Cadmium passivation by four Passivators: Isotherm adsorption, desorption and mechanisms

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Abstract. In order to select passivator that can effectively passivate bivalence cadmium (Cd\(^{2+}\)) in combined soil, this study will firstly operate an outdoor research and preliminary experiment which have already selected steel slag, phosphate rock, palygorskite and charcoal as passivators. This paper will operate indoor isothermal experiments of adsorption and desorption, the specific surface area - pore radius distribution instrument to measure the phase composition, specific surface and the characteristics of pore radius of passivators. The main result shows that: (1) The results of indoor isothermal experiments of adsorption and desorption show that steel slag, palygorskite and phosphate rock all have a good adsorption of heavy metal ion bivalent cadmium; the adsorption isotherm is conforming to L equation and F equation. These four passivators’ adsorption on Cd\(^{2+}\) tend to increase as the initial concentration increases. Under the condition of same initial concentration, these four passivators have different adsorption capacities on Cd\(^{2+}\). Under the condition of same equilibrium concentration, these four passivators’ adsorptions on Cd\(^{2+}\) is steel slag > phosphate rock > palygorskite > charcoal and under the condition of low concentration. (2) Experiments of adsorption and desorption show that steel slag has a relatively small desorption on heavy metal ion Cd\(^{2+}\), ground phosphate rock, charcoal and palygorskite have an increasing desorption on this heavy metal ion as the adsorptions increase. Specifically, when the adsorption reaches its peak, desorption on Cd\(^{2+}\) is charcoal > palygorskite > phosphate rock > steel slag. After the comparisons we could find that among these four passivators, charcoal has a relatively huge desorption on Cd\(^{2+}\). (3) Among these four passivators, charcoal and palygorskite have relatively huge specific surfaces and pore volumes. The passivation mechanism of heavy metal is mainly physical adsorption and ion exchange adsorption. Though steel slag and phosphate rock have relatively smaller specific surfaces and pore volumes, they have higher pH values. The passivation mechanism of heavy metal is mainly chemical precipitation reaction.

1. Introduction
Due to the rapid development of industry and human activities’ interference, heavy metal pollution in farmland’s soil has seriously threatened the safety of crop and human health. In the face of heavy metal pollution in farmland, the chemical repairing technology of passivation stands out of many other
repairing techniques for it fixes quickly, has a short time of repairing, is easy to operate and has a low cost. The key point of repairing technique is the selection of passivator.

Currently, as the heavy metal pollution of soil is becoming more and more serious, the governance technology relative to heavy metal pollution of soil is constantly developing. The heavy metal in the soil is difficult to be completely removed, thus the strategy to reduce the biological activity of heavy metal and to repair the soil by adopting chemical passivation method is widely concerned and recognized. Some industrial by-products, agricultural waste materials and clay minerals have been widely used in the remediation of the heavy metal pollution of soil. After the adding of palygorskite and other mineral materials by Ma et al. (2012)[1] and Liu et al. (2013)[2] and A Middea et al. (2013)[3] to the soil polluted by heavy metal, the effect of palygorskite on the changes in biological effectiveness of heavy metal has been studied and the results show that the effective contents of Lead (Pb), Copper (Cu) and Zinc (Zn) in soil have decreased with the palygorskite treatment[4]. After the adding of hydroxyapatite to different soils by Chen et al. (2006) [5]and Omoniyi Kehinde Israel et al.(2011)[6]and Krishna Brundavanam Ravi et al. (2013)[7], Brundavanam Sridevi et al. (2015)[8] and Lucia Forte et al. (2017)[9] the effect of hydroxyapatite on Pb in the soil has been studied and the result shows that the adsorption amount of Pb by soil has obviously increased after adsorption and desorption tests and the adsorption mechanism of hydroxyapatite on Pb was discussed to generate precipitation of phosphate which is of great significance for solid waste recycling and resource recycling and which also provides a reference for the treatment of heavy metal pollution of farmland soil.

The experiment has chosen the four passivators (phosphate rock, charcoal, palygorskite and steel slag) in the pre-passivation tests and carried out the isothermal adsorption and desorption experiments on heavy metal bivalent cadmium (Cd\(^{2+}\)) indoors to study the effect of the four passivators on this heavy metal and to explore the adsorption mechanism briefly.

