



Article Sorption Characteristics and Fraction Distribution Changes of Selenite in Soil

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Abstract: Sorption properties play a key role in the mobility of selenium (Se) and fraction distribution changes, leading to the bioavailability of Se in the soil environment. Thus, the effect of soil physicochemical properties on the sorption of exogenous selenite was investigated to predict the rate and capacity of sorption. Correlation analysis and multiple linear regression were used to observe the relationship between sorption characteristics and soil properties. Sequential extraction was used to observe the fractions of Se at different ages in soil. Results indicated that sorption isotherms followed the Langmuir equation, and the sorption capacity ranged from 50.7 to 567 mg·kg⁻¹ with pseudo-second-order sorption kinetics. The correlation and multiple linear regression analyses showed that sorption parameters were significantly positively correlated with dithionite-citrate-bicarbonate-extracted Fe (Fe_{DCB}), dithionite-citrate-bicarbonate-extracted Al (Al_{DCB}), amorphous Fe (Fe_{OX}), and soil organic matter (SOM), whereas pH was negatively correlated. Sequential extraction analyses revealed that the fraction distribution of Se in soil varied with the age, and the content of elemental Se increased with prolonged aging. Fe_{DCB}, Al_{DCB}, Fe_{OX}, pH, and SOM play important roles in selenite sorption onto soils. Selenite sorption onto soil can be reduced to a lower-state Se, such as elemental Se and selenides, during the aging process. This information on the environmental behavior of Se is used to develop agronomic strategies for increasing Se levels in food crops and improving human health.

Keywords: Selenite; sorption properties; fraction distribution; soil characteristics; multiple linear regressions

1. Introduction

Selenium (Se), as a component of antioxidant enzymes, contributes to animal and human growth. Se has been discovered in 25 selenoproteins, which play significant roles in many metabolic processes [1]. However, the biological range of Se content is very narrow between deficiency, physiological, and toxic [2]. Se affects human health when dietary intake is less than 40 μ g per day or more than 400 μ g per day [3]. In general, Se levels in human bodies are controlled through diet, and Se in food generally depends on its content and distribution fraction in soil [4]. In addition, Se exists in different oxidation states, including Se(VI), Se(IV), Se(0), and Se(–II). In natural soil conditions, Se(VI) and Se(IV) are the main inorganic Se forms. Se(VI) predominates in alkaline soils and has a higher mobility than Se(IV), which commonly occurs in neutral or acidic soils and is easily sorbed on oxyhydroxides [5]. Considerably low Se levels in soil (<0.05 mg·kg⁻¹) occur in parts of China, USA, and some European countries, such as Finland and New Zealand [6]. Although endemic Se poisoning has been found in several provinces (Hubei and Shanxi) [7], most of China is in a low-Se area, and approximately 72% of the national land area is Se-deficient [8]. Se-enriched fertilizers

can be used to increase the Se concentration in plants, improve the Se content in the human body, and effectively decrease Kashin–Beck disease [9].

Nevertheless, the sorption and transformation of Se-enriched fertilizers in soil would lead to bioavailability reduction [10]. Moreover, Se sorption is impacted by soil properties and environmental factors, such as pH, Eh, soil minerals, and soil organic matter (SOM) [6]. Therefore, Se sorption onto soil, soil minerals, and SOM should be investigated to further understand its environmental behaviors. Previous studies on Se sorption have mostly considered pure materials [11–14]. For example, Zhang and Sparks [14] investigated selenate and selenite adsorption/desorption onto goethite. They concluded that the selenate was fixed on goethite through electrostaticity, whereas selenite sorption onto goethite was due to ion exchange. Manceau and Charlet [13] found that inner-sphere surface complexes were formed with selenate sorption on both goethite and ferric hydroxide, similar to phosphate and selenite, and binuclear bridging complexes with A-type OH groups were formed. In addition, they asserted that pH and ionic strength were the main control factors influencing the sorption process. Jordan et al. [11] concluded that the mechanism of selenite sorption on maghemite was controlled by pH, and bidentate binuclear corner-sharing and bidentate mononuclear edge-sharing inner-sphere surface complexes were formed at low and high pH, respectively. Kamei-Ishikawa et al. [12] found that selenite sorption onto humic acid (HA) followed the Freundlich isotherm and was affected by pH.

Se sorption on soil is more complex than that of pure materials, because soil is a complex heterogeneous material. Thus, Se sorption on soil depends on both soil properties and environmental factors. Dhillon and Dhillon [15] reported that the sorption capacity of selenite was greater in acidic soils. Lessa et al. [16] found that selenate adsorption was greater in clayed than in sandy soils. Other studies reported that the retention of selenate and selenite on soils is related to the contents of organic matter (OM) and amorphous oxides of aluminum and iron, besides pH and texture [17,18].

In addition, Se can be redistributed among soil components after entering into soils. The mobility and bioavailability of Se can be influenced by its speciation and fractions in soils [8,19]. However, the fraction distribution of Se changes during the aging process. Some studies reported that the metal bioavailability was different between natural field and freshly spiked soils due to the aging process [20,21]. For example, Settimio et al. [22] found that some soluble silver transformed into metallic and exchangeable Ag. To date, the aging of heavy metals in soil has been commonly studied, but few studies have involved Se aging. Tolu et al. [23] reported that the soluble Se fractions decreased and the organic matter-bound Se fraction increased during incubation, although this process is slow. Li et al. [10] found that available Se rapidly transformed into the stable fraction in three different tested soils in the initial 42 days, and declined thereafter. The sorption properties of Se and the mechanism of redistribution in soil remain unclear.

