A calcined shell powder used for minimizing aluminum concentration in the soil of tea plantations

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ABSTRACT

In this study, the effect of shell powder on the adsorption and desorption behavior of aluminum in soil of tea plantations was explored. With increasing amounts of shell powder, the adsorption of the aluminum by the soil gradually increased. As the initial pH value of aluminum solution increased, the amount of soil aluminum adsorption gradually increased. The Elvich equation was the best fitting curve for the two soil adsorption kinetics, while the best fitting curve for the desorption kinetics of the original soil (OS) was a double constant equation. The best fitting curve for OS and shell powder (SS) was the Freundlich equation and Langmuir equation, respectively. The theoretical maximum adsorption capacity of OS and SS on aluminum was 975.0 and 4191 mg/kg, respectively. In conclusion, the addition of shell powder can improve the aluminum adsorption capacity of the soil and reduce the activity of aluminum in the soil.

Aluminum is one of the most abundant metal elements in soil [1]. Most of the aluminum in the soil exists in the form of minerals [2]. The active aluminum in the soil is mainly released by the soil itself. With the weathering of the soil and acid pollution, which causes the release of aluminum from the primary minerals, and the activity of aluminum in the soil gradually increases [3]. The acidification of the soil accelerates the accumulation of active aluminum in the soil, and the soil aluminum pollution in areas with severe soil acidification is also an important concern [4–6].

At the same time, the enrichment of aluminum by plants will also aggravate the aluminum pollution of the soil, especially for tea plants. Most tea plantations have excessively high level of active aluminum in the soil. Meanwhile, the enrichment of soil acid aluminum caused by plants is a typical process of soil acidification. The pH of soil gradually decreases to very low level with the growth of tea plants [7]. Tea plants can grow in slightly acidic soils, but too much acidity and aluminum content will reduce tea production [7]. Thus, controlling the excessive acidification of the soil in tea plantations is key to maintaining the stable production of tea plants growth. Many studies have used the method of increasing soil pH to control the excessive acidification of the soil in tea plantations [8,9].

Through its enrichment in the food chain, the aluminum in the soil can have a toxic effect on plants and even soil microorganisms, which in turn affects animals and ultimately has a toxic effect on the human body [10,11]. The roots of plants are the first to be affected by aluminum [12,13]. Under the effect of aluminum toxicity, the cell division of plant roots is inhibited, as is root elongation. Aluminum in plants can also change the cell wall structure of plants, leading to the death of plant cells [14,15]. Aluminum is generally considered to be a neurotoxin [16–18]. After entering the human body, aluminum can accumulate in various organs, which can lead to Alzheimer’s, Parkinson’s disease, dialysis encephalopathy and osteomalacia [17,19,20]. Therefore, controlling aluminum pollution in the soil is of great significance to agriculture and human health.

The aluminum in the soil can be divided into exchanged aluminum, adsorbed inorganic hydroxyaluminum, organic complex aluminum, iron oxide-bound aluminum, interlayer aluminum, amorphous aluminosilicate and gibbsite and mineral aluminum [21]. Among these, exchanged aluminum and adsorbed inorganic hydroxyaluminum have the strongest toxicity. Therefore, reducing the biological toxicity of these aluminum is the current focus of this research [22–24].

At present, the toxicity of aluminum is mainly reduced through controlling soil acidity, by applying organic acids, activated carbon, humic acid and other biologically active substances [25,26]. Shells, as a good source of calcium, could also be used as an effective alternative to control this aluminum
pollution. Shells are mainly composed of calcium carbonate [27,28]. The porous surface and strong alkalinity of the ground after adding ground shell demonstrate the effectiveness of this method at improving acidic soils, with shell powder effectively increasing soil pH. In several studies, shell powder was used to treat soil acidification and heavy metal pollution [29–32]. In this present study, shell powder was added to soil to investigate changes in the adsorption and desorption behavior of aluminum in the soil, which providing a reference for the treatment of aluminum soil pollution.

1 Materials and Methods

1.1 Sample collection and preparation

1.1.1 Soil collection

The soil samples were collected from red soil in fields near Jiu Village, Yongkang City, Zhejiang Province, China. The samples were to the laboratory, the soil was flattened in a clean plastic pot and placed in a ventilated location for air drying. After that tweezers were used to remove visible insect residues, branches, leaves and other organisms in the soil, and then the soil was passed through a 20-mesh sieve for further analyses.

1.1.2 Preparation and characterization of shell powder

After washing, drying and grounding with universal pulverizer, the mussel shells were passed through a 100-mesh sieve and calcinated at 600°C for 1 h, and then ground again to obtain shell powder for later use. The shell powder was mixed with water at a mass ratio of 1:9, then stirred for 2 min and left to stand for 30 min. The supernatant was taken for the determination of the reference pH value.

