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Benzene sulfonate modified ZnCr-LDH and its enhanced adsorption properties for anionic dyes

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Abstract

A benzene sulfonate modified hydrotalcite (SO₃-LDH) was synthesized by a facile one-pot hydrothermal technique, which can efficiently remove methyl orange (MO), Congo red (CR) and orange II (OII) from aqueous solution. After modified by benzene sulfonate, the microstructure of hydrotalcite changes obviously, from the cellular structure to the stacking structure formed by the face-face contact of hydrotalcite nanosheets, which resulted in much more exchangeable nitrate ions to remain in the interlayer space. The pre-insertion of benzene sulfonate as a pillar expanded the interlayer gallery, which facilitated the pollutant anions (MO, CR and OII) into the interlayer of LDH in the subsequent adsorption process. The maximum adsorption capacity of SO₃-LDH for MO, CR and OII was 4200.8 mg/g, 1252.0 mg/g and 1670.6 mg/g respectively, which is approximately 1.86 times, 1.8 times and 2.32 times that of the pristine NO₃-LDH, respectively. The removal mechanism of anionic dyes was determined as anion exchange between NO₃⁻ ions and dye molecules. The adsorption behavior for MO and OII is multilayer adsorption, while the adsorption behavior for CR is monolayer adsorption. The adsorption process mainly was controlled by the chemical bonding between the dye molecules and adsorbent active sites. The benzene sulfonate modified LDH has a great potential to be used as a high-efficient adsorbent to remove anionic dyes from aqueous solution.

Keywords: Layered double hydroxide; Benzene sulfonate modification; Adsorption; Methyl orange (MO); Congo red (CR), Orange OII (OII).
1 Introduction

With the widespread application of dyes in textile, leather, papermaking and other chemical industries, a large amount of polluted water containing poisonous and hardly-degradable organic dyes is discharged (Tao et al. 2017). Undoubtedly, these dye wastewater will lead to serious environmental issues such as color pollution, light penetration interference, damage aquatic organisms, even harm to human health. Therefore the effective treatment of dyeing wastewater is one of the most serious concerns of the current era. So far, many techniques have been used to treatment dyeing wastewater, such as adsorption methods (Zheng et al. 2019), chemical methods (Liu et al. 2013), biological degradation methods (Pakshirajan and Kheria 2012), photocatalytic oxidation methods (Dinari et al. 2016; Mohapatra and Parida 2012), flocculation precipitation methods (Morshed et al. 2013), membrane filtration methods (Liu et al. 2018), and the combined treatment of different methods (Ou et al. 2015). In these methods, adsorption is a simple, effective and low-cost way to remove of dyeing wastewater (Zheng et al. 2019). Various kinds of adsorbents have been used for dyeing wastewater treatment, such as activated carbon (Maneerung et al. 2016), clay minerals (Zhang et al. 2019b), polymeric resins, transition metal composite (Zheng et al. 2017) and nanocomposites(Zheng et al. 2019). However, the adsorption capacity is limited. Therefore, efficient adsorbents with high adsorption capacity and fast adsorption rate are urgently needed.

As one kind of useful multi-functional materials, layered double hydroxides (LDH) based on a brucite-like (Mg(OH)$_2$) structure have been widely used as adsorbents for the removal of anionic contaminants from dyeing wastewater owing to their layered and uniformly distributed structure, flexible self-assembly and efficient modification of chemical compositions, large surface area, high porosity and controllability of layer interval and anionic exchangeability (Mahjoubi et al. 2018; Tao et
al. 2017). Usually, the exchangeable anions compensating the positive charge of the LDH interlayers include NO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$ and Cl$. A kind of ultra-small NiAl-Cl-LDH displayed favorable removal performance toward MO was reported (Jing et al. 2019), which showed 900.1 mg/g maximum theoretical adsorption capacity at pH = 7 and 298 K. The anion nitrate in the interlayer of MgAl-NO$_3$-LDH can also be exchanged by methyl orange (MO), orange II (OII) and orange G (OG) (Darmograi et al. 2015), and the corresponding maximum adsorption capacity were 1800.3 mg/g, 945.9 mg/g and 769.0 mg/g respectively. In a more classical case (Mahjoubi et al. 2018), ZnAl layered double hydroxides intercalated with carbonate, nitrate, chloride and sulphate ions exhibited exceptional maximum adsorption capacities of 1684.0, 2270.0, 2455.0 and 2758.0 mg/g for MO, respectively. These precursors can be effectively exchange with anionic dyes in wastewater.