In this study, the sorption characteristics of selenite on 12 soils from different areas with different physicochemical properties were investigated, and the relationship between sorption characteristics of selenite and soil properties was studied. Additionally, sequential extraction was used to obtain Se fractions at different ages in selected soils. This information on the environmental behavior of selenite is used in developing agronomic strategies to increase Se levels in food crops.

2. Materials and Methods

2.1. Soil Samples

In order to observe soils with different physicochemical property, 12 soils were selected from 10 provinces in China (Figure 1), including arid and paddy soil. The soil samples used in this study were collected from different agricultural areas (0–20 cm). Soil samples were homogenized and ground after air-drying before the determination of physicochemical properties.



Figure 1. Map showing locations of samples in this study. (Site1 = Baoding; Site2 = Linqu; Site3 = Chongzuo; Site4 = Hefei; Site5 = Xuyi; Site6 = Yichun; Site7 = Yichang; Site8 = Liuyang; Site9 = Xiangtan; Site10 = Quanzhou; Site11 = Guiyang; Site12 = Liaocheng).

Soil pH values, SOM content, texture, and total contents of Fe, Al, and Mn were determined in accordance with the methods reported in previous studies [24]. Soil Fe, Al, and Mn amorphous oxides were extracted with acidified ammonium oxalate buffer (0.175 mol·L⁻¹ of ammonium oxalate + 0.1 mol·L⁻¹ of oxalic acid, pH 3.0) [25]. Free Fe, Al, and Mn oxides were obtained with dithionite–citrate–bicarbonate buffer solution [25]. Total Se in soil was measured by hydride generation atomic fluorescence spectrometry (HG–AFS; 230E, Beijing Haiguang Company, Beijing, China) after soil digestion (HNO₃:HCl = 3:1; *v:v*) in a boiling water bath [26]. Fe, Al, and Mn concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES; ICP7500, Shimadzu, Kyoto, Japan). All measurements were in triplicate.

2.2. Sorption Experiments

Soil samples were ground to pass through a 0.25 mm sieve before sorption experiments. Potassium selenite (K_2SeO_3 , analytic reagent grade, Sigma, St. Louis, MI, USA) was dissolved to form 100 mg·L⁻¹ of selenite stock solutions. A batch equilibration method was conducted to study the sorption isotherms of selenite in all sorption experiments. Furthermore, 10 mmol·L⁻¹ of 2-(*N*-morpholino) ethanesulfonic acid monohydrate (MES) was used for buffering at pH 6.0, and ionic strength was kept constant at 10 mmol·L⁻¹ in all experiments by NaCl addition. The initial concentrations of selenite in sorption experiments were 0, 1.0, 2.0, 4.0, 8.0, 10, and 16 mg·L⁻¹, and the soil-to-water ratio was 1:50. After 24 h shaking in an air-bathing constant-temperature vibrator (25 ± 1 °C) and centrifugation at 9000 rpm, the sorption supernatant liquid was filtered (0.22 µm of cellulose). The concentration of selenite in the filter liquor was determined by ICP–AES. All measurements were in duplicate.

Kinetic experiments were conducted under the following conditions. Briefly, 2.5 g of soil was spiked with 125 mL 2.0 mg·L⁻¹ of K₂SeO₃ solution (pH 6 and ionic strength at 10 mmol·L⁻¹) in a 200 mL polyethylene centrifuge bottle. Then, all bottles were oscillated for 48 h, and three samples were randomly collected at 0.167, 0.5, 1, 2, 4, 6, 20, 30, and 48 h. Desorption tests were performed immediately after sorption experiments. Thus, 10 mmol·L⁻¹ of KCl (20 mL) or 10 mmol·L⁻¹ of KH₂PO₄ (20 mL) was added to the soil remaining from the sorption experiments to extract the soluble and ion-exchange state selenite [15], with shaking reciprocation for 2 h. The Se in the supernatant was determined by the same method as the desorbed selenite.

Soil aging: in this study, only one soil (Liaocheng) was selected for the aging experiment; the selected soil had the lowest Se content. The experimental process during the initial 48 h was the same as that for the kinetic experiments. After 48 h oscillation, the aging experiments began, and the remaining bottles for the selected soil were kept in the dark at 25 °C. Three samples were randomly collected at 0, 10, and 60 days, centrifugation was performed at 9000 rpm, and the supernatant liquid was filtered.

2.3. Sorption Models

2.3.1. Sorption Isotherm

The sorption isotherm data were fitted by Langmuir and Freundlich models. The Langmuir equation can describe valid monolayer sorption onto a surface, which contains a finite number of sorption sites. This method assumes uniform energies of sorption onto the surface and that no adsorbate transmigration occurs. The Langmuir equation is written as:

$$Q_e = KQ_M C_e / (1 + KC_e) \tag{1}$$

where C_e is the equilibrium concentration of Se in the solution (mg·L⁻¹), Q denotes the sorbed concentration (mg·kg⁻¹), Q_M (mg·kg⁻¹) indicates the sorption maximum, and K represents the sorption constant.