1.1.2.1 Inductively coupled plasma mass spectrometry (ICP-MS) analysis

The shell powder was digested in a mixture of concentrated nitric acid, concentrated hydrochloric acid, hydrogen peroxide and hydrofluoric acid at 180°C, and then the content of heavy metals was determined by ICP-MS [33].

1.1.2.2 Fourier infrared spectrometry (FTIR) analysis

Two milligrams of shell powder were weighed, about 100 mg potassium bromide powder was added, and then the resulting liquid was thoroughly mixed. After compression, the sample was analyzed using infrared spectroscopy. The measuring range was 4000–400 cm⁻¹ [34].

1.1.2.3 X-ray diffractometer (XRD) analysis

The shell powder was analyzed by XRD with an X-ray diffractometer, with 0.04° 2θ as the step. The 2-s diffraction analysis was carried out in the range of 2θ 20–70° [35].

1.1.2.4 Thermogravimetric analyzer (TG) analysis

The curve of shell powder loss with temperature was measured by TG [36]. The sample dosage in this experiment was 20 mg. The experiment was carried out in a nitrogen gas atmosphere. The temperature range was from room temperature to 1000°C, and the heating rate was 10°C/min. By observing the change in quality that occurs in the sample with increasing temperature, the content of organic and inorganic matter in the sample can be estimated.

1.1.2.5 Specific surface area (SSA) analysis

The sample specific surface area (SSA) and particle size were measured with a Micromeritics ASAP 2010 (Micromeritics Instrument Corporation, Norcross, GA, USA), and the weight of the sample was measured between 0.2 and 0.3 g. First, the sample was heated to 180°C, kept for 12 h and then the sample was degassed. Nitrogen was adsorbed and desorbed on the sample in a liquid nitrogen environment, and nitrogen adsorption capacity was measured [37].

1.2 Soil treatment

The mixing of shell powder and soil created a dilution gradient. An aliquot of 90 g of soil was added to the Ziplock bag of the appropriate size, then 10 g of shell powder was added. The soil and shell powder were mixed with a medicine spoon. Finally, by shaking the Ziplock bag repeatedly, a uniform soil was obtained containing 10% shell powder. After calculations, an appropriate amount of soil containing 10% shell powder was added to soils of different quality and mixed well to obtain soil with a different shell powder content.

1.3 Determination of aluminum

The chromazurine color method was used to determine aluminum content [38]. Briefly, ethylenediamine-hydrochloric acid buffer (pH 6.7 ~ 7.0), polyethylene glycol octyl phenyl ether (TritonX-100) and cetyl pyridinium bromide (in the presence of CPB), trivalent aluminum ions reacted with chromazurol S to form blue-green quaternary micelles. The absorbance value was measured at a wavelength of 620 nm and compared with the standard series for quantification. The standard series consisted of aluminum solutions containing 0, 0.500, 1.00, 2.00, 3.00, 4.00 and 5.00 μg of aluminum.
1.4 The adsorption experiment of soil aluminum

1.4.1 A single factor’s influence on soil adsorption of aluminum

1.4.1.1 Effect of shell powder addition on the adsorption of aluminum in soil.

An amount of 0%, 0.05%, 0.15%, 0.30%, 0.50% or 0.75% of shell powder was added to the soil. After that, 1 g of each of the now enriched soils was added to a 100-mL centrifuge tube. Then, 20 mL of 100 mg/L aluminum solution was added, and the resulting solution was maintained at 25°C. After shaking the solution for 12 h at 180 r/min, the supernatant was analyzed to determine the aluminum ion concentration and the amount of soil aluminum adsorption. The pH value of the 100mg/L aluminum solution was adjusted to 2, 3, 4, 5 or 6, respectively. Aluminum solutions 20mL in volume with different pH values were placed in a 100mL centrifuge tube containing 1g of soil. After shaking for 12h, the supernatant was taken to determine the aluminum ion concentration, and the amount of soil aluminum adsorption.

1.4.1.2 Effect of the initial pH value of aluminum solution on the adsorption of aluminum by soil.

1.4.1.3 Effect of aluminum solution ionic strength on soil adsorption of aluminum.

Aliquots of 100 mg/L aluminum ion solutions were prepared containing, 50, 100, 150, 200 and 250 mg/L sodium ions. These solutions with different ionic strengths were added to a 100 mL centrifuge tube, containing 1 g of soil. After shaking for 12 h, the supernatant was taken to determine the aluminum ion concentration, and the amount of soil aluminum adsorption.

