The Sorption of Iodine by Modified Layered Double Hydroxides from Aqueous Solutions: Effects of Intercalation Groups and Cationic Ratio

Ling Zhang, Miaomiao Zhang, Hongting Zhao and Dong Zhang*

Department of Environmental Science and Engineering, College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, China
Email: zhangdong@hdu.edu.cn

Abstract. Layered double hydroxides (LDHs) have been considered as one of promising sorbents to treat radioactive iodine contaminated soil. In the study, we investigate the effects of intercalation anions and cationic ratio of LDHs on the sorption of iodine from aqueous. The results from kinetic and isotherm sorption experiments showed that intercalation of organic anions (e.g., SDBS, SDS) and higher Mg:Al ratio (e.g., 4:1) have a benefit for the sorption of iodine. The sorption affinity (L·kg⁻¹) of iodine with LDHs followed the order: SDS (604.5) > SDBS (528.2) > Cl⁻ (514.2) > CO₃²⁻ (461.8) > SO₄²⁻ (311.4) and 4:1 (2912) > 3:1 (514.2) > 2:1 (281.2). It seems that the intercalation of SDBS and SDS provide additional aromatic structures, which is responsible to the specific binding between aromatic carbon with iodine.

1. Introduction
Radioactive iodine is considered to be a risk-contributing contaminant and has potentially acutely and chronically toxic to human due to its easily uptake and bioaccumulation. Tremendous amount of radiiodine (e.g., ¹²⁹I, ¹³¹I) has been released into our environment as the form of iodine, iodide, and iodate through nuclear bomb testing, release of improperly disposed spent nuclear fuel, wastewater discharging of thyroid cancer treatment sections, and accident in nuclear power plants [1-4]. Many studies indicated that interactions between aromatic carbon in organic matter and iodine occurred (formation of carbon-iodine bonds), which determines the transportation of radiiodine in soil [5-8]. However, due to relatively low organic carbon content for most soil, radiiodine is much mobile in soil systems and subsequently high ecological risk [8, 9]. Therefore, soil amendments are needed to control the transport of low-concentration iodine in soil.

Numerous studies have been conducted to design, develop, apply and assess useful and effective materials with concern of ecological safety, including Portland cement [10], metallic oxides [11], biochar [9], superfine powered activated carbon [12], modified montmorillonite [13] and layered double hydroxides (LDHs) [14, 15]. LDHs, as an anionic mineral, showed good affinity and capability for iodine sorption. However, the effects and mechanisms of structure and property on the removal and sorption of iodine are still unknown. Therefore, in the present study, we investigated kinetics and isotherm sorption of iodine by LDHs with different intercalation anions and cationic ratio to evaluate the effects of property of LDH on the interaction of iodine with anionic mineral clays.
2. Materials and Methods

2.1. Chemical reagents
Mineral salts used for LDHs synthesis including magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$·6H$_2$O), aluminium nitrate nonahydrate (Al(NO$_3$)$_3$·9H$_2$O), potassium carbonate, sodium sulfate, and sodium chloride were all AR grade and purchased from Aladdin Reagent Co. (Shanghai). Two anionic surfactants e.g., sodium dodecyl benzene sulfonate (SDBS), and sodium dodecyl sulfate (SDS) were used to organic modification for LDHs and also purchased from the same company. We chose iodine isotope to represent radioactive iodine in all experiments to avoid the potential radioactive risk. No purification and/or pre-treatment were carried out for all reagents and were directly used.

2.2. Preparation of LDHs with different intercalation anions and cationic ratios
The LDHs with different intercalation anions and interlay cations were prepared by coprecipitation method as described in our previous study [14]. A series of LDHs with different intercalation anions and cationic ratios were used, including Mg$_3$Al$_2$(SO$_4$)$_3$·LDH, Mg$_3$Al$_2$(CO$_3$)$_3$·LDH, Mg$_3$Al$_2$(Cl)·LDH, Mg$_3$Al$_2$(SDBS)·LDH, Mg$_3$Al$_2$(SDS)·LDH, Mg$_3$Al$_2$(Cl)·LDH, and Mg$_3$Al$_2$(Cl)·LDH.