In addition, a large number of organic molecules can be incorporated into the interlayer space, such as aliphatic and aromatic carboxylates, sulfonates, alkyl sulfate anions and organic dyes (Mandal et al. 2009). The organo-modification could change the surface hydrophilicity into hydrophobic nature to strengthen the removal of organic pollutants in aqueous solution by the similar dissolve mutually theory (Taviot-Guého et al. 2018). Soft-template synthesis has become highly desirable in the process of organo-modification for LDH. In Soft-template synthesis method, sulfonates and alkyl sulfate anions as a soft template agent can intercalate into the LDH host structure via ion exchange with a specific anion (e.g., NO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$, OH$^-$, Cl$^-$). The intercalated anionic surfactants will expand the base spacing of LDH host structure, which facilitated the pollutant anions into the interlayer gallery of LDH. Dodecyl sulfate anion (DS$^-$) intercalated magnesium iron layered double hydroxide (MgFe-DS-LDH) was prepared by the co-precipitation method in the presence of SDS aqueous solution (X. Ruan et al. 2013), the adsorption capacity of the organic contaminants (naphthalene, nitrobenzene, acetophenone)
by MgFe-DS-LDH was much greater than that of the pristine MgFe-CO$_3$-LDH and MgFe-NO$_3$-LDH. Recently, a hierarchical organic three-dimensional MgAl-SDS-LDH was also successfully synthesized via a one-step hydrothermal strategy using sodium dodecyl sulfate (SDS) as a soft template agent (Zhang et al. 2019a), which can efficiently remove MO with the maximum adsorption capacity of 377.9 mg/g. The organic modified hydrotalcite samples were potential sorbents for the abatement of organic contaminants. In this work, a benzene sulfonate modified hydrotalcite (SO$_3$-LDH) was synthesized by a facile one-pot hydrothermal technique using methyl orange as a soft template agent, and then the products were used to remove MO, CR and OII from aqueous solutions. The microstructure, adsorption isotherms, adsorption kinetics and adsorption mechanism of the material were systematically investigated. We found that MO, CR and OII were removed by anion exchange. The adsorption properties of modified hydrotalcite was significantly better than that of unmodified hydrotalcite, and showed very high adsorption capacity for the anionic dyes of MO, CR and OII.

2 Materials and methods

2.1 Materials

All of the chemicals used in this study were of analytical grade. Zn(NO$_3$)$_2$·6H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, NaOH, methyl orange (MO), congo red (CR) and orange OII (OII) were purchased from MACKLIN (China). The distilled water was used in all experiments.

2.2 Preparation of unmodified and modified hydrotalcite

Unmodified hydrotalcite was prepared by one-pot hydrothermal method. A mixed salt solution containing Zn(NO$_3$)$_2$·6H$_2$O (0.67M) and Cr(NO$_3$)$_3$·9H$_2$O (0.33M) was titrated with the solution of sodium hydroxide (2.0 M) up to pH 10.0 at room temperature, and stirred vigorously for 30 minutes. The suspension was hydrothermally treated at 65 °C for 12 h, then washed with distilled water for
several times until the pH was neutral, and dried at 65 °C for 12 h. The obtained product was named 
NO$_3$-LDH.