1.4.1.4 Effect of soil addition on soil adsorption of aluminum.

Different amounts of soil (0.5, 1.0, 1.5, 2.0 or 2.5 g) were added to a 100-mL centrifuge tube. Then 20 mL of 100 mg/L aluminum solution was added and shaken for 12 h. The supernatant was taken to determine the aluminum ion concentration, and the amount of soil aluminum adsorption.

1.4.2 Analysis of the kinetics of aluminum adsorption

1.4.2.1 Soil adsorption kinetics experiment.

An aliquot of 1 g of soil was added into a 100 mL centrifuge tube. Then 20 mL of 100 mg/L aluminum solution was added and shaken for 5, 10, 20, 40 or 60 min, or 2, 4, 6, 12, 24 h, at 25°C and 180 r/min. Subsequently, the supernatant was analyzed to determine the aluminum ion concentration.

1.4.2.2 Soil desorption kinetics experiment.

An aliquot of 1 g of soil was added into a 100 mL centrifuge tube and weighed. Then, 20 mL of 100 mg/L aluminum solution was added and shaken for 8 h at 25°C and 180 r/min. It was equilibrated for 12 h, then centrifuged at 8000 r/min for 20 min to be able to extract the supernatant after the solution was passed through a 0.45 μm filter membrane. Then 20 mL of 0.1 mol/L KCl solution was added to the centrifuge tube containing the filter residue and shaken for 5, 10, 20, 40 or 60 min, and 2, 4, 6, 12 or 24 h, at 25°C and 180 r/min. The supernatant was then taken to determine the aluminum ion concentration and to calculate the release of aluminum from the soil after adsorption.

1.4.3 Study on the thermodynamics of aluminum adsorption and desorption in soil

1.4.3.1 Soil desorption thermodynamic experiment.

An aliquot of 1 g of soil was added into a 100-mL centrifuge tube and weighed. Then, 20, 40, 80, 120, 160, 200, 240 or 280 mg/L of aluminum solutions were added and centrifuged at 180 r/min and 25°C. After being shaken for 8 h, the supernatant was taken to determine the aluminum content. These filters are weighed and used for standby.

1.4.3.2 Soil desorption thermodynamic experiment.

The filter residue was taken from the experiment described in 1.3.3.1. Then, 1 mol/L KCl solution was added to the extract for 24 h, and then the aluminum ion content was measured in the supernatant and the amount of desorbed aluminum was calculated.

1.5 Data processing

All the experiments were carried out at least three times, and the experimental results were expressed as means ± one standard deviation. Analysis of variance (ANOVA) was performed and significant differences were determined by least significant difference (LSD) tests with a confidence interval of 95%, using SPSS v. 13.0. (SPSS Inc., Chicago, IL, USA). The fitting of kinetics and thermodynamics equations was completed using Origin®8.6 software. The fitting equations are listed in Tables 1 and 2.

2 Results and discussion

2.1 Composition and characteristics of shell powder

2.1.1 Composition and characteristics of shell powder.

As shown in Table 3, the shell powder contained arsenic 0.36 ± 0.014 mg/kg, lead 0.81 ± 0.015 mg/kg, mercury 0.012 ± 0.0032 mg/kg, cadmium
1.07 ± 0.083 mg/kg, chromium 0.097 ± 0.0071 mg/kg and copper 1.09 ± 0.089 mg/kg, and the contents of six metal ions were all relatively low. The pH of shell powder reached 11.21 ± 0.36, which indicating a strong alkalinity and can improve the soil pH value and ultimately enhanced the adsorption capacity of the soil to aluminum. TG analysis showed that the calcined shell powder contained more than 98% calcium carbonate. The average particle size of the shell powder was 154.42 ± 2.72 μm, and the specific surface area was 0.3483 ± 0.017 m²/g. Both smaller particle size and a larger specific surface area can enhance the adsorption capacity of the soil powder.

2.1.2 Fourier infrared spectrometer analysis

The values 712.7, 875.4, 1424.6, 1797.0 and 2512.6 present in the figure were all the infrared characteristic peaks of calcium carbonate, as shown in Figure 1(a) [39]. The absorption peak at 712.7 cm⁻¹ belonged to calcium carbonate C-O out-of-plane bending vibration; the absorption peak at 875.4 cm⁻¹ was attributed to calcium carbonate C-O in-plane bending vibration; the absorption peak at 1424.6 cm⁻¹ indicating to calcium carbonate C-O asymmetric stretching vibration; the absorption peak of 1797.0 cm⁻¹ was attributed to the C = O stretching vibration of calcium carbonate; the absorption peak at 2512.6 cm⁻¹ was caused by the combined frequency of 1797.0 cm⁻¹ and 712.7 cm⁻¹. Several absorption peaks represented the vibration of CO₃²⁻ in calcium carbonate, but the absorption peak at 1424.6 cm⁻¹ had a relatively strong red shift, which indicating that some changes had taken place in the groups on the surface of the shell powder after calcination [36]. The wide absorption band centered at 3421.6 cm⁻¹ could be attributed to the stretching mode of hydroxyl radicals and amino groups.