2.3. Batch sorption of iodine by different LDHs and analytical method for iodine
The iodine sorption from aqueous phase by different LDHs were conducted in triplicate using batch technique followed the description of our previous study[14]. In the sorption assays (e.g., kinetic and isotherm), certain amount of LDHs (20 mg) were weighted and added into glass tubes (22 mL) with series concentration of iodine (initial concentrations ranged from 0 to 200 mg·L$^{-1}$). Controls without LDHs were also conducted to evaluate the possible systematic loss. In the sampling time (kinetic) or equilibrium time (isotherm), LDHs sorbed iodine was separated from solutions by centrifuging for 15 min at 3000 g. The aqueous iodine was measured followed our previous method using spectrophotometer (Shimadzu UV-Vis 2600, Japan) at wavelength of 460 nm [16].

3. Results and Discussion
The influence of sorption time on the removal efficiency and sorption amount of iodine by LDHs from aqueous solutions were conducted and illustrated in figure 1. Results indicated that within 24 h, the sorption of iodine by all 7 LDHs reached equilibrium, and the maximal sorption amounts of iodine ranged from 110606 to 183485 mg·kg$^{-1}$, depending on different anions or cationic ratios. Taking cationic ratio as an example (figure 1b), Mg$_3$Al$_2$Cl·LDH showed the fast and most sorption performance, while the Mg$_3$Al$_2$Cl·LDH sorbed much slower and fewer iodine.

**Figure 1.** Iodine kinetic sorption by Mg/Al-LDHs with different (a) intercalation anions and (b) cationic ratio.
For further evaluation of the sorption rate of iodine by different LDHs, several kinetic models such as Morris-Weber model ($Q_e = k_1 e^{-t/\tau} + Q_0$), Lagueren model ($\log(Q_0 - Q_e) = \log Q_0 - k_1 t$), pseudo-second-order (PSO) model ($t/t_{0.5} = 1/k_2 Q_e^2 + t/\tau$), were used. Over a comprehensive consideration of both correlation coefficient ($R^2$) and sorption capacity (data not shown), the obtained dynamic data was well fitted to the PSO model, and the kinetic constants were summarized in Table 1.

According to the parameters, pseudo-second-order kinetic constant ($k_2$) differed with different intercalation anions and cations. The values of $k_2$ ranged from 5.784×10^{-6} to 1.516×10^{-4} g·mg^{-1}·min^{-1}, which covered more than two orders of magnitude. Furthermore, the initial sorption rate $h$ (mg·g^{-1}·min^{-1}, equals to $k_2 Q_e^2$) was useful to illustrate the initial sorption process. We calculated the constant $h$ and the values were shown in Table 1. The values also indicated Cl-LDH with 4:1 of Mg/Al ratio sorbed iodine very fast.

In order to evaluate the sorption affinity between LDHs and iodine, isotherm sorption was carried out and illustrated in Figure 2. Same as kinetic sorption, LDHs with higher cationic ratio (e.g., Mg:Al=Cl-LDH) showed higher equilibrium sorption amount (figure 2b). The intercalation of organic anions (e.g., SDBS, SDS) indicated higher sorption capacity (figure 2a) compared with inorganic anions (e.g., sulfate, carbonate).

| LDHs          | $k_2$, g·mg^{-1}·min^{-1} | $Q_0$, mg·g^{-1} | $h$, mg·g^{-1}·min^{-1} | $R^2$  |
|---------------|---------------------------|-----------------|-------------------------|--------|
| Mg:Al=3:1     | SO_4^{2-} 5.784×10^{-6}   | 151.5           | 0.1328                  | 0.9528 |
|               | CO_3^{2-} 1.119×10^{-5}   | 158.7           | 0.2820                  | 0.9896 |
|               | SDBS 4.195×10^{-5}        | 116.3           | 0.5672                  | 0.9889 |
|               | SDS 2.383×10^{-5}         | 138.9           | 0.4596                  | 0.9785 |
| Mg:Al=4:1     | Cl^1 1.194×10^{-5}        | 185.2           | 0.4095                  | 0.9563 |
| Mg:Al=2:1     | Cl^1 9.046×10^{-6}        | 188.7           | 0.3220                  | 0.9739 |