Modified hydrotalcite was also synthesized via one-pot hydrothermal method at a constant 
solution pH of 10. In detail, the modifier of methyl orange was dissolved in 50mL water and prepared 
into a 60 mmol/L solution. Then, a mixed salt solution (50 mL) containing Zn(NO$_3$)$_2$·6H$_2$O (0.67 M) 
and Cr(NO$_3$)$_3$·9H$_2$O (0.33 M), and a 2.0 M NaOH solution were simultaneously added into the 
modifier solution, the pH was maintained at 10. The mixture solution poured into hydrothermal reactor 
and aged at 65 °C for 12 h, and then washed repeatedly with distilled water. Finally, it was dried at 
65 °C for 12 h. The obtained product was named SO$_3$-LDH.

2.3 Characterization of ZnCr-LDH

Powder XRD diagrams were recorded on a X-ray diffractometer (X’pert$^3$ Powder, PANalytical) 
equipped with a Beta filter Nickel at a scanning rate of 5.166°/min. The applied radiation is Cu Kα 
from a long fine-focus Cu tube operating at 40 kV and 40 mA. The FTIR spectra of the samples were 
recorded using potassium bromide pellet technique (0.5 wt.% sample) on a NICOLET VERTEX 
70V-spectrometer at the condition of 40 scans and 4 cm$^{-1}$ resolution. The morphologies of samples 
were investigated using a scanning electron microscope (S4800 LV) with the accelerating voltage of 50 
kV.

2.4 Adsorption experiments

The adsorption studies were carried out by batch method, the adsorption experiments was 
performed in a series of 250 mL beakers containing 0.01g adsorbent and 100 mL of the MO, CR or OH 
solution at the desired concentration. The initial dye concentration from 100 to 1000 mg/L. The 
solution pH was adjusted to 5 with 0.1M HCl or 0.1M NaOH solution. Stirred the suspension at room
temperature until adsorption equilibrium. After MO, OII or CR solution adsorbed by the SO₃-LDH samples, it was respectively named as SO₃-LDH-MO, SO₃-LDH-OII or SO₃-LDH-CR. Similarity, After MO, OII or CR solution adsorbed by the NO₃-LDH samples, it was respectively named as NO₃-LDH-MO, NO₃-LDH-OII or NO₃-LDH-CR. Then, the suspensions were centrifuged at 4000 rpm for 20 min. The supernatant concentration was determined using a PERSEE TU-1810 UV-vis spectrometer. The MO, OII and CR removal performance was evaluated by calculating the adsorbed capacity at equilibrium \( Q_e \) (mg/g) and at any time \( Q_t \) (mg/g), and is given as Eq. (1) and (2):

\[
Q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)
\]

\[
Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)
\]

where \( C_0 \) (mg/L) corresponds to the dye initial concentration, \( C_e \) (mg/L) is the dye equilibrium concentration, \( C_t \) (mg/L) is the dye concentration in the aqueous solution at any time \( t \) (min), \( V \) (L) is the solution volume, and \( m \) (g) is the adsorbent mass.

3 Results and discussion

3.1 Characterization of materials

3.1.1 XRD analysis

Fig.1 shows the XRD patterns of unmodified and modified hydrotalcite. The XRD pattern of pristine NO₃-LDH is consisted of sharp and symmetrical diffraction peaks indicating good crystallinity (Kloprogge et al. 2004; Kloprogge et al. 2005; Parida and Mohapatra 2012). The basal peaks for (003), (006) and (009) crystal planes and non-basal peaks for the (015), (012) and (110) planes can be observed from Fig. 1a. The (003) peak indicates the basal reflection of interlayer anion in LDH materials. The interlayer distance of (003) basal plane \( d_{003} \) of the pristine NO₃-LDH is 8.269 Å. For the modified sample (SO₃-LDH), the \( d_{003} \) value is 8.654 Å, and larger than that of NO₃-LDH, a new
peak appears at 19.698°, and the diffraction peak of (006) basal plane is absent, which indicates that some benzene sulfonate anions enters the interlayer space of (003), (006) and (009) basal planes.