The Freundlich model is as follows:

$$Q_e = K C_e^{\frac{1}{n}} \tag{2}$$

where *K* and *n* are related to the site heterogeneity of the adsorbent.

2.3.2. Sorption Kinetics

Sorption kinetic data were fitted using the reversible Langmuir kinetics, pseudo-second-order rate, Elovich, and double-constant rate equations, which have been widely used in adsorption kinetics. The kinetic equations can be described as follows:

Reversible Langmuir kinetics equation:

$$Q_t = t/(a_1 \times t + b_1) \tag{3}$$

Pseudo-second-order rate equation:

$$\frac{t}{Q_t} = \frac{1}{Q_e^2 K_2} + \frac{1}{Q_e} t$$
(4)

The initial adsorption rate, h, was obtained from the intercept in Equation (4):

$$h = Q_e^2 \times K_2 \tag{5}$$

Elovich equation:

$$Q_t = \frac{1}{K} \ln(1 + \alpha K t) \tag{6}$$

Double constant equation:

$$Q_t = a t^b \tag{7}$$

where Q_t is the amount of selenite adsorbed (mg·kg⁻¹) at time t (h), Q_e indicates the retained amount (mg·kg⁻¹) at the equilibrium time, and a_1 , b_1 , K_1 , K_2 , α , a, b, and K represent the sorption constants.

2.4. Sequential Extraction

The fraction distribution was analyzed by the modified sequential extraction method according to Kulp and Pratt [27] and Wang et al. [28]. (1) Water-soluble Se: 1 g of soil sample was mixed with 25 mL of Milli-Q water in a 50 mL centrifuge tube and then oscillated in a reciprocating shaker (175 oscillations min⁻¹ at 25 °C) for 2 h. Then, the mixture was centrifuged for 20 min at 3500 r·min⁻¹, and the supernatant was collected after filtration. The cleaned residue was used for the next step; (2) Ligand-exchangeable Se: 25 mL of 0.1 M KH₂PO₄ + K₂HPO₄ buffer (pH 7.0) was added to the above-mentioned tube and shaken at 3500 r·min⁻¹ for 2 h; (3) Organic matter-bound Se: 25 mL 0.1 mol·L⁻¹ of NaOH (90 °C) was added to each remaining soil sample for 2 h in a 90 °C water bath, and the centrifuge tubes were shaken; (4) Elemental Se: 25 mL 1 mol·L⁻¹ of Na₂SO₃ solution (pH was adjusted to 7.0 with HCl) was added to the above-mentioned tubes, and then, tubes were placed in an ultrasonic bath for 8 h. (5) Residual Se: the soil residuals were digested with mixed acid (HNO₃:HClO₄ = 4:1) in a Teflon crucible at 170 °C. The Se concentrations in the filter liquor were measured by HG–AFS.

Sigma Plot 12.0 was used for curve fitting [29]. The stepwise multiple linear regression technique of SPSS 19.0 was used to derive the relationship between the soil physicochemical properties and Se sorption capacity [30].

3. Results and Discussion

3.1. Soil Characterization

On the basis of American soil taxonomy, soils used in this study were classified as alfisols, ultisols, inceptisols, and entisols [31]. Table 1 shows the soil properties and the wide variation among the 12 soils. The SOM contents ranged from 0.06 to 4.6%, the pH varied from 5.5 to 6.9, and the concentration of Se ranged from 0.38 mg·kg⁻¹ to 0.72 mg·kg⁻¹. Total Fe, Al, and Mn concentration in soils varied considerably, and the lowest and highest total Fe contents were 1.3% and 5.7%, respectively. The total Al and Mn concentrations ranged from 2.5% to 14% and from 104 mg·kg⁻¹ to 321 mg·kg⁻¹, respectively. In addition, the Fe_{DCB} content of these soils ranged from 429 mg·kg⁻¹ to 2104 mg·kg⁻¹, and ultisols exhibited a high Fe_{DCB} content (913–2104 mg·kg⁻¹).

3.2. Selenite Kinetic Sorption in Soil

Figure 2 shows the time-dependent sorption of selenite onto the 12 soils. Sorption was greatest with Liuyang soil: approximately 4.4 times that of Liaocheng soil, which had the least. Most of the selenite sorption equilibrium can occur within 6 h, except for Chongzuo and Xiangtan soils. The R² for the reversible Langmuir kinetics and double-constant equation ranged from 0.894 to 0.986 and from 0.888 to 0.991 (Table 2), respectively, whereas the pseudo-second-order rate equation provided good fits with R², from 0.992 to 0.999 (Table 2). In addition, the initial adsorption rates (*h*) differed among those soils, varying from 24.4 (Xiangtan soil) to 148 (Liuyang soil). The Elovich rate equation also provided good fits, with all R² values exceeding 0.904. The initial sorption rate of Liuyang soil was the largest among all soils, indicative of its high iron and aluminum oxide contents. By contrast, Xiangtan soil had the lowest initial sorption rate, which could be related to its OM content.

