Effects of exogenous silicon on the adsorption kinetics characteristics of arsenic in soils of acidic paddy fields in northeast China

Dan Yang, Yayun Wang, Tianyu Yang, Lei Guo and Na He*

College of Land and Environment, Shenyang Agricultural University, Shenyang, Liaoning, 110866, China

*corresponding author’s e-mail: 513912817@qq.com

Abstract. To explore the effects of exogenous silicon on the adsorption characteristics of arsenic in paddy field soils, the impacts of silicon on adsorption kinetic characteristics of arsenic in the acidic paddy field soil in northern China were studied under neutralizing alkaline of Sodium Silicate and balancing Na+ of different treatments. The results indicated that silicon reduced the adsorption amount of arsenic in soils and shortened the adsorption equilibrium time. The adsorption process of arsenic in the soil could be well described by Elovich equation. Silicon increased the equation parameters α and β values, which indicated that exogenous silicon could accelerate the initial arsenic adsorption rate in soils and reduce the reaction rate during the absorption process.

1. Introduction
As a toxic metalloid element prevailing in the natural, arsenic was introduced into soils through industrial activities such as mining and smelting as well as excessive usage of arsenic-containing pesticides and fertilizers. According to the joint announcement of “Survey on National Soil Pollution Conditions” issued by Ministry of Environment Protection and Ministry of Land and Resources in 2014, the point over-standard rate was 2.7%, ranking after cadmium (7.0 %) and nickel (4.8 %). Rice (Oryza sativa L.) is more likely to absorb arsenic from soils than other crops. There are arsenic contaminated soils in main rice-planted areas in China [1]. The bioaccumulation of arsenic in rice imposes huge risks on food safety and ecological environment. Therefore, there is an imperative demand on seeking effective methods for minimizing Arsenic contamination in soil.

The literatures have shown that the application of silicon not only could stimulate the seed germination and seedling growth under arsenic stresses as well improve the rice yield, but also greatly lower down the absorption and transportation of arsenic in rice[2]. The application of exogenous silicon may affect the physical and chemical properties of soils, which may further change the bioavailability of arsenic in soils. Yet the mechanism of the effect of silicon on arsenic chemical behaviors in soil remains unresolved. The objective of this research was to explore the effects of exogenous silicon on the adsorption kinetics characteristics of arsenic in the acidic paddy fields in northern China, eliminating differences of pH and accompanying ions, to provide a basis of the impact of exogenous silicon on arsenic changes in soil to mitigate arsenic accumulation in rice.
2. Materials and Methods

2.1 Soils
Soil samples were collected in Xinbin County of Fushun City in Liaoning Province (125° 20’ 44.4” E, 41° 34’ 9.1” N). The basic physical and chemical properties of soil samples are as bellow in Table 1.

Table 1. Physical and chemical properties of the soil

| pH   | Organic matter (g·kg⁻¹) | Available N (N·mg·kg⁻¹) | Available P (P·mg·kg⁻¹) | Available K (K·mg·kg⁻¹) | Amorphous iron oxides (Fe·mg·kg⁻¹) | Free iron oxide (Fe·mg·kg⁻¹) | Available Si (SiO₂·mg·kg⁻¹) | Total As (As·mg·kg⁻¹) |
|------|------------------------|--------------------------|-------------------------|-------------------------|-----------------------------------|-------------------------------|-----------------------------|-----------------------|
| 5.01 | 24.92                  | 62.27                    | 21.2                    | 103.9                   | 4.93                              | 13.09                        | 45.50                       | 11.891                |

2.2 Kinetic absorption
Several soil samples (1.25 g) were placed into 50 mL centrifugal tubes. 25 mL solutions, containing two different Na₂SiO₃ concentrations (0 and 100 mg·L⁻¹, SiO₂) and one Na₂HAsO₄ concentration (40 mg·L⁻¹, As), were added it to each tube. The alkalinity of Na₂SiO₃ are neutralized with HNO₃, and the differences in Na⁺ are eliminated by the appropriate amounts of NaNO₃ (0.01 mol·L⁻¹). Each treatment shall be performed for 3 times. Then seal the above-mentioned centrifugal tubes and set in the constant-temperature oscillator under different concussion durations of 15, 30, 60, 120, 240, 480, 960 and 1440 min. The treated samples were centrifuged for 5 min. The supernatant is further filtered and diluted for later use after centrifugation.