3.1.2 FTIR analysis

Fig. 2a shows the FTIR spectra of modifier. A broad peak at 3447 cm$^{-1}$ is attributed to the stretching mode of the OH bond of the hydroxyl groups and water molecules (Rojas Delgado et al. 2004). The position at 3180 cm$^{-1}$ is associated with the peak of aromatic C−H stretch vibration in modifier molecule. The position at 2808 cm$^{-1}$ is the peak of aliphatic C−H stretching vibration associated with CH$_3$ in modifier. A sharp aromatic C−C stretching band is observed at 1605 cm$^{-1}$. The band at 1520 cm$^{-1}$ is assigned to N=N. The peaks at 1365 and 1119 cm$^{-1}$ are attributed to the C−N bands (Zhang et al. 2019a) These peaks appear at 1421 cm$^{-1}$, 1165 cm$^{-1}$ and 1036 cm$^{-1}$, which originate from the stretching and vibrational mode of S=O in the sulfonate group (−SO$_3^−$). The peak at 1007 cm$^{-1}$ is related to the in-plane bending vibration of C−H, and the rest peaks are ascribed to the out-of-plane bending bands of C−H in aromatic nucleus.
Fig. 2. FT-IR spectra for (a) Modifier, (b) SO$_3$-LDH and (c) NO$_3$-LDH

Fig. 2b and 2c shows the FTIR spectra of modified and unmodified samples. The FTIR spectra of NO$_3$-LDH revealed the characteristic bands of hydrotalcite-like compounds. The broad and strong band centered at 3400 cm$^{-1}$ is attributed to the stretching mode of the OH bond of the hydroxyl groups and H$_2$O molecules. The weak band at 1632 cm$^{-1}$ is assigned to the bending vibration of the interlayer water, and disappeared in the sample of SO$_3$-LDH. It shows that the hydrophobicity of hydrotalcite is enhanced after modification. The strong absorption peak at 1384 cm$^{-1}$ is attributed to the antisymmetric stretching mode of the NO$_3^-$ anion. The bands below 1000 cm$^{-1}$ are due to M–O deformations and translational bands. The band at 831 cm$^{-1}$ Zn–OH is out of plane bending mode. The band at 789 cm$^{-1}$ is assigned to the Cr–OH deformation mode, and the bands at 571 cm$^{-1}$ and 514 cm$^{-1}$ are ascribed to the Cr–OH translation.
The modification of hydrotalcite by benzene sulfonate anions is also confirmed by the FTIR spectra. The aromatic C−C stretching band is observed at 1605 cm\(^{-1}\). The bands at 1520 cm\(^{-1}\) is assigned to N=N. The peak at 1119 cm\(^{-1}\) is attributed to the C−N bands. Stretching and vibrational bands of the sulfonate group (−SO\(_3^−\)) are observed at 1421 cm\(^{-1}\), 1165 cm\(^{-1}\) and 1036 cm\(^{-1}\), and the band of in-plane bending vibration of C−H is observed at 1007 cm\(^{-1}\). For modified hydrotalcite, the bands attributed to benzene sulfonate an including C–H, aromatic C−C, C−N, N=N and SO\(_3^−\) were evident in the spectra, proving the benzene sulfonate anions of the modifier intercalation into the interlayer of LDH.

3.1.3 SEM analysis

SEM image of the pristine NO\(_3^−\)-LDH (Fig.3a) indicates a cellular structure assembled by the side-face contacted ultra-fine LDH nanosheets (Costa et al. 2009). The thickness of LDH nanosheets is about 20nm. For SO\(_3^−\)-LDH (Fig.3b), the cellular structure basically disappears, and the LDH nanosheets are packed together via face-face contact. Therefore, there are more sandwich structures formed by the stacking of LDH nanosheets via face-face contact, which causes much more nitrate ions to remain in the interlayer space, and further improves the anion exchange capacity of SO\(_3^−\)-LDH.