3.3. Batch Sorption of Selenite in Soils

Figure 3 shows the results of selenite sorption onto the 12 soils. Liuyang and Baoding soils showed the highest and lowest sorption capacities of selenite, respectively. Table 3 presents several parameters from the Langmuir and Freundlich models on sorption energy and capacity. As Table 3 shows, the Langmuir and Freundlich isotherms fit the experiment data well, with $R^2 > 0.965$. However, the Langmuir fits the data better than the Freundlich isotherm ($0.990 < R^2 < 0.997$ compared with $0.965 < R^2 < 0.992$, Table 3). Lessa et al. [16] also proved that selenite sorption data were better fitted to the Langmuir model than to the Freundlich model. The maximum sorption capacity (Q_M) varied widely, ranging from a low of 50.7 mg·kg⁻¹ on Baoding soil to a high of 567 mg·kg⁻¹ on Liuyang soil.

re _{total} Artotal	initiotal PCO	Αιοχ	winox	TeDCB	AIDCB	MUDCB	36	C1 (0())				
		т		TeDCB	INDCB	WINDCB	56	Clay (%)	Silt (%)	Sand (%)		
		Incer	Inceptisol									
$31 2.8 \pm 0.12 5.4 \pm 0.24$	318 ± 10.1 494 ± 2	$.1 392 \pm 17.1$	113 ± 8.45	546 ± 21.1	86.0 ± 6.85	148 ± 9.46	0.40 ± 0.008	5.50	39.9	54.6		
2.3 ± 0.13 4.9 ± 0.16	236 ± 9.56 471 ± 13	.9 417 ± 31.1	141 ± 11.2	486 ± 15.9	133 ± 11.1	135 ± 11.7	0.43 ± 0.009	4.41	33.1	62.5		
3.9 ± 0.21 9.3 ± 0.45	113 ± 8.23 975 ± 36	.7 603 ± 19.8	52.0 ± 3.1	1118 ± 87.6	205 ± 9.87	33.0 ± 1.98	0.57 ± 0.023	10.6	53.6	35.8		
Alfisols												
$022 3.3 \pm 0.18 2.5 \pm 0.12$	321 ± 15.2 354 ± 12	$.5 2340 \pm 80.9$	655 ± 31.2	617 ± 21.3	279 ± 18.8	209 ± 17.8	0.39 ± 0.014	21.9	45.0	33.1		
2.4 ± 0.15 6.0 ± 0.20	295 ± 14.1 203 ± 14.1	.7 794 ± 65.2	191 ± 9.12	1673 ± 92.1	264 ± 19.7	229 ± 18.4	0.47 ± 0.029	36.9	53.8	39.3		
		Ulti	sols									
1.32 ± 0.085 7.7 ± 0.46	104 ± 7.35 485 ± 2	$.8 452 \pm 36.4$	25.0 ± 2.42	1178 ± 13.6	229 ± 13.5	26.0 ± 1.74	0.69 ± 0.007	20.1	66.6	13.3		
5 2.44 ± 0.14 6.5 ± 0.54	147 ± 6.89 233 ± 13	$.6 854 \pm 42.7$	67 ± 4.19	1998 ± 27.1	312 ± 21.1	86.0 ± 2.81	0.53 ± 0.011	6.90	51.2	41.9		
$5 4.42 \pm 0.25 5.9 \pm 0.36$	253 ± 12.1 278 ± 12.1	$.3 940 \pm 59.6$	127 ± 9.92	2104 ± 16.4	452 ± 16.9	84.0 ± 2.36	0.41 ± 0.018	5.80	56.9	37.3		
2.81 ± 0.18 7.0 ± 0.29	232 ± 13.6 225 ± 9.6	$12 1080 \pm 76.9$	113 ± 7.89	1208 ± 10.6	192 ± 8.46	107 ± 1.91	0.46 ± 0.016	5.40	39	55.6		
2 2.77 ± 0.11 8.4 ± 0.37	287 ± 9.81 580 ± 24	$.1 1160 \pm 87.1$	203 ± 18.7	1146 ± 16.1	453 ± 23.8	138 ± 4.36	0.49 ± 0.019	5.00	39.4	55.6		
5.74 ± 0.29 14 ± 0.85	185 ± 8.97 480 ± 33	$.0 3560 \pm 101$	113 ± 5.16	913 ± 18.6	459 ± 29.1	46.0 ± 2.75	0.72 ± 0.012	9.60	49.6	40.8		
Entisol												
7 2.55 ± 0.17 4.6 ± 0.31	274 ± 15.1 351 ± 19	$.2 294 \pm 19.2$	106 ± 4.98	429 ± 17.4	74.0 ± 6.98	127 ± 3.57	0.38 ± 0.014	5.00	35.8	59.2		