2.1.3 XRD

The X-ray diffraction energy spectrum of the calcined shell powder had a high degree of fit with the PDF#72-1214 card, and the FOM was only 0.6, as shown in Figure 1(b), [40]. No peaks of other crystals were

![Figure 1](image_url). Characteristics of shell powder. FTIR patterns of shell powder (a), XRD patterns of shell powder (b), and TG diagram of shell powder (c).
found in the energy spectrum, or the characteristic peaks of other crystals were covered by the larger intensity of the characteristic peaks of calcium carbonate. It can be determined that most of the crystal forms of calcium carbonate in the shell powder that calcined at 600°C were a type of calcite.

2.1.4 TG
The mass of shell powder slowly decreased when heated from 0°C to 400°C, at which point it stopped, with a resultant mass change of about 2.88%, as shown in Figure 1(c). This might be caused by the gradual ashing of the organic components in the shell powder. It can be inferred that the organic components in the selected mussel shell samples were approximately 2.88% of the entire organism mass. When the temperature rose to about 700°C, the quality of the shell powder began to decline rapidly. This was because the calcium carbonate in the shell powder began to gradually decompose from the heating. The decomposition of the shell powder was most rapid at 782.0°C. The decomposition rate of calcium carbonate in the shell powder reached its peak. When the temperature was close to 800°C, the quality of shell powder stopped decreasing and remained unchanged, which indicating that all the calcium carbonate in it had been converted into calcium oxide [41]. It can be inferred that the decomposition temperature of the mussel shell powder used in this experiment was about 700–800°C.

2.2 Effect of additional amounts of shell powder on the amount of aluminum adsorption in soil
As the amount of shell powder increased, the amount of aluminum adsorbed by the soil gradually increased, as shown in Figure 2. As the additional amount of shell powder increased from 0% to 0.75% of soil, the amount of aluminum adsorption increased from 409.8 to 1246.0 mg/kg. This increase in adsorption reached 204.0%.

Shell powder itself is a kind of strong alkaline powder [42]. When the shell powder was added to the soil, it significantly increased the pH of the soil. As the amount increased, the pH of the soil gradually increased. When the pH of the soil changed from acidic to neutral, the soil’s capacity to accept aluminum increased, which reflect the increase in the soil’s capacity to absorb aluminum. The tea plants enrich with the acid aluminum reduces the tea yield. The application of shell powder reduced the accumulation of acid aluminum in the soil [43]. Shell powder has a strong physical adsorption capacity due to its loose and porous surface, which can also increase the adsorption capacity of the soil to aluminum. Thereby passivating the aluminum in the soil.

2.3 Effect of the initial pH value of aluminum solution on the amount of aluminum adsorption in soil
The higher the initial pH value of the aluminum solution, the stronger the adsorption capacity of the soil for aluminum (as shown in Figure 3). When the initial pH value was 2, the soil could not adsorb aluminum in the solution and instead released some of it. When the pH value was increased, the adsorption capacity of the soil to aluminum gradually increased. In addition, when the pH value reached 6, the adsorption capacity was greatest. The adsorption capacity of 0.5 to aluminum under different initial pH values of aluminum solution was weaker than that of SS, but when the pH value reached 6, the adsorption capacity of the two to aluminum was similar. The pH value factor is proved an important indicator that affected the activity of aluminum. Earlier studies also showed that when the soil pH increased, the active aluminum ions in the soil were

![Figure 2](image_url)  
Figure 2. The change of soil aluminum adsorption with different additional amounts of shell powder.
significantly reduced, and the capacity of the soil for aluminum increased. At the same time, the adsorption capacity of the soil for aluminum increased and aluminum ions were less likely to be released.