3.2 Adsorption performance of unmodified and modified samples

In order to compare the adsorption performance of unmodified and modified LDH for different
dyes. The 10 mg adsorbent was dispersed in 100 mL MO, OII and CR solutions with an initial concentration of 1000 mg/L. The pH was adjusted to 5, stirred the suspension at room temperature. The adsorption capacity of NO$_3$-LDH and SO$_3$-LDH for dyes are shown in Fig.4a. The maximum adsorption capacity of MO by SO$_3$-LDH was about 4200.8 mg/g, and significantly higher than that of NO$_3$-LDH (2252.8 mg/g). The maximum adsorption capacity of CR and OII by SO$_3$-LDH was about 1252.0 mg/g and 1670.6 mg/g respectively, and higher than that of NO$_3$-LDH (695.4 mg/g and 719.8 mg/g). Therefore, SO$_3$-LDH has better adsorption performance for MO, CR and OII dyes.

![Fig.4. Adsorption of dyes by NO$_3$-LDHs and SO$_3$-LDH (a) ; Spectral scanning curve of (b) MO, (c) CR and (d) OII before and after SO$_3$-LDH adsorption](image)

In addition, the stability of the SO$_3$-LDH as adsorption material was also studied. The three dye solutions before and after adsorbed by SO$_3$-LDH were diluted 20 times, respectively, and then...
spectroscopically scanned by UV-vis spectrophotometer. As can be seen from Fig. 4b, after SO$_3$-LDH adsorbed MO, the intensity of characteristic peak of methyl orange was significantly reduced. Obviously, SO$_3$-LDH can efficiently adsorb methyl orange in aqueous solution. Similarly, we can see from Fig. 4c and Fig. 4d, the intensity of CR and OII characteristic peak was also reduced after adsorbed by SO$_3$-LDH, but the location and number of the peak were not changed. Therefore, during the adsorption process, the dye molecules intercalation into the interlayer of LDH will not be exchanged into aqueous solution. It shows that the interlaminar sulfonate groups (−SO$_3$−) are confined in the two-dimensional interlayer space by electrostatic interactions and/or hydrogen bonds with the host layer, and are not readily to be exchanged by the anions of other dyes (Mandal et al. 2009).

### 3.3 Adsorption kinetics

To further investigate the adsorption rate of the three anionic pollutants by the SO$_3$-LDH sample, the adsorption kinetics data was respectively analyzed by Pseudo-first-order and Pseudo-second-order kinetic models (Zhang et al. 2019a), as the following equation Eq. (3) and (4):

The pseudo-first-order: 

$$q_t = q_e [1 - \exp(-k_1 t)]$$  \hspace{1cm} (3)

The pseudo-second-order: 

$$q_t = \frac{k_2 q_e^2 t}{1 + q_e K_2 t}$$  \hspace{1cm} (4)

Where $k_1$ (min$^{-1}$) and $k_2$ (g/mg/min) are the rate constant of two models.

Fig. 5 displays the adsorption kinetic curves of SO$_3$-LDH for OII, CR and MO. All the kinetic curves show that the adsorption rate is high in the initial phase, then gradually slows down, and finally reaches equilibrium. With the increase of dyes concentration, the $k_2$ value is obviously reduced. The change of $K_2$ values suggests that dyes concentration has a great influence on the adsorption rate. Some experimental data are deviated from the fitting curve for the pseudo-first-order kinetic model, while almost all the experimental data are distributed on the fitted curve for the pseudo-second-order kinetic model. The corresponding parameters as shown in table 1, the R$^2$ values of the all curves fitted by the
pseudo-second-order kinetic model are closer to 1 compared with the curve fitted by pseudo-first-order kinetic model. Furthermore, the $Q_{\text{exp}}$ values for the pseudo-second-order model are closer to the experimental values ($Q_{\text{exp}}$). Therefore, the pseudo-second-order kinetic model is more suitable to explain the adsorption kinetics of these pollutants, the adsorption rate of SO$_3$-LDH on three dyes is mainly controlled by the chemical bonding between the dye molecules and adsorbent active sites.