))24011138 1532 151219	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} & & & & & & & & & & & & & & & & & & &$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} $	$\begin{array}{c} 1 \\ 2.8 \pm 0.12 \\ 2.8 \pm 0.12 \\ 3.4 \pm 0.13 \\ 4.9 \pm 0.16 \\ 3.9 \pm 0.21 \\ 9.3 \pm 0.45 \\ 113 \pm 8.23 \\ 975 \pm 36.7 \\ 603 \pm 19.8 \\ 52.0 \pm 3.1 \\ 114 \pm 11.2 \\ 486 \pm 15.9 \\ 133 \pm 11.1 \\ 141 \pm 11.2 \\ 486 \pm 15.9 \\ 133 \pm 11.1 \\ 118 \pm 87.6 \\ 205 \pm 9.87 \\ \hline \\ $	$\begin{array}{c} 1 \\ 2.8 \pm 0.12 \\ 2.3 \pm 0.13 \\ 3.9 \pm 0.21 \\ 3.9 \pm 0.21 \\ 9.3 \pm 0.45 \\ 113 \pm 8.23 \\ 9.5 \pm 0.45 \\ 113 \pm 8.23 \\ 9.75 \pm 36.7 \\ 603 \pm 19.8 \\ 52.0 \pm 3.1 \\ 114 \pm 11.2 \\ 486 \pm 15.9 \\ 133 \pm 11.1 \\ 135 \pm 11.7 \\ 144 \pm 11.2 \\ 486 \pm 15.9 \\ 133 \pm 11.1 \\ 135 \pm 11.7 \\ 135 \pm 11.1 \\ 135 \pm 11.7 \\ 205 \pm 9.87 \\ 33.0 \pm 1.98 \\ \hline $	$\begin{array}{c} 1 \\ 2.8 \pm 0.12 \\ 2.3 \pm 0.13 \\ 3.9 \pm 0.21 \\ 3.9 \pm 0.21 \\ 3.9 \pm 0.21 \\ 9.3 \pm 0.45 \\ 113 \pm 8.23 \\ 975 \pm 36.7 \\ 603 \pm 19.8 \\ 975 \pm 36.7 \\ 603 \pm 19.8 \\ 52.0 \pm 3.1 \\ 1118 \pm 87.6 \\ 205 \pm 9.87 \\ 33.0 \pm 1.1 \\ 135 \pm 11.7 \\ 135 \pm 11.7 \\ 135 \pm 11.7 \\ 135 \pm 11.7 \\ 0.43 \pm 0.009 \\ 0.57 \pm 0.023 \\ 0.55 \pm 0.17 \\ 0.46 \pm 0.31 \\ 0.45 \pm 0.54 \\ 0.47 \pm 0.29 \\ 0.52 \pm 0.12 \\ $	$\begin{array}{c} 2.8 \pm 0.12 & 5.4 \pm 0.24 & 318 \pm 10.1 & 494 \pm 21.1 & 392 \pm 17.1 & 113 \pm 8.45 & 546 \pm 21.1 & 86.0 \pm 6.85 & 148 \pm 9.46 & 0.40 \pm 0.008 & 5.50 \\ 2.5 & 2.3 \pm 0.13 & 4.9 \pm 0.16 & 236 \pm 9.56 & 471 \pm 15.9 & 417 \pm 31.1 & 141 \pm 11.2 & 486 \pm 15.9 & 133 \pm 11.1 & 135 \pm 11.7 & 0.43 \pm 0.009 & 4.41 \\ 3.9 \pm 0.21 & 9.3 \pm 0.45 & 113 \pm 8.23 & 975 \pm 36.7 & 603 \pm 19.8 & 52.0 \pm 3.1 & 1118 \pm 87.6 & 205 \pm 9.87 & 33.0 \pm 1.98 & 0.57 \pm 0.023 & 10.6 \\ \hline \\ $	$\begin{array}{c} \begin{array}{c} 2.8 \pm 0.12 \\ 2.8 \pm 0.12 \\ 3.9 \pm 0.21 \\ 3.9 \pm 0.21 \\ 3.9 \pm 0.21 \\ 9.3 \pm 0.45 \\ 113 \pm 8.23 \\ 975 \pm 36.7 \\ 603 \pm 19.8 \\ 975 \pm 36.7 \\ 603 \pm 19.8 \\ 52.0 \pm 3.1 \\ 1118 \pm 87.6 \\ 205 \pm 9.87 \\ 33.0 \pm 1.98 \\ 205 \pm 9.87 \\ 33.0 \pm 1.98 \\ 0.57 \pm 0.023 \\ 10.6 \\ 53.6 \\ \end{array} \begin{array}{c} \begin{array}{c} 39.9 \\ 33.1 \\ 33.1 \\ 133 \pm 11.1 \\ 135 \pm 11.7 \\ 0.43 \pm 0.009 \\ 4.41 \\ 33.1 \\ 33.1 \\ 135 \pm 11.7 \\ 0.43 \pm 0.009 \\ 4.41 \\ 33.1 \\ 135 \pm 11.7 \\ 0.43 \pm 0.009 \\ 4.41 \\ 33.1 \\ 135 \pm 11.7 \\ 0.43 \pm 0.009 \\ 4.41 \\ 33.1 \\ 10.6 \\ 53.6 \\ \end{array} \\ \begin{array}{c} \begin{array}{c} \\ \end{array} \\ \hline \end{array} \\ \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \\ \hline \end{array} \\ \hline \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \hline \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \hline \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c$		

Table 1. Location, Classification, and Some Properties of Soils.

Note: ^a data are given as mean \pm SD (n = 3); OM, Fe_{total}, Al_{total}: %; Mn_{total}, Fe_{OX}, Al_{OX}, Mn_{OX}, Fe_{DCB}, Al_{DCB}, Mn_{DCB}, Se: mg kg⁻¹.