2.3 Sample analysis
The basic physical and chemical properties of soils are determined by regular methods. The total arsenic amount in soils is digested by aqua regia, and tested by HG-AFS, and the same method also applies to the determination of the arsenic amount in the absorption equilibrium solution.

3. Results and analysis

3.1 Absorption kinetic characteristics of arsenic in soils
With an initial arsenic solution concentration equivalent to 40 mg·L⁻¹ at 25°C, the absorption amount of arsenic in soils increased from fast to slow, approaching to saturation with sustained time. The arsenic absorption amount of silicon addition treatments was lower than that of Control treatments reaching a maximal arsenic absorption amount about 327.98 mg·kg⁻¹ and 370.47 mg·kg⁻¹ respectively within 1440 min. The As absorption amount of Si addition groups reached to 94.3% of the maximum absorption value at 120 min, whereas the control’s reached only to 93% at 240 min(Figure 1). The results showed that the absorption process of arsenic in soils was affected by exogenous silicon.

Figure 1 Adsorbed dynamic character of As on the paddy field soil
3.2 Equation of kinetic absorption of arsenic in soils

Elovich equation is found to be well fitted, and the results are presented in Table 2. \( Q_t \) (mg·kg\(^{-1}\)) is the absorption amount of arsenic at time \( t \) (min); \( A \) and \( B \) are parameters in the kinetic equation.

| Arsenic intensity (mg·L\(^{-1}\)) | Elovich equation       | \( r \)       | \( A \)       | \( B \)       |
|-----------------------------------|------------------------|--------------|--------------|--------------|
| 0                                | \( Q_t = 38.4422t + 114.5456 \) | 0.9589**     | 756.6037     | 0.0260       |
| 100                              | \( Q_t = 29.7649t + 133.6329 \) | 0.9226**     | 2651.6661    | 0.0336       |

* P<0.05; ** P<0.01. \( r_{0.05} = 0.811 \), \( r_{0.01} = 0.917 \).

According to Table 2, the fitting degree of Elovich equation reaches a significant level of 1%, indicating that it can be used to describe the absorption of arsenic in these experiments. And it can be further refined based on Low’s studies by defining \( A \) as \( (1/\beta)\ln(\alpha\beta) \) and \( B \) as \( 1/\beta \).[3] The equation becomes

\[
Q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t
\]

The \( \alpha \) (mg·g\(^{-1}\), min\(^{-1}\)) is in positive correlation with the initial absorption rate, while the desorption constant \( \beta \) (g·mg\(^{-1}\)) is in negative correlation with the reaction rate \[4\]. The calculated equation parameters are presented in Table 2. Compared with the control group, \( \alpha \) and \( \beta \) values of the treatment group increased, showing that silicon can accelerate the initial absorption rate of arsenic while reduce the overall reaction rate.

4. Discussion

The absorption of arsenic in soils is affected by multiple factors, such as pH, surface charges, organic matters, metallic oxides, clay minerals, etc.[5]. Extensive studies have shown that Fe-, Mn- and Al-oxides (or hydroxides) in soil colloid had strong affinity to arsenic.[6]

The experiment proved that the application of silicon inhibited the absorption of arsenic, and the relevant absorption amount in the treatment groups was lower than that of the control groups at anytime. The possible reason is that the arsenic in soil solutions is exclusively absorbed mainly via the Anion coordination exchange mechanism.[7], and silicon and arsenic have similar chemical properties, both of which are tetrahedral oxyanion. Silicates and arsenates compete with each other for the binding sites on the surface of Fe-Mn-Al oxides.[8], resulting to reduce the absorption of arsenic in soils. Thus, the application of silicon weakened the absorption of arsenic, and accelerate the absorption process of arsenic to reach the equilibrium sooner.