![Fitted plots of the pseudo-first-order and pseudo-second-order kinetic models for (a) OII, (b) CR and (c) MO adsorption by SO$_3$-LDH](image)

**Fig. 5.** Fitted plots of the pseudo-first-order and pseudo-second-order kinetic models for (a) OII, (b) CR and (c) MO adsorption by SO$_3$-LDH
### Table 1 Parameters in the two kinetic models for OII, CR and MO adsorption by SO₃-LDH

| Pollutants | Concentration / (mg/L) | $q_{e,exp}$ / (mg/g) | $q_{e,cal}$ / (mg/g) | $k_1$ / (mg/g/min) | $R^2$ | $q_{e,cal}$ / (mg/g) | $k_2$ / (mg/g/min) | $R^2$ |
|------------|------------------------|----------------------|----------------------|--------------------|-------|----------------------|--------------------|-------|
| OII        | 100                    | 878.8                | 856.7                | 0.09038            | 0.9003 | 884.7                | 0.000223           | 0.9974 |
|            | 200                    | 1189.6               | 1156.0               | 0.09085            | 0.8467 | 1195.0               | 0.000164           | 0.9967 |
|            | 400                    | 1395.5               | 1367.8               | 0.09660            | 0.8892 | 1409.0               | 0.000157           | 0.9993 |
|            | 600                    | 1516.0               | 1479.2               | 0.09745            | 0.8406 | 1524.9               | 0.000145           | 0.9970 |
|            | 800                    | 1591.2               | 1551.5               | 0.09785            | 0.8382 | 1599.3               | 0.000139           | 0.9968 |
|            | 1000                   | 1670.6               | 1641.6               | 0.09624            | 0.8979 | 1691.3               | 0.000130           | 0.9975 |
| CR         | 100                    | 778.6                | 745.7                | 0.05332            | 0.9154 | 788.8                | 0.000113           | 0.9984 |
|            | 200                    | 1092.0               | 1044.1               | 0.05083            | 0.9142 | 1060.9               | 0.000075           | 0.9968 |
|            | 400                    | 1203.0               | 1151.8               | 0.05169            | 0.9178 | 1219.5               | 0.000070           | 0.9963 |
|            | 600                    | 1231.0               | 1176.9               | 0.05039            | 0.9183 | 1248.1               | 0.000066           | 0.9967 |
|            | 800                    | 1242.8               | 1186.6               | 0.05027            | 0.9170 | 1258.8               | 0.000065           | 0.9971 |
|            | 1000                   | 1252.0               | 1193.5               | 0.04993            | 0.9149 | 1266.6               | 0.000064           | 0.9968 |
| MO         | 100                    | 964.5                | 961.4                | 0.74524            | 0.7019 | 964.8                | 0.007360           | 0.9959 |
|            | 200                    | 1698.8               | 1663.8               | 0.36132            | 0.7557 | 1697.1               | 0.000600           | 0.9964 |
|            | 400                    | 2654.0               | 2603.1               | 0.34295            | 0.7787 | 2656.8               | 0.000350           | 0.9976 |
|            | 600                    | 3290.0               | 3228.0               | 0.35421            | 0.7979 | 3290.9               | 0.000300           | 0.9986 |
|            | 800                    | 3766.0               | 3680.5               | 0.30957            | 0.7919 | 3767.4               | 0.000210           | 0.9980 |
|            | 1000                   | 4200.8               | 4118.9               | 0.30506            | 0.8150 | 4213.7               | 0.000180           | 0.9958 |

