isotherm.

The behavior of the Se(IV) biosorption by citrus peels, Ca-alginate, and Ca-alginate@citrus was characterized by fitting equilibrium experimental data to the Langmuir (Figure 2A) and Freundlich (Figure 2B) isotherm models. A negative slope between $c_e$ and $c_e/q_e$ indicates that the Se(IV) biosorption did not follow the Langmuir isotherm model (Figure 2A). The plots of $c_e$ versus $q_e$ indicate that the Se(IV) biosorption follows the Freundlich isotherm model, and that Se(IV) sorption on the surface of biosorbents occurs in heterogeneous layers (Figure 2B). This result is consistent with the previous literature showing Freundlich fit for Se(IV) sorption using different sorbents.

### Table 2. Determination of Biosorption Mechanism Using the Diffusion Model

| biosorbents       | Morris–Weber model (intraparticle diffusion) | Boyd’s model (fixed-film diffusion) |
|-------------------|---------------------------------------------|------------------------------------|
|                   | $k_i$ | $R^2$ | $k_f$  | $R^2$ |
| citrus peels      | 3.4   | 0.74  | 0.013  | 0.99  |
| Ca-alginate       | 3.6   | 0.80  | 0.011  | 0.98  |
| Ca-alginate@citrus| 1.7   | 0.81  | 0.008  | 0.91  |

Figure 2. Fitting of Se(IV) biosorption with (A) Langmuir isotherm model and (B) Freundlich isotherm model.
such as layered double hydroxide (LDH) nanoparticle and iron oxide impregnated carbon nanotubes.

The isotherm constants measured for Se(IV) biosorption using the three biosorbents are presented in Table 3. The $K_L$ values for citrus peels, Ca-alginate, and Ca-alginate@citrus are calculated as 0.005, 0.4, and 0.1 ((mg·g$^{-1}$)·(mg·L$^{-1}$)$^{-1/n}$), respectively, whereas the value of $n$ was 0.4 for all three biosorbents. A value of $n < 1$ indicates an energetically unfavorable condition for Se(IV) biosorption on the surface of citrus peels, Ca-alginate, and Ca-alginate@citrus. However, as the initial biosorption occurs, the biosorbent surface gets modified by the adsorbed Se(IV), resulting in favorable condition for additional biosorption.

In this work, the maximum Se(IV) biosorption capacity of citrus peels, Ca-alginate, and Ca-alginate@citrus were measured as 116.2, 72.1, and 111.9 mg·g$^{-1}$, respectively. Citrus peels showed higher biosorption capacity than that of Ca-alginate, with and without embedded peels. The comparable maximum biosorption capacity of citrus peels and Ca-alginate@citrus beads indicates that the entrapment of citrus peels by Ca-alginate beads did not affect the biosorption capacity of Ca-alginate@citrus. Biosorbents used in this study were compared to different biosorbents for their maximum biosorption capacity for Se (Table 4). Iron oxide impregnated carbon nanotubes showed the maximum Se(IV) adsorption capacity of 111 mg·g$^{-1}$, which is lower than that of Ca-alginate@citrus observed in the present study. When compared to the maximum Se(IV) adsorption capacity of other adsorbents such as iron oxy-hydroxides, Fe-metal organic framework (Fe-MOF) and Al-impregnated Fe-MOF (Al@Fe-MOF), magnetite nanoparticles, $FeO_x$-chitosan nanocomposites, MgO nanosheets, and Fe/Si and Al/Si coprecipitate, the citrus peels and Ca-alginate@citrus in the present study showed superior maximum biosorption capacity.

### Table 3. Determination of Isotherm Parameters Using Langmuir and Freundlich Isotherm Models

| biosorbents         | $q_{max}$ (mg·g$^{-1}$) | $K_L$ (L·mg$^{-1}$) | $R^2$ | $1/n$ | $K_F$ ((mg·g$^{-1}$)·(mg·L$^{-1}$)$^{-1/n}$) | $R^2$ |
|---------------------|--------------------------|---------------------|-------|-------|---------------------------------------------|-------|
| citrus peels        | 35.08                    | -0.15               | 0.76  | -1.58 | 370.42                                      | 0.96  |
| Ca-alginate         | 36.23                    | -0.16               | 0.84  | -0.61 | 354.65                                      | 0.94  |
| Ca-alginate@citrus  | 52.63                    | -0.28               | 0.86  | -0.38 | 196.15                                      | 0.96  |