2. Materials and methods

2.1. Experimental materials

Passivators used in the present study were phosphate rock, charcoal, palygorskite and steel slag. Charcoal was purchased from the agricultural market of Wujiaying Village, Chenggong District, Kunming, Yunnan Province; the other three passivators were purchased from Bairuisi Company, Kunming. Testing solution was prepared with ultra-pure water. The basic nature of the four passivators is shown in Table 1.

### Table 1. pH value, specific surface area and pore characteristics of the passivation agents

| passivator   | pH value | specific surface area \(\text{m}^2\cdot\text{g}^{-1}\) | pore volume \(\text{cm}^3\cdot\text{g}^{-1}\) | pore radius \(\text{nm}\) |
|--------------|----------|-----------------------------------------------|----------------------------------------|-------------------|
| phosphate rock | 8.79     | 1.37                                         | 0.004                                   | 3.59              |
| charcoal     | 7.45     | 97.93                                        | 0.03                                    | 3.22              |
| palygorskite | 7.38     | 54.80                                        | 0.04                                    | 3.22              |
| steel slag   | 8.80     | 2.32                                         | 0.008                                   | 3.60              |

2.2. Experimental methods

2.2.1. Adsorption experiment. Preparation for solution: The concentration of background solution \(\text{NaNO}_3\)-\(\text{NaCl}\) was 0.01mol/L; the concentration of mother solutions \(\text{CdCl}_2\) is 1000mg/L respectively which is prepared by ultra-pure water and of which the value of pH is regulated by \(\text{HNO}_3\), \(\text{HCl}\) or \(\text{NaOH}\).

Cd adsorption experiment: a total of 2g phosphate rock, charcoal, palygorskite and steel slag have been weighed and selected on the polyethylene centrifuge tubes with a content of 5ml respectively, set the mass concentrations of \(\text{Cd}^{2+}\) as 0mg/L, 5mg/L, 10mg/L, 20mg/L, 40mg/L, 60mg/L, 80mg/L,
100mg/L, mother solution CdCl₂ with different volume have been weighed and selected into centrifuge tubes and dilute with NaCl of 0.01mol/L to 25ml. After 24 hours of constant temperature oscillation at 25°C (the velocity of vibration: 200 r/ min), it has been static for 24 hours, supernatant fraction has been filtered and selected to be measured by centrifugation for 10 minutes (the velocity of centrifugation: 4000 r/min). Each experiment was repeated three times. Cd is determined by atomic absorption spectrophotometer (America, Viran AA240FS), and the adsorption amount of Cd²⁺ on adsorbent is calculated by subtraction method.

Desorption experiments: 25ml solution NaNO₃ or NaCl with the background ion of 0.01mol/L have been added into residue after the end of the adsorption experiment, seal, let it be static for 24 hours. After 24 hours of oscillation at 200 r/min at 25°C constant temperature oscillation box, centrifugate for 10 minutes at 4000 r/min and take it out and filter and obtain the supernatant fluid. Cd²⁺ is determined by atomic absorption spectrophotometer (America, Viran AA240FS).

2.2.2. Data processing. Data was processed with Excel Microsoft 2003 and description of data of adsorption experiments with model L and model F which both are adsorption isotherm. The phase composition of passivators are analyzed by X-ray diffraction (Japan, D/max-2200) and the specific surface area, pore volume and pore radius of passivators are determined by low temperature N₂ adsorption method of the specific surface area - pore radius distribution instrument (America, Quantachrome, NOVA 2200e).

3. Results

3.1. Isothermal adsorption of different passivators for Cd²⁺

3.1.1. Isothermal adsorption curve of the four kinds of passivators for Cd²⁺. Under the same temperature and pressure conditions, the adsorption of the four kinds of passivators for Cd²⁺ were measured and the specific isothermal adsorption curve is shown in Figure 1. There was a high adsorption capacity of the four passivators for Cd²⁺, which increased continuously with increasing concentration of Cd²⁺ within the initial concentration of the solution in the range of 0~100mg/L. In the adsorption process, the adsorption of the four kinds of passivators for Cd²⁺ had some differences. The adsorption of phosphate rock, palygorskite and steel slag had undergone a rapid growth from low concentration to high concentration whereas charcoal increased slowly at low concentration and increased quickly at high concentration throughout the adsorption process.