### 3.4 Adsorption isotherms

Equilibrium data, generally known as sorption isotherms are elementary necessity to comprehend the mechanism of the sorption [25]. There are a number of isotherm models such as Langmuir isotherm model, Freundlich isotherm model, Temkin isotherm model and the Dubinin–Radushkevich isotherm model (Liu and Wang 2021; Maneerung et al. 2016). The Langmuir monolayer adsorption and Freundlich multilayer adsorption models are commonly applicable to solid-liquid adsorption systems (Kausar et al. 2018; Tao et al. 2017).
Fig. 6. Isotherm model for (a) OII, (b) MO and (c) CR adsorption on SO₃-LDH

Table 2 Parameters of isotherm model for OII, MO and CR adsorption on SO₃-LDH

| Isotherm model | Pollutants | Parameters | \( R^2 \) |
|---------------|------------|------------|----------|
| Langmuir      | OII        | \( q_m (\text{mg/g}) \) | 1553.6   | 0.08785 | 0.8442 |
|               | MO         | \( q_m (\text{mg/g}) \) | 4169.5   | 0.01986 | 0.8932 |
|               | CR         | \( q_m (\text{mg/g}) \) | 1267.1   | 0.07130 | 0.9995 |
| Freundlich    | K_(F)(\text{mg/g})(\text{mg/L})^n | 1/n | \( R^2 \) |
|               | OII        | 610.96     | 0.14897  | 0.9991  |
|               | MO         | 619.38     | 0.29917  | 0.9990  |
|               | CR         | 609.32     | 0.11212  | 0.8798  |
Fig. 6 displays the Langmuir and Freundlich isotherm curves for the OII, CR and MO adsorbed by SO$_3$-LDH. The corresponding adsorption models (Zhang et al. 2019a) are expressed as follows Eq. (5) and (6):

Langmuir: \[ q_e = \frac{Q_m k_L C_e}{1 + K_L C_e} \] (5)

Freundlich: \[ q_e = K_F C_e^{1/n} \] (6)

Where \( Q_m \) is the maximum adsorption capacity of adsorbents (mg/g), \( K_L \) is the Langmuir adsorption equilibrium constant (L/mg), which is related to the affinity of the binding site of the adsorbent, the larger the value, the stronger the adsorption capacity. \( K_F \) is the Freundlich adsorption equilibrium constant ((mg/g) (mg/L)$^n$), which is related to the adsorption affinity, and \( n \) reflects the supporting force of the adsorption process. If the empirical constant \( 1/n \) is between 0.1 and 0.5, it means easy adsorption. If \( n=1 \), it is linear adsorption; If \( 1/n \) is greater than 2, adsorption is difficult to occur.

The adsorption isotherms of SO$_3$-LDH for OII, MO and CR are shown in Fig. 6. As shown in table 2, for OII and MO, the correlation coefficients ($R^2$) for the Langmuir isotherm respectively are 0.8442 and 0.8932, while the $R^2$ values for the Freundlich isotherm respectively are 0.9991 and 0.9990. Thus, Freundlich isotherm model is better to predict the OII and MO adsorption process. The Freundlich assumed that the adsorption occurs on heterogeneous surfaces with non-uniform adsorption sites. The \( K_F \) value respectively are 610.96 and 619.37, which suggests MO and OII have good adsorption affinity with the surface of the adsorbent. The value of \( 1/n \) are 0.14897 and 0.29917 within the range of 0.1–0.5, which indicates a favorable supporting force of the adsorption for OII and MO adsorption by SO$_3$-LDH. The results shows that the adsorption of OII and MO by SO$_3$-LDH is relatively easy to happen and belongs to multi-layer adsorption with strong adsorption affinity (Kausar
et al. 2018). For CR, the $R^2$ for the Langmuir isotherm is larger than the Freundlich isotherm models. Langmuir isotherm model greatly predicted the CR adsorption process, the adsorption occurs on a homogeneous adsorbent surface and belongs to single-layer adsorption.