### Table 4. Comparison of the Se(IV) Absorption Capacity of Different Absorbents

| absorbent       | maximum adsorption capacity (mg·g$^{-1}$) | refs       |
|-----------------|-------------------------------------------|------------|
| Ca-alginate     | 72.1                                      | present study |
| citrus peel     | 116.2                                     |            |
| Ca-alginate@citrus | 111.9                                    |            |
| Al/Si coprecipitate | 25.9                                      | 47         |
| Fe/Si coprecipitate  | 22.5                                      |            |
| MgO nanosheets  | 103.5                                     | 46         |
| iron oxide impregnated carbon nanotubes | 111       | 16         |
| hematite-coated magnetic nanoparticle | 25       | 44         |
| magnetic nanoparticle | 15.3                                     |            |
|FeO$_x$-chitosan nanocomposite | 15.6     | 45         |
| layered double hydroxide/chitosan nanocomposite | 17 | 39 |
|Fe-MOF           | 42.4                                      | 43         |
|Al@Fe-MOF composite | 75.3                                      | 42         |
|iron oxy-hydroxides | 23                                        | 42         |

### 3.4. Effect of Operational Parameters

#### 3.4.1. pH

Se(IV) biosorption capacity of citrus peels, Ca-alginate, and Ca-alginate@citrus varied upon altering the pH from 2 to 12 (Figure 3A). The speciation of Se(IV) in an aqueous solution is dependent on pH. Between pH 2 and 8, the dominant form of Se(IV) remains as HSeO$_3$$^-$$^-$, increase in pH to 12 results in the domination of SeO$_3$$^-$$^2$. In the present study, the increase in pH from 2 to 8 resulted in increased Se(IV) biosorption capacity for all the biosorbents. The optimized pH for citrus peels was determined to be 8 at which its biosorption capacity was observed as 28.2 ± 0.04 mg·g$^{-1}$.

carbon nanotubes showed the maximum Se(IV) adsorption capacity of 111 mg·g$^{-1}$, which is lower than that of Ca-alginate@citrus observed in the present study. When compared to the maximum Se(IV) adsorption capacity of other adsorbents such as iron oxy-hydroxides, Fe-metal organic framework (Fe-MOF) and Al-impregnated Fe-MOF (Al@Fe-MOF), magnetite nanoparticles, FeO$_x$-chitosan nanocomposites, MgO nanosheets, and Fe/Si and Al/Si coprecipitate, the citrus peels and Ca-alginate@citrus in the present study showed superior maximum biosorption capacity.

Figure 3. Effect of (A) pH, (B) initial Se(IV) concentration, and (C) biosorbent dosing on equilibrium Se(IV) biosorption by citrus peels, Ca-alginate, and Ca-alginate@citrus.

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Further increase in pH to 12 reduced the Se(IV) biosorption. Point of zero charge (pH_{pzc}) could explain such a reduced biosorption capacity at highly alkaline pH. The pH_{pzc} of citrus peels and Ca-alginate beads are reported to be near-neutral.\(^\text{49}\) Therefore, the increase of pH above 7 could convert the net surface charge of the biosorbents to negative leading to lower Se(IV) adsorption. A similar decrease in Se(IV) adsorption capacity above pH 6 has been reported in the previous literature.\(^\text{44,60}\)

### 3.4.2. Initial Se Concentration

Se(IV) biosorption capacity of citrus peels, Ca-alginate, and Ca-alginate@citrus varied upon altering the initial concentration of Se(IV) (Figure 3B). Increasing the original Se(IV) concentration from 10 mg L\(^{-1}\) enhanced the Se(IV) biosorption capacity of Ca-alginate and Ca-alginate@citrus, which reached to saturation at 75 mg L\(^{-1}\). Increasing the original Se(IV) concentration further to 100 mg L\(^{-1}\) did not result in a significant increase of Se(IV) biosorption capacity for these two biosorbents. The optimized initial concentration of Se(IV) (in terms of biosorption efficiency, Figure S1) was found to be 50 mg L\(^{-1}\) in citrus peels and 75 mg L\(^{-1}\) both in Ca-alginate and Ca-alginate@citrus. Such saturation of Se(IV) biosorption in Ca-alginate at lower initial concentration was because of the availability of less biosorption sites on its surface as compared to that of citrus peels and Ca-alginate@citrus.\(^\text{16}\) The biosorption of Se(IV) by citrus peels and Ca-alginate@citrus was found higher than that of Ca-alginate throughout all the initial Se(IV) concentration studied. Such higher biosorption capacity at a higher initial Se(IV) concentration is because of higher Se(IV) mass transfer at the surface of these two biosorbents.\(^\text{16}\) The result shows that biosorption capacity of citrus peels remained unaffected even after entrapping within Ca-alginate beads; moreover, it provides structural integrity (Ca-alginate@citrus) to be useful for developing an effective biofiltration technology for Se(IV) removal.