![Figure 1. Adsorption isotherm curve of the four kinds of passivators on Cd²⁺](image-url)
3.1.2. The comparison of the adsorption capacity of the four kinds of passivators on Cd\(^{2+}\) with the same initial concentration and the same equilibrium concentration. By comparison with the change in equilibrium concentration and adsorption capacity of the four kinds of passivators for Cd\(^{2+}\) under same initial concentration(Figure2), it can be seen that with the increase of the initial concentration, the equilibrium concentration also increased and the equilibrium concentration of the four kinds of passivators appeared that the equilibrium concentration of charcoal was greater than that of phosphate rock, and the equilibrium concentration of palygorskite was greater than that of steel slag under the same initial concentration. However, the equilibrium concentration of charcoal was always higher than that of the other three passivators throughout the adsorption process. The adsorption capacity of the four kinds of passivators increased with the increase of initial concentration, and adsorption capacity of charcoal in the four kinds of passivators was always lower than that of the other three passivators. Under the same equilibrium concentration, the adsorption of the four kinds of passivators for Cd\(^{2+}\) differs as follows: steel slag > phosphate rock= palygorskite > charcoal. It is likely that phosphate rock and steel slag can increase the pH value of the soil in the four kinds of passivators to increase the amount of negative charges on the soil colloid surface and to enhance the electrical adsorption of heavy metal so that the adsorption of Cd\(^{2+}\) has increased.

3.1.3. Isothermal fitting curve of four passivators for Cd\(^{2+}\). The isothermal adsorption of four passivators for Cd\(^{2+}\) is expressed by the formula in the following Figures (Figure3-1 ~ Figure3-4) fitted through Model L and Model F. The adsorption of four passivators for Cd\(^{2+}\) complied with Model L and Model F. It shows that by comparing adsorption isotherm curve of the four passivators for Cd\(^{2+}\), Model L in isothermal fitting curve of phosphate rock and charcoal for Cd\(^{2+}\) is relatively correlated with the experimental data, both of with were close to 1 and is higher than the correlation coefficient of Model F. This demonstrates that this two kinds of passivators complies more with Model L.
However, model F in isothermal fitting curve of palygorskite and steel slag for Cd\(^{2+}\) was relatively correlated with the experimental data and it was higher than the correlation coefficient of Model L, indicating that Model F complied more with the adsorption process for these two passivators.

**Figure 3-1.** Adsorption isotherm of equation for phosphate rock on Cd\(^{2+}\)

**Figure 3-2.** Adsorption isotherm of equation for steel slag on Cd\(^{2+}\)

**Figure 3-3.** Adsorption isotherm of equation for palygorskite on Cd\(^{2+}\)
3.2. The adsorption of different passivators for Cd²⁺

The relationship between absorption and desorption capacity of different passivators for Cd²⁺ is shown in Figure7. The desorption of the four passivators for Cd²⁺ was increased with the increase of adsorption, and the desorption of the four passivators for Cd²⁺ differ greatly under the same condition as follows: charcoal > palygorskite > phosphate rock > steel slag. The desorption of steel slag throughout the desorption process is basically 0 mg/g. The reasons may be that the adsorption of steel slag for Cd²⁺ is mainly chemical absorption with strong adsorption selectivity and affinity which is difficult to desorption.

4. Discussion on the major functioning mechanism

It can be concluded from the analysis on the relationship between adsorption, initial concentration and equilibrium concentration of different passivators for heavy metal that the adsorption of Cd²⁺ by the four passivators showed an increasing trend with the increase of initial concentration. Under the same initial concentration, there are differences in the adsorption capacity of the four passivators for Cd²⁺.

(1) Under the same equilibrium concentration, the adsorption of the four passivators for Cd²⁺ showed an increasing trend with the increase of equilibrium concentration. Under the same equilibrium concentration, the adsorption of different passivators for Cd²⁺ was different as following: steel slag > phosphate rock; palygorskite > charcoal under the low concentration conditions.
(2) The isothermal fitting equation of phosphate rock and charcoal for Cd$^{2+}$ complied with the adsorption process of model L, whereas the isothermal fitting equation of steel slag and palygorskite for Cd$^{2+}$ with model F.