| Pollutants | Adsorbents            | pH   | Temperature (°C) | Adsorption isotherm | $q_m$ (mg/g) | References                      |
|------------|-----------------------|------|------------------|---------------------|-------------|---------------------------------|
| MO         | SO$_3$-LDH            | 5    | 25               | Freundlich          | 4200.8      | In this work                    |
|            | MgAl-LDH              | 3-11 | 25               | Freundlich          | 377.9       | (Zhang et al. 2019a)            |
|            | SNIFe-LDH             | 3    | 25               | Freundlich          | 387.6       | (Zubuir et al. 2018)            |
|            | NiFe-Cl-LDH           | 5-6  | 30               | Langmuir            | 769.2       | (Gao et al. 2018)               |
|            | ZnMgAI-LDH            | 3.0  | 25               | Freundlich          | 883.2       | (Zheng et al. 2012)             |
|            | ZnAl-Cl-LDH@Al(OH)$_3$| 4.5  | 25               | Langmuir            | 1013.5      | (Guo et al. 2018)               |
|            | MgAl-Cl-LDH           | -    | 25               | Langmuir            | 1112.0      | (Xu et al. 2017)                |
|            | Co$_3$Fe-NO$_3$-LDH   | 7.1-7.3| 25           | Langmuir            | 1290.0      | (Ling et al. 2016)              |
|            | ZnAl-CO$_3$-LDH       | 3.5-4.5| -              | Langmuir            | 1684.0      | (Mahjoubi et al. 2018)          |
| CR         | ZnAl-Cl-LDH           | 3.5-4.5| -              | Langmuir            | 2455.0      | (Mahjoubi et al. 2018)          |
|            | ZnAl-SO$_3$-LDH       | 3.5-4.5| -            | Langmuir            | 2758.0      | (Mahjoubi et al. 2018)          |
|            | SO$_3$-LDH            | 5    | 25               | Langmuir            | 1252.0      | In this work                    |
|            | Mg$_2$Al-LDH/CF       | -    | 25               | Langmuir            | 271.0       | (Sun and Chen 2020)             |
|            | ZnFe$_2$O$_4$/MgAl-LDH| -    | 25               | Langmuir            | 294.1       | (Sun et al. 2020)               |
|            | Zn-LDH                | 3    | -                | Freundlich          | 591.8       | (El Khanchaoui et al.)          |
|            | ZIF-ZnAl-LDH          | -    | 45               | Langmuir            | 909.1       | (Li et al. 2020)                |
|            | Ni/MgAl-LDH           | 7    | 30               | Langmuir            | 1250.0      | (Lei et al. 2017)               |
| OII        | SO$_3$-LDH            | 5    | 25               | Freundlich          | 1670.6      | In this work                    |
|            | Calcined MgAl-LDH     | -    | -                | Langmuir            | 602.0       | (Yan et al. 2016)               |
|            | LDH/PEG               | -    | 50               | Langmuir            | 724.6       | (Mandal et al. 2019)            |
|            | Mg$_2$Al-NO$_3$-LDH   | 7    | 40               | Langmuir            | 1265.0      | (Mustapha Bouhent et al. 2011)   |
|            | HTMacro-cal           | 7    | 25               | Langmuir            | 1521.2      | (Géraud et al. 2007)            |
|            | NiAlTi-LDH            | 8    | 25               | Langmuir            | 2000.0      | (Rathee et al. 2020)            |

In order to position the adsorption performance of SO$_3$-LDH, Comparison of the adsorption capacity of this work and that of LDH material reported in literature is shown in table 3. The results show that the experimental $Q_m$ of SO$_3$-LDH in this work is significantly superior to all of the reported LDHs containing different interlayer anions, and shows very high adsorption capacity. In general, the
as-synthesized SO$_3$-LDH is a promising adsorbent for the removal of anions from dye containing effluents.

3.5 Adsorption mechanism

3.5