To assess the sorption affinity, several isotherm models were used such as linear model ($Q_e=K_0 C_0$), Langmuir model ($C_e/Q_e=1/Q_0 (1+K_1 C_0)$), Freundlich model ($\log Q_e=\log K_f + n \log C_0$), and Temkin model ($Q_e=BnK_f+Bn C_0$). The isotherm sorption parameters were listed in Table 2. It seemed that LDHs with different anions or cations followed different models. Basically, LDHs with organic anion intercalations fitted Langmuir model, while inorganic anion intercalated LDHs followed linear model.

![Figure 2](image-url)  
**Figure 2.** Iodine isotherm sorption by Mg/Al-LDHs with different intercalation anions (a) and cationic ratio (b).
The partition coefficient ($K_d$) is a useful constant to assess the sorption affinity of pollutants with sorbents, which can be obtained from linear model. According to $K_d$ values in table 2 and figure 3, intercalation anions and cationic ratios of LDHs indeed were significant parameters for the sorption of iodine by LDHs. With a certain Mg/Al ratio (e.g., 3:1), organic anion intercalation increased the sorption affinity for iodine (figure 3a). The aromatic rings in SDBS and SDS provided additional sorption sites for iodine through carbon–iodine binding, which was accordance with the sorption of iodine by soil organic matter [7, 8] and biosorbents [9, 16]. For the LDHs with the same anion intercalation, cationic ratio was another important parameter to affect the sorption affinity (figure 3b). It is notable that 4:1 LDH showed much higher affinity (2912 L·kg$^{-1}$), compared with 3:1 LDH (514.2 L·kg$^{-1}$) and 2:1 LDH (281.2 L·kg$^{-1}$). This result was consistent with study released by Theiss et al. [17].

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Effects of intercalation anions (a) and cationic ratio (b) on the sorption affinity of iodine.

| LDHs | Mg: Al anion | Linear $K_d$, L·kg$^{-1}$ | R$^2$ | Langmuir $K_L$, L·mg$^{-1}$ | R$^2$ | Freundlich $K_F$, L·g$^{-1}$ | R$^2$ | Temkin $K_T$, mol·kg$^{-1}$ | R$^2$ |
|------|-------------|--------------------------|-------|----------------------------|-------|----------------------------|-------|----------------------------|-------|
| 3:1  | SO$_4^{2-}$ | 311.4 | 0.238 | 0.1023 | 0.996 | 7.563 | 0.868 | 536.2 | 0.925 |
| 3:1  | CO$_3^{2-}$ | 461.8 | 0.986 | 0.0375 | 0.860 | 24.54 | 0.585 | 4039 | 0.527 |
| 3:1  | SDBS       | 528.2 | 0.882 | 0.1423 | 0.962 | 34.27 | 0.740 | 77458 | 0.672 |
| 3:1  | SDS        | 604.5 | 0.770 | 0.0351 | 0.981 | 7.175 | 0.992 | 260.4 | 0.977 |
| 3:1  | Cl$^-$     | 514.2 | 0.859 | 0.0169 | 0.646 | 1.423 | 0.786 | 77.20 | 0.843 |
| 4:1  | Cl$^-$     | 2912 | 0.989 | 0.2343 | 0.672 | 16.57 | 0.649 | 588.8 | 0.724 |
| 2:1  | Cl$^-$     | 281.2 | 0.841 | 0.1023 | 0.996 | 0.064 | 0.854 | 18.06 | 0.912 |

**Table 2.** Isotherm sorption constants for iodine by modified LDHs.

4. Conclusions
LDHs were useful and easily modified sorbent for the effective removal of iodine from aqueous environments. Intercalated anions and cation ratios were two important parameters influencing sorption performance for iodine. According to kinetic and isotherm sorption, organic anion intercalation with aromatic structure and higher Mg/Al ratio was preferable for iodine sorption.

**Acknowledgments**
Appreciation for the financial supported from Project of the Natural Science Foundation of Zhejiang Province (LY19B070009), and the National Natural Science Foundation of China (41977017).
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