Soil	Soil Double Constant		Reversible Langmuir Kinetics		Pseudo-Second-Order Model				Elovich				
	a#	$b^{\#}$	R ²	$a_1^{\#}$	$b_1^{\#}$	R ²	$Q_e^{\#}$	$K_2^{\#}$	h [#]	R ²	α#	K [#]	R ²
Baoding	20.8	0.147	0.987	0.0287	0.0140	0.986	36.07	0.0259	33.7	0.998	1.01×10^{3}	0.264	0.969
Liaocheng	17.5	0.0810	0.988	0.0310	0.0125	0.894	24.67	0.0437	26.6	0.996	1.69×10^{5}	0.659	0.904
Lingu	21.6	0.151	0.888	0.0149	0.0174	0.922	36.19	0.0375	49.1	0.997	557	0.227	0.930
Hefei	38.7	0.228	0.979	0.0110	0.0052	0.965	89.76	0.00667	53.7	0.998	229	0.0745	0.992
Xuyi	55.7	0.158	0.947	0.0117	0.0164	0.964	99.61	0.00886	87.9	0.997	1.41×10^3	0.0858	0.942
Yichun	26.1	0.221	0.963	0.0124	0.0506	0.958	60.17	0.00880	31.8	0.995	177	0.117	0.978
Yichang	41.6	0.197	0.986	0.0066	0.0047	0.972	87.09	0.00729	55.3	0.996	449	0.0878	0.997
Liuyang	84.4	0.180	0.969	0.0476	0.0038	0.898	160.7	0.00572	148	0.999	$1.19 imes 10^3$	0.0479	0.988
Xiangtan	23.1	0.325	0.984	0.0212	0.0083	0.961	80.06	0.00381	24.4	0.992	44.6	0.0637	0.973
Quanzhou	30.6	0.144	0.961	0.0184	0.0193	0.953	51.25	0.0213	55.9	0.998	1.33×10^3	0.178	0.953
Guiyang	32.0	0.263	0.984	0.0127	0.0109	0.949	86.41	0.00502	37.5	0.995	120	0.0713	0.988
Chongzuo	32.4	0.217	0.991	0.0122	0.0250	0.960	74.43	0.00683	37.8	0.992	257	0.0993	0.981

Table 2. Regressed Kinetic Parameters for Selenium (IV) Sorption onto The 12 Soils.

Note: ${}^{\#}a_1$, $\overline{b_1}$, K_1 , K_2 , a, b, α and K are the kinetic sorption constants, h is the initial adsorption rate. The average of two replicates was used to fit with models, and R² represents the coefficient of determination for all treatments (p < 0.01); m/v of soil to solution = 0.5 g/25 mL. All data are presented as the average of two replicates, and the error bar represents the standard deviation.



Figure 2. Sorption of selenite onto 12 different soils as a function of contact time (**a**) inceptisol; (**b**) alfisols; (**c**) ultisols; (**d**) entisol with reaction conditions: pH = 6, ionic strength = 0.01 mol·L⁻¹ of NaCl, T = 298 K, initial selenite concentration = 2.0 mg·L⁻¹.

		Langmuir		Freundlich				
Soil	K (L·mg ⁻¹)	Q_M (mg·kg ⁻¹)	R ²	1/n	$K_f ((mg \cdot kg^{-1})(mg \cdot L^{-1}))^{-1/n}$	R ²		
Baoding	0.460	50.7	0.993	0.351	18.3	0.973		
Liaocheng	0.0805	118	0.997	0.657	11.3	0.992		
Linqu	0.244	98.1	0.980	0.475	23.1	0.990		
Hefei	0.126	383	0.996	0.653	48.8	0.982		
Xuyi	0.177	361	0.997	0.591	61.3	0.982		
Yichun	0.311	216	0.991	0.471	56.8	0.990		
Yichang	0.392	276	0.993	0.456	81.8	0.988		
Liuyang	0.503	567	0.990	0.534	178	0.984		
Xiangtan	0.109	391	0.994	0.657	45.6	0.990		
Quanzhou	0.276	175	0.995	0.475	43.2	0.967		
Guiyang	0.216	320	0.998	0.553	63.5	0.982		
Chongzuo	0.263	261	0.993	0.507	60.3	0.965		

Table 3. Langmuir and Freundlich Equation Parameters Calculated Using Nonlinear Curve-Fitting for Adsorption Isotherms of 12 Soils.

Note: The average of two replicates was used to fit with models, and R^2 represents the coefficient of determination for all treatments (p < 0.01).

In this context, the highest sorption capacity of Liuyang soil could be attributed to its physiochemical properties. Liuyang soil possessed the highest Fe_{DCB} content and a lower pH, whereas Baoding soil had the lowest OM, lower iron concentration, and highest pH (Table 1). In general, the selenite sorption capacities tended to be related to the high content of Fe/Al oxides and OM. Positive relationships between the crystalline and amorphous contents of Fe and Al and the sorption capacity were previously observed [15,17]. In addition, Li and coworkers reported that SOM, including HA and fulvic acid, may influence sorption for selenite, as Se binds to OM by a complex action [17].



Figure 3. Sorption isotherms of selenite onto 12 different soils (**a**) inceptisol; (**b**) alfisols; (**c**) ultisols; (**d**) entisol. Reaction conditions: pH = 6, ionic strength = 0.01 mol·L⁻¹ of NaCl, T = 298 K, and m/v of soil to solution = 0.5 g/25 ml.