At pH 2 and pH 3, there were the most obvious changes in adsorption capacity was observed. For SS, when the pH increased from 2 to 3, the soil aluminum adsorption capacity increased from −41.17 to 1478.89 mg/kg, with an increased range of 1520 mg/kg. Meanwhile, when the pH increased from 3 to 5, the soil aluminum adsorption capacity changed by 372.0 mg/kg. pH increased from 5 to 6, it only increased by 15.25 mg/kg. For OS, increasing in pH from 2 to 3 and from 5 to 6, the soil aluminum adsorption capacity increased by 703.7 and 864.1 mg/kg, respectively. While the adsorption capacity was relatively smaller, when the pH was increased from 3 to 5. This phenomenon was possibly related to the change in the form of aluminum. When the environmental pH is extremely low, most of the active aluminum in the soil is converted into free aluminum (aluminum ions). These aluminum ions compete with the aluminum ions in the solution and occupy a limited adsorption site on the soil. There may be release of aluminum ions from the soil. When the pH value was of medium acidity, the higher pH value of the solution was also conducive to the passivation and adsorption of aluminum. When the pH was neutral, the presence of aluminum in the solution was not sufficiently stable and the aluminum was easily settled. This could also be a reason that the soil aluminum adsorption capacity at pH 6 was close to that of OS and SS. Therefore, it can be inferred that for a tea plantation with a slightly acidic soil environment, the adsorption capacity of the soil to aluminum can be effectively enhanced after the treatment of shell powder, thus by reducing the activity of aluminum.

2.4 Effect of aluminum solution ionic strength on the amount of aluminum adsorption by the soil

As the ionic strength of the aluminum solution increased, the adsorption capacity of the original soil for aluminum gradually increased (Figure 4). As the sodium ion strength increased from 50 to 250 mg/L, the original soil showed an increase in aluminum adsorption capacity. The adsorption capacity increased from 349.8 to 502.3 mg/kg. As the ionic strength of the aluminum solution increased, the adsorption capacity of the soil treated with shell powder did not change significantly, as the adsorption capacity decreased from 1511 to 1427 mg/kg.

The ionic strength of the solution affects the adsorption behavior between the adsorbent and the adsorbate [44]. A strong electrolytic solution activates the adsorption sites on the surface of the adsorbent, but there might also be competition with the
adsorbate [45]. Proper ionic strength could help to increase the adsorption capacity of the adsorbent and increase the saturated adsorption capacity of the adsorbent. In this current study, ionic strength had a small effect on the adsorption of aluminum by the soil, but these two soils exhibited opposite effects. The reason for this might be due to sodium ions, which activated the adsorption sites of the soil to a certain extent but sodium ions competed with aluminum ions due to the adsorption sites created by the addition of shell powder.

### 2.5 Effect of soil addition on the amount of soil aluminum adsorption

As the amount of soil added to the aluminum solution increased, the amount of aluminum adsorption per unit of soil decreased (Figure 5). With the increase of added soil, the amount of aluminum adsorption per unit soil of OS decreased from 600.3 to 380.2 mg/kg, while the amount of aluminum adsorption per unit soil of SS decreased from 2025 to 750.0 mg/kg.

The adsorption capacity of aluminum per unit soil of SS decreased significantly. This might be because the shell powder effectively improved the ability of the soil to adsorb aluminum, and only a small amount of soil could adsorb more aluminum ions. Increasing the additional amount of soil makes a limited contribution to the amount of adsorption under the condition of limited aluminum ions. So, the adsorption amount of aluminum per unit of soil after the shell powder treatment was significantly reduced. The soil added with 0.5 g, the solid–liquid ratio was relatively small. The soil was in contact with the solution completely and the soil could have been supersaturated with aluminum adsorption. When the amount of soil added daily basis, showed an increase from 1.0 to 2.0 g, the solid–liquid ratio was moderate. In this OS soil could only absorb a small proportion of the aluminum ions in the solution and the maximum aluminum adsorption capacity of the soil was lesser. When the amount of added soil increased, the same concentration of aluminum ions resulted in more OS soil, which reaching adsorption balance. Thus, the amount of aluminum adsorption by the soil did not change significantly. When the amount of added soil was 2.5 g, the solid–liquid ratio was relatively high, and the aluminum solution in the experiment did not result in the soil reaching adsorption balance and the amount of aluminum adsorption per unit soil decreased.

![Figure 5](image1.png)

*Figure 5.* The change of soil adsorption of aluminum under different amounts of soil added to aluminum solution: OS—original soil, SS—soil treated with 0.75% shell powder.