It can be concluded from the analysis on the relationship between adsorption and desorption in of the four kinds of passivator on Cd$^{2+}$ that desorption in of other kinds of passivators increases with increase of adsorption in addition to the few changes in the adsorption of steel slag on Cd$^{2+}$ throughout the whole process of the desorption of Cd$^{2+}$ is as that: charcoal $>$ palygorskite $>$ phosphate rock $>$ steel slag at the maximum adsorption; it shows from comparison that in the four kinds of passivators, the desorption in of charcoal to Cd$^{2+}$ is large, which is mainly due to the fact that the adsorption of charcoal on heavy metal mainly focuses on physical adsorption and it is easy for desorption.

In terms of the passivation mechanism, charcoal has a larger specific surface area and structure of pore volume which focuses on the physical adsorption and ion exchange adsorption of the passivation of heavy metal [14]; as for steel slag and phosphate rock, though specific surface area and pore volume of them were relatively smaller than other passivators. They have relatively large value of pH and passivation mechanism of heavy metal may give priority to chemical precipitation reaction.

It can be seen from Table1 that the characteristics of the pH value, specific surface area and pore radius of the four passivators. The pH value of several passivators are of partial alkalinity, and the pH of steel slag and phosphate rock are the highest, reaching 8.80 and 8.79. However, the pH value of charcoal and palygorskite are relatively low, reaching 7.45 and 7.38, respectively. In addition, the specific surface area of charcoal and palygorskite are larger than that of steel slag and phosphate rock, reaching 97.93 m$^2$·g$^{-1}$ and 54.80 m$^2$·g$^{-1}$. However, the specific surface area of steel slag and phosphate rock was only 2.32m$^2$·g$^{-1}$ and 1.37m$^2$·g$^{-1}$. The pore volume was similar to that of the specific surface area, and pore radius showed no obvious change. The specific surface area and pore volume are also two important factors during the passivation process.

This study will measure the adsorption isotherm through adsorption quantity, initial concentration and equilibrium concentration to discuss the adsorption process and the probable mechanism of heavy metal. There are a lot of factors that influence the adsorption. In order to have a further study on heavy metal’s adsorption, a large amount of work need to be carried out. How ion strength, temperature, heavy metal’s chemical property and co-existing ion influence the adsorption need to be discussed.

(3) The study will analyze and discuss about the mechanism that passivators passivate heavy metals by analyzing characterizations of the XRD, pore volume, pore radius and specific surface area. Due to the complexity of soil’s fundamental property, we need to take other interactive factors into the consideration of the mechanism between heavy metal and passivators. We could use X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) to present its characteristics and have a further discussion about the combining point and mechanism of heavy metal and passivators.

5. Conclusion
Conclusions can be drawn from these experiments:

(1) The results of indoor isothermal experiments of adsorption and desorption show that steel slag, palygorskite and phosphate rock all have a good adsorption of heavy metal ion Cd$^{2+}$; the adsorption isotherm is conforming to L equation and F equation. These four passivators’ adsorptions on Cd$^{2+}$ is tend to increase as the initial concentration increases. Under the condition of same initial concentration, these four passivators have different adsorption capacities on heavy metal ion. Under the condition of same equilibrium concentration, these four passivators’ adsorptions on Cd$^{2+}$ is steel slag $>$ phosphate rock $>$ palygorskite $>$ charcoal.

(2) Experiments of adsorption and desorption show that steel slag has a relatively small desorption on heavy metal ion Cd$^{2+}$; ground phosphate rock, charcoal and palygorskite have an increasing desorption on this heavy metal ion as the adsorptions increase. Specifically, when the adsorption reaches its peak, desorption on Cd$^{2+}$ is charcoal $>$ palygorskite $>$ phosphate rock $>$ steel slag. After the
comparisons we could find that among these four passivators, charcoal has a relatively huge desorption on Cd²⁺.

(3) Among these four passivators, charcoal and palygorskite have relatively huge specific surfaces and pore volumes. The passivation mechanism of heavy metal is mainly physical adsorption and ion exchange adsorption; though steel slag and phosphate rock have relatively smaller specific surfaces and pore volumes, they have higher pH values. The passivation mechanism of heavy metal is mainly chemical precipitation reaction.

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