3.4. Selenite Desorption

Selenite desorption by potassium chloride varied from 2.15% (Liuyang soil) to 46.1% (Xiangtan soil); the desorption of 10 out of 12 soils was lower than 20%, as shown in Figure 4. In comparison, the desorption rate of selenite by potassium dihydrogen phosphate varied from 24.4% (Liuyang soil) to 45.7% (Hefei soil). Thus, the amount of adsorbed selenite replaced by chloride ions was less than that of potassium dihydrogen phosphate. However, the finding was opposite in Xiangtan soil. Moreover, the selenite sorption onto Xiangtan soil was more easily desorbed than that on the other soils. This phenomenon may be related to its high OM concentration.



Figure 4. Desorption of selenite by 0.01 M of KCl and 0.01 M of KH₂PO₄ in soils.

3.5. Relationship between Sorption Parameters and Soil Properties

Correlation analysis between sorption parameters (including Q_M , K_f , and h) and soil properties was conducted to identify the key factors influencing selenite sorption onto soils. Table 4 shows the coefficient correlations and p-values. Significant positive correlations were observed for OM, Fe_{DCB}, Al_{DCB}, Fe_{OX}, silt content, and Q_M (p < 0.05). Both Fe_{DCB} and Al_{DCB} were positively correlated with K_f (p < 0.01), with correlation coefficients greater than 0.80, and pH was negatively correlated with K_f (p < 0.05). The initial adsorption rate (h) was positively correlated with Fe_{DCB} (p < 0.01), whereas pH negatively influenced initial sorption rate ($\mathbb{R}^2 = -0.700$, p < 0.05). In general, Fe_{DCB}, Fe_{OX}, Al_{DCB}, OM content, and pH were the key factors for selenite sorption onto soils.

	Q _{MA}	ĸ	K _f		h		
	Correlation p Coefficient p		Correlation Coefficient	p	Correlation Coefficient	p	
pН	-0.563	0.057	-0.675 *	0.016	-0.700 *	0.011	
ОМ	0.598 *	0.04	0.079	0.541	0.074	0.819	
Fe _{total}	0.455	0.137	0.422	0.172	0.261	0.412	
Al _{total}	0.256	0.422	0.08	0.805	-0.195	0.544	
Mn _{total}	-0.048	0.882	-0.187	0.561	0.237	0.458	
Fe _{DCB}	0.678 *	0.015	0.815 **	0.001	0.714 **	0.009	
Al _{DCB}	0.601 *	0.039	0.664 *	0.018	-0.012	0.970	
Mn _{DCB}	-0.018	0.955	-0.268	0.400	0.329	0.296	
Fe _{OX}	0.663 *	0.019	0.804 **	0.002	0.676	0.016	
Al _{OX}	0.317	0.315	0.188	0.559	0.543	0.068	
Mn _{OX}	0.148	0.645	-0.073	0.822	0.187	0.561	
Sand	-0.663 *	0.019	-0.498	0.100	-0.442	0.150	
Slit	0.708 *	0.01	0.560	0.058	0.522	0.082	
Clay	0.373	0.145	0.230	0.275	0.017	0.958	

Table 4. Correlation Coefficient and *p*-Values of Sorption Parameters Related to The Physicochemical Properties of The Soils.

Note: * significant at the 0.05 probability level; ** significant at the 0.01 probability level.

In other words, numerous factors can influence the sorption capacity of selenite onto soil. Hence, the multiple linear regressions were used to describe the relationship between soil properties and sorption maximum (Table 5). The regression results showed that SOM, besides Fe_{DCB} , has a positive effect on selenite sorption. Figure 5 shows the relationship between predicted Q_M and sorption amount at the designed initial selenite concentration, and a significant positive correlation was expressed ($R^2 = 0.8071$, p < 0.01).

Model	Multiple Linear Equation	R ²	p	S.E.					
	The stepwise regression for Q_M								
1	$Q_M = 0.176[Fe_{DCB}] + 71.8$	0.459	0.0154	113					
2	$Q_M = 0.130[\text{Fe}_{\text{DCB}}] + 37.5[\text{OM}] + 50.5$	0.535	0.0319	111					
3	$Q_M = 0.0338[Fe_{DCB}] + 9.30[silt] + 58.8[OM] - 311$	0.846	0.00129	67.8					
4	$Q_M = 0.0240 [Fe_{\rm DCB}] + 0.105 [Al_{\rm DCB}] + 8.87 [{\rm silt}] + 57.5 [{\rm OM}] - 305$	0.852	0.00400	71.2					
	The stepwise regression for K_f								
1	$K_f = 0.0616[Fe_{DCB}] - 11.3$	0.667	0.00123	26.1					
2	$K_f = 0.0533[Fe_{DCB}] + 1.11[Fe_{OX}] - 52.9$	0.721	0.00321	25.1					
3	$\dot{K_f} = 0.0454[\text{Fe}_{\text{DCB}}] + 0.847[\text{Fe}_{\text{OX}}] + 0.0709[\text{Al}_{\text{DCB}}] - 50.6$	0.752	0.00834	25.2					

Note: S.E. means standard error of the estimate.



Figure 5. Relationship between experimental sorption capacity and predicted Q_M by Model 3 in Table 5; experimental data are sorption amount at the designed initial selenite concentration (16 mg·L⁻¹).