### 2.6 Effect of shell powder on the kinetics of soil adsorption and desorption of aluminum

The adsorption of aluminum by the two soil types can be divided into two stages: fast reaction and slow reaction, which was due to the limited number of binding sites on the soil surface (Figure 6). Moreover, binding sites can be divided into high-energy and low-energy sites. At the beginning of adsorption, aluminum was mainly bound to high-energy sites on the soil surface. Consequently, there was less aluminum on the soil surface and more high-energy sites, which indicating the fast adsorption reaction. When the high-energy sites were gradually saturated and the aluminum content adsorbed on the soil surface increased, the adsorption reaction gradually slowed due to the principle of adsorption and repulsion. After adsorption and desorption reaching equilibrium, the aluminum content on the soil surface did not showed any change. The rapid adsorption reaction of the OS during the first hour, the adsorption capacity reached 89.1% of the maximum capacity. Meanwhile, the reaction was fastest in the first 5 min, it reaching more than 50% of the maximum adsorption capacity. The adsorption rapid reaction stage of the SS reached 83.30% of the maximum adsorption capacity during the first
two hours of reaction, and the reaction was fastest in the first 5 min, which reaching 36.30% of the maximum adsorption capacity. While, the OS reached equilibrium after 4 h and the recorded maximum adsorption capacity was 415.4 mg/kg. In addition, the SS reached approximate equilibrium after 8 h, and the maximum adsorption capacity was about 1419 mg/kg.

The amount of aluminum adsorption on the two soils changed over time and was fitted with four kinetic models: the double constant model, the Elovich model, the first-order kinetic model, and the parabolic diffusion model (Table 1). Based on R² values, the two-constant model and the Elovich model were the best fits, while the first-order kinetic model fitted the two soils poorly. The degree of fit of the parabolic diffusion model to the SS data was better than that to the OS data. The Elovich model fitted the two soils best. Therefore, we primarily used the Elovich model to describe the adsorption process of aluminum on the two soils, but we also applied the double constant model. However, both the Elovich model and the two-constant model were suitable for describing the kinetic process of a complex reaction, which showed that the process of soil adsorption of aluminum is a complex one that might involve multiple reactions [46]. The Elovich model is suitable for describing the chemical adsorption behavior of heterogeneous solid surfaces [47]. Therefore, both the Elovich model and the double constant model can be used to discuss the adsorption kinetic characteristics of the two soils.

In the Elovich model of $S = B*t + A$, when the time $t$ is 1 h, the fitting parameter $A$ is equal to the average adsorption rate of the reaction for 1 h. The rapid reaction stage of the two groups of soils includes the first hour of the reaction, and parameter $A$ can be used as a parameter for the reaction rate at this time. This shows that the reaction rate in the rapid reaction stage of the OS was significantly lower than that of the SS. When the reaction time was longer than 1 h, the change of the adsorption amount $S$ according to the Elovich model was mainly determined by $B$. In these two sets of adsorption equations, $B$ represents the reaction rate parameter of the slow reaction stage. In the slow reaction stage, the reaction rate of the OS was greater than that of the SS.

The desorption processes of the two soils were not consistent (as shown in Figure 7) but these could be divided into two stages: fast reaction and slow reaction. The rapid reaction stage of the original soil reached 87.13% of the maximum desorption before 2 h, and the desorption equilibrium was achieved within 6 h.

### Table 1. Composition and characteristics of shell powder.

| Heavy metal elements of shell powder (mg/kg) | Calcium carbonate | pH | Mean grain size (μm) | SSA (m²/g) |
|---------------------------------------------|-------------------|----|----------------------|------------|
| Arsenic                                     | 0.36 ± 0.014      | 1.96 | 718.5                | 262.4      |
| Lead                                        | 0.81 ± 0.015      | 0.997 ± 0.0071 | 0.9946              | 0.9820     |
| Mercury                                     | 0.012 ± 0.0032    | 1.09 ± 0.089 | −394.5              | −674.6     |
| Cadmium                                     | 1.07 ± 0.083      | −0.01109 | 198.9               | 0.3483     |
| Chromium                                    | 0.097 ± 0.071     | −0.01500 | 0.01950             | 0.01109    |
| Copper                                      | 1.09 ± 0.089      | −0.01416 | 1.0914              | 1.0914     |

### Table 2. Fitting parameters of soil dynamics equation.

| Kinetic equations | Parameters | Adsorption | Desorption |
|-------------------|------------|------------|------------|
| Double constant   | $\ln(S) = B*\ln(t)+A$ | A          | 5.818      | 5.886      |
|                   | $B$        | 0.9640     | 0.1500     | 0.1402     |
|                   | $R^2$      | 0.7890     | 0.9439     | 0.9429     |
| Elovich           | $S = B*\ln(t)+A$ | A          | 339.7      | 368.3      |
|                   | $B$        | 36.435     | 156.3      | 58.17      |
|                   | $R^2$      | 0.8534     | 0.9750     | 0.9343     |
| First-order kinetics | $\ln(S) = A + B*t$ | A          | 5.798      | 5.859      |
|                   | $B$        | 0.0130     | 0.0244     | 0.0195     |
|                   | $R^2$      | 0.2071     | 0.3168     | 0.3096     |
| Parabolic diffusion model | $S/S_{\text{max}} = A + B*t^{1/2}$ | A          | 0.7008     | 0.5635     |
|                   | $B$        | 0.0864     | 0.1550     | 0.1219     |
|                   | $R^2$      | 0.4914     | 0.8081     | 0.6403     |