### 3.4.3. Biosorbent Dose

Biosorbent dosing influencing the Se(IV) biosorption on the surface of citrus peels, Ca-alginate, and Ca-alginate@citrus is presented in Figure 3C. Increasing biosorbent dose from 0.5 g L\(^{-1}\) significantly enhanced the Se(IV) biosorption capacity of the biosorbents. The biosorption efficiency (Table S1, Figure S1) reached near-saturation at 5 g L\(^{-1}\) dosing in citrus peels and Ca-alginate beads, and at 1 g L\(^{-1}\) in Ca-alginate@citrus. The biosorption capacity and efficiency of the biosorbents at different dosing concentrations are also shown in Table S1 and Figure S1. The Ca-alginate and citrus peels showed lower biosorption efficiency and capacity than that of Ca-alginate@citrus at biosorbent dosing concentration between 0.5 and 3 g L\(^{-1}\). The biosorption capacity of the Ca-alginate and citrus peels showed similar biosorption behavior at all biosorbent dosing \(\geq 1\) g L\(^{-1}\) (Figure S1). Higher biosorption capacity of Se(IV) by Ca-alginate@citrus at lower dosing exhibits its economic advantage as a novel biosorbent for Se(IV) contaminated waters.

#### 3.5. Biosorbent Characterization

The scanning electron micrograph shows the surface morphology of biosorbents before and after Se(IV) adsorption at 15X and 1000X magnification (Figure 4). As observed from the micrograph, the Ca-alginate bead looks spherical with a smooth surface before Se(IV) was adsorbed. Roughening of the surface of Ca-alginate beads occurred upon Se(IV) adsorption (Figure 4A). A similar observation of Ca-alginate beads with a smooth surface before adsorption was reported earlier.\(^\text{51}\) Roughening of its surface upon adsorption of metals such as Cu, Pb, and Pt was reported in the literature.\(^\text{52,53}\) The rough surface morphology of citrus peels and Ca-alginate@citrus provide them a higher surface area as compared to Ca-alginate beads (Figures 4B,C). Such rough and heterogeneous surface morphology results in higher adsorption capacity.\(^\text{34}\) The SEM micrograph of Se(IV)-loaded biosorbents as shown in Figure 4A–C indicates the adsorption and homogeneous distribution of Se(IV) over the entire surface of the biosorbents.

In this work, we evaluated the biosorption of Se(IV) from the aqueous solution using bare citrus peels, Ca-alginate, and Ca-alginate@citrus. The pseudo-second-order kinetics defines the Se(IV) biosorption on the surface of these three biosorbents. The biosorption of Se(IV) at the heterogeneous layer of the biosorbents is explained by the Freundlich isotherm model, which showed a closer fit \((R^2 = 0.94–0.96)\) with the experimental data. The fixed-film diffusion model explains the mechanism of Se(IV) biosorption by the three biosorbents. The optimization of pH, initial Se(IV) concentration, and biosorbent dosing significantly improved the Se(IV) biosorption efficiency and capacity of the biosorbents. Surface characteristics of the biosorbents indicate that citrus peels contribute to the increased surface area in Ca-alginate@citrus. Comparatively, the similar adsorption capacities of citrus peels and Ca-alginate@citrus indicate that the entrainment of citrus peels by Ca-alginate did not affect its adsorption capacity; moreover, it provided structural integrity. The durability of Ca-alginate@citrus with comparable biosorption capacity to that of citrus peels would increase its prospect as a novel biosorbent in field-scale applications for the develop-
ment of high-efficiency filtration systems to treat Se(IV) contaminated waters.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01347.

Effect of different parameters on Se(IV) adsorption by citrus peels, Ca-alginate, and Ca-alginate@citrus are included in Table S1 and biosorption efficiency plots are shown in Figure S1 (PDF).

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**Author Contributions**

S.D. and A.K. contributed equally to this work. A.K. and S.A. designed the experiments. A.K. conducted the experiments. S.D. and A.K. contributed equally to this work. A.K. and S.A. helped improve this paper.

**Notes**

The authors declare no competing financial interest.

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