This study showed that the absorption kinetic characteristics of arsenic could be well presented by Elovich equation, indicating that the absorption process of arsenic in soils with silicon treatment was still a non-uniform diffusion process.[9]. After the addition of silicon, the adoption amount of arsenic reduced and the parameter \( \alpha \) increased, so the absorption equilibrium came earlier. Chien and Clayton[10] stated that the parameter \( \beta \) could be generally considered as the indicator of reaction rate, and the higher was \( \beta \) value, the slower was the reaction. \( \beta \) value augment with application silicon proved that exogenous silicon could decrease the absorption rate and inhibit the absorption of arsenic in soils. The reason for the slower adoption rate was that the binding sites of arsenic in soils were occupied by silicon.

5. Conclusion

(1) Under the temperature condition of 25 °C, The adsorption of arsenic on soil was first rapid, then slow and reached balance at last. Exogenous silicon lowered down the absorption amount of arsenic in soils and made adoption equilibrium reach earlier. (2) Elovich equation could be used to describe the absorption of arsenic in soils. The application of silicon resulted in higher \( \alpha \) and \( \beta \) values, indicating
that exogenous silicon accelerated the initial absorption rate of arsenic in soils, while decelerated the reaction rate of the overall process.

Acknowledgments
This study was supported by Basic research projects of Liaoning higher education institutions under a grant number LSNQN201713 and Natural Science Foundation of China under a grant number 41101275.

References
[1] Ji, D.L., Meng, F.S., Xue, H. (2016) Situation and prospect of soil arsenic pollution and its remediation techniques at home and abroad. J. J. Environ. Eng. Technol. 6(1): 90-99.
[2] Seyfferth, A.L., Limmer, M.A., Dykes, G.E. (2018) On the use of silicon as an agronomic mitigation strategy to decrease arsenic uptake by rice. In: Donald L., S. (Eds.), Advances in Agronomy, Volume 149. Elsevier, Netherlands. pp. 49-91.
[3] Low, M.J.D. (1960) Kinetics of chemisorption of gases on solids. J. Chem. Rev. 60(3):267-312.
[4] Ho, Y.S., Ng, J.C.Y., McKay, G. (2000) Kinetics of Pollutant Sorption By Biosorbents: Review. J. Sep. Purif. Methods 29(2): 189-232.
[5] Huling, J.R., Huling, S.G., Ludwig, R. (2017) Enhanced adsorption of arsenic through the oxidative treatment of reduced aquifer solids. J. Water Res. 123: 183-191.
[6] Crognale, S., Amalfitano, S., Casentini, B. (2017) Arsenic related microorganisms in groundwater: a review on distribution, metabolic activities and potential use in arsenic removal processes. J. Rev. Environ. Sci. Biotechnol. 16(4): 647-665.
[7] Chen, T.B. (1996) Arsenic in soil solution and its effect on the growth of rice(Oryza Sativa L.) J. Acta Ecol.Sin. 16(2):147-153.
[8] Hu, K.W., Guan, L.Z., Yan, L. (2002) Effect of supply silicon on adsorption and desorption action of phosphorus in paddy soil J. Plant Nutr. Fert. Sci. 8(2): 214-218.
[9] Wu, F.C., Tseng, R.L., Juang, R.S. (2009) Characteristics of Elovich Equation Used for the Analysis of Adsorption Kinetics in Dye-chitosan Systems. J. Biochem. Eng. 150(2-3): 366-373.
[10] Chien, S.H., Clayton, W.R. (1980) Application of Elovich equation to the kinetics of phosphate release and sorption in soils. J. Soil Sci. Soc. Am. J. 44(2): 265-268.