Note: A and B denote the parameters in the kinetic equation, $S$ (mg/kg) denotes the adsorption amount, $T$ (h) denotes the time, and $S_{\text{max}}$ denotes the maximum adsorption amount.

### Table 3. Fitted parameters of equations for soil isothermal adsorption of aluminum.

|                     | Langmuir | Freundlich | Temkin |
|---------------------|----------|------------|--------|
| Soil                | C/qm     | K_{m}      | R^2    |
| OS                  | 975.0    | 0.01109    | 0.9620 |
| SS                  | 4191     | 0.01950    | 0.9877 |
|                     | In q = ln C/n + ln K_{p} | q = a*lnC+b |
| OS                  | 48.83    | 2.01       | 0.9946 |
| SS                  | 262.4    | 1.96       | 0.9820 |
|                     | n        | a          | b      |
| OS                  | 198.9    | −394.5     | 0.9751 |
| SS                  | 718.5    | −674.6     | 0.9386 |

Note: $K_{m}$, $n$, $a$, $b$ are thermodynamic parameters, $C/q_{\text{m}}$ is the maximum adsorption capacity, $q$ (mg/kg) is the adsorption capacity and $C$ (mg/L) is the equilibrium concentration.
The maximum desorption was about 503.7 mg/kg. The rapid reaction stage of the soil treated with shell powder reached 83.87% of the maximum desorption before 1 h, and the desorption equilibrium was achieved within 6 h. Maximum desorption was about 161.3 mg/kg.

The relationship between the amount of aluminum desorption by the two soils with time was fitted with four kinetic models: the double constant model, the Elovich model, the first-order kinetic model and the parabolic diffusion model (Table 1). Based on R², the model fittings followed a similar pattern to those for adsorption. The two-constant model and the Elovich model were fits better while the first-order kinetic model was not suitable for either soil type. The best fit model for the OS was the two-constant model, while the best fit model for the SS was the Elovich model.

2.7 Effect of shell powder on the thermodynamics of soil adsorption and desorption of aluminum

The amount of aluminum adsorption by the soil in the SS was significantly greater than that in the OS (Figure 8). The maximum adsorption capacity of the SS reached 2974 mg/kg, while the maximum adsorption capacity of the OS only reached 745.2 mg/kg. Under the same initial aluminum concentration, the aluminum adsorption capacities of each group were also greater than those of the SS. This shows that the treatment of soil with shell powder improves the adsorption capacity of the soil for aluminum. With an increase in aluminum ion concentration, the adsorption capacity increased rapidly, but the increase in the adsorption capacity of the OS was always slower than that of the SS. Earlier studies have shown that there are high-energy and low-energy sites in the adsorption process. For SS, when the aluminum ion concentration was low, the adsorption was mainly at the high-energy site. During this period, the adsorption rate was large, and the slope of the curve was also relatively large. As the concentration of aluminum ions increased, the high-energy sites gradually became saturated, and the adsorption sites shifted from high-energy to low-energy. At this time, the adsorption repulsion caused the adsorption rate to gradually decrease, which made the curve gradually slow down and the slope decrease. Compared with the curve of the SS, the slope of the OS’s curve was relatively small across the adsorption process, and the change was not clear. This might be due to the existence of shell powder providing a large number of high-energy sites, which greatly enhanced the ability of soil to adsorb aluminum.