Both crystalline and amorphous iron oxides were key factors for sorption capacity of selenite on soils. For example, Liuyang soil has the highest Fe_{DCB} content, and selenite sorption capacity is the highest too. Generally, the effect of iron oxides on contaminants and nutrients in soil is due to their large specific surface area and pH-dependent, positively charged surface. Meanwhile, the change in iron oxide crystalline state influences the metalloid sorption in soil [32,33]. Dhillon and Dhillon [15] suggested that iron oxides in the clay fraction have major influences on the retention of selenite by different types of Indian soils.

pH is an important factor that affects Se sorption onto soil, and soils with low pH exhibit high sorption capacity. On the one hand, pH can influence soil minerals and OM properties. For example, iron oxides exhibit further positive charges at low pH, thereby enhancing selenite sorption onto soil, and increased OH⁻ inhibits selenite sorption due to competition for sorption sites [34,35].

The results of this study indicated that soil OM was positively correlated with selenite sorption capacity, as determined by the Langmuir model. Several researchers have believed that OM influences Se sorption and desorption in soils with high OM contents, whereas oxy-hydroxides control sorption in soils with low OM [23,36]. The effect of OM on Se sorption in soil could be: (1) Binding of selenite to functional groups, such as amines in HA, through ligand exchange. Previous studies indicated that the arsenic could be bound to SOM through ligand exchange [37]. (2) The presence of cationic metals that could act as bridges for Se sorption to OM (Fe, Ba, Cr, Mg, and Mn are present in HA) [38].

3.6. Se Fraction Distribution Change with Age

The fraction distribution of Se at different ages was studied by the sequential extraction procedure, as shown in Figure 6a. First, at the beginning of soil aging, the distribution of Se was found in exchangeable (34.8%), water-soluble (27.6%), organic matter-bound (19.8%), and residual (16.0%) fractions. By contrast, the percentages of exchangeable and water-soluble Se fractions in total Se content decreased to 14.9% and 14.4%, and elemental and residual Se increased to 10.9% and 42.4% during the 60-day aging process, respectively. In other words, the sum of water-soluble and exchangeable Se was the predominant fraction and occupied 62.4% of the total Se in soil when exogenous Se entered into the soil. Furthermore, Se would change to the insoluble fraction (elemental and residual) with prolonged aging.



Aging time (d)

Figure 6. Changes of Se fraction distribution during the aging process. Se fraction occupied the total Se proportion at different ages (**a**); Se concentration in five fractions of soil aged for 0, 10, and 60 days (**b**).

In addition, the water-soluble Se is the main form in plant uptake and utilization, which could reflect the bioavailability of Se. Figure 6b shows that the content of water-soluble Se in soil decreased rapidly within the first 10 days of aging and then declined slightly (p < 0.01). Water-soluble Se content decreased from 6.60 mg·kg⁻¹ at the beginning of the aging process to 3.78 and 2.90 mg·kg⁻¹ at 10 and 60 days of aging, respectively. By contrast, no significant change was observed in the organic matter-bound Se with prolonged aging.

Nevertheless, the fractions of soluble and exchangeable metals could reflect their availability, because they are the parts that plants can absorb easily [39]. The fraction of water-soluble and exchangeable Se declined rapidly during the initial period (10 days), followed by a slow decrease (Figure 6). These phenomena were observed in previous studies [40,41], which could be due to the mechanism of selenite sorption. Selenite sorption onto soil includes two steps. The first step is the formation of outer-sphere surface complexes at the β -layer, and the second step is a ligand exchange process and formation of the inner-sphere surface complexes [14]. Additionally, some biogeochemical reactions also impact the fraction of Se in soil. The organic matter can enhance the Se(IV) reduced to insoluble Se(0) and/or Se(-II), which may precipitate with metal or substitute for sulfur in organic compounds [23]. Previous studies suggested that microbial reduction also results in the decrease of soluble and exchangeable Se [42,43]. Therefore, the sorption and aging of Se were a multistep process, including physical sorption, complexation, and redox reactions, which are related to soil properties and microbe community. The transformation mechanisms of Se in soil still need further research.

4. Conclusions

The relationship between sorption parameters and soil properties was investigated by statistical analysis to elucidate which properties controlled selenite sorption. Kinetic experiments showed that selenite sorption followed a pseudo-second-order reaction model, with sorption rate positively correlated with Fe_{DCB} and negatively correlated with soil pH. The batch sorption data were better described by the Langmuir model than by Freundlich model, and the sorption capacity ranged from 50.7 to 567 mg·kg⁻¹. Sorption parameters were significantly positively correlated with Fe_{DCB}, Al_{DC}B, Fe_{OX}, and SOM, whereas pH was negatively correlated. Thus, Fe_{DCB}, Fe_{OX}, Al_{DCB}, OM, pH, and soil texture controlled selenite sorption onto soil. The water-soluble and exchangeable Se fractions declined rapidly during the initial period, and the fraction of insoluble Se increased with prolonged aging. The variances of soil physicochemical properties in different areas result in different sorption behaviors of exogenous Se, so soil composition should be analyzed and the redistribution should be considered when Se fertilizers are applied in the future. This study could provide a reference for the application of Se fertilizers.

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