The Langmuir, Freundlich and Temkin equations were used to fit the adsorption isotherms of OS and SS to aluminum. The parameters obtained by the fitting are listed in Table 2. The results showed that the three curves had a good fit for the two soil adsorption isotherms. According to R², the best fit for the OS was the Freundlich equation, and the best fit for the SS was the Langmuir equation. Langmuir isotherms derive from the assumption that all adsorption sites were the same and that adsorption at the active site was independent of whether adjacent sites were occupied or not [48]. The Langmuir model was more inclined to describe the formation of monolayer adsorption [49]. The Langmuir equation was used to obtain the maximum values of aluminum adsorption in the two groups of soils, which were 975.0 mg/kg in the OS and 4191 mg/kg in the SS. This was the theoretical value obtained by equation fitting, and there was some difference between these and the maximum observed values, but the difference was not large and might be achieved by increasing the concentration of the aluminum solution. It has been assumed that the Freundlich model is superior to the Langmuir model when simulating the adsorption of metal elements on a heterogeneous surface is solid. The Freundlich isotherm is an empirical equation that assumes multiple layers of adsorption on an inhomogeneous surface composed of different types of
adsorption sites [48]. In the Freundlich model, $K_F$ reflects the strength of the adsorption capacity of the adsorbent to the adsorbate, and ‘$n$’ can be used as the strength of the soil’s adsorption of metal elements. The larger the value of $n$, the greater the adsorption force and the more affinity. In the Temkin equation, the larger the value of ‘$a$’, the stronger the adsorption capacity of the soil to metal elements. It can be seen from Table 2 that no matter the model applied (Langmuir, Freundlich or Temkin equation), the adsorption capacity of the soil in the SS was stronger than that in the OS, but from the ‘$n$’ of the Freundlich model, it was found that the affinity of the OS to aluminum was higher than that of SS. Therefore, OS adsorption of aluminum was more likely to be multi-layer adsorption on a non-uniform surface, while SS adsorption of aluminum was more likely to be single-layer adsorption.

The desorbent used in this study was a 1 M KCl solution because it effectively desorbs aluminum ions in the soil. With an increase in the amount of aluminum adsorption, the desorption by soil aluminum in the OS and SS increased from 109.1 to 630.5 mg/kg, and from 43.15 to 615.7 mg/kg, respectively. While the desorption percent increased from 75.8% to 84.6%, and from 12.5% to 20.7% (Figure 9). Both the desorption amount and desorption percent increased with the increase of aluminum adsorption, but the desorption was never complete. The aluminum remaining in the soil was combined with high-energy sites, which had a relatively weak effect on plants. It can be seen from the desorption rate that the desorption rate of the SS was much lower than that of the OS, which means that most of the aluminum in the SS had a relatively large binding force with the soil, and thus it was difficult to desorb the aluminum using KCl solution.

When the concentration of aluminum and the amount of adsorption were low, the aluminum adsorption in soil mainly occurred at high-energy sites. Judging from the change in resolution rate, the preferential adsorption should be a specific adsorption.

This part of the adsorbed aluminum was difficult to desorb with desorbents. When the high-energy sites were saturated, the adsorption of aluminum into the soil mainly occurred at the low-energy sites. This portion of the aluminum was easier to desorb with desorbents, has a higher bioavailability, and has a stronger toxic effect on plants. This shows that shell powder enhances the specific aluminum adsorption of soil and greatly reduces the desorption capacity of soil aluminum. It might be that shell powder provides a large number of high-energy sites or changes the adsorption properties between soil and aluminum.

3 Conclusion

Shell powder has a strong alkaline pH of 11.21 ± 0.36, which indicating that it can improve the pH value of the soil and has a certain influence on the adsorption of aluminum in the soil. More importantly, both the specific surface area and particle size of shell powder are small, suggesting their strong adsorption capacity for aluminum. The main component of shell powder was shown to be calcium carbonate (>98%), and the main crystalline form of calcium carbonate is aragonite. All these characteristics have a great influence on the soil adsorption and desorption of aluminum.

Consequently, the larger the additional amount of shell powder, the stronger the adsorption capacity of the soil to aluminum. The higher the pH value, the stronger the adsorption capacity of the soil to aluminum. The ionic strength of the aluminum solution enhanced the ability of the original soil to absorb aluminum, while it weakened the ability of the soil after the shell powder treatment to absorb aluminum, though the effect was not obvious. The larger the amount of soil added, the greater the adsorption capacity of aluminum, but the unit adsorption capacity decreased. Therefore, it can be speculated that, shell powder can be used to improve the soil of tea plantations. It can also effectively increase the pH of the soil and absorb a large amount of active aluminum by reducing the effect of acid aluminum enrichment on tea plants in terms of acid aluminum’s toxic effect.

The Elovich equation was the best fitting curve of the two soil adsorption kinetics, while the best fitting curve of the original soil desorption kinetics was the double constant equation. The best fitting curve of soil desorption kinetics after shell powder treatment was the Elovich equation.

Thermodynamic equation fitting indicated that the best fitting curve of the original soil was the Freundlich equation, and the best fitting curve of the soil after shell powder treatment was the Langmuir equation. In the process of soil improvement, shell powder strongly enhanced the adsorption capacity of the soil to aluminum. This also weakened the desorption capacity of aluminum and effectively reduced its biological toxicity.
Disclosure statement

No potential conflict of interest was reported by the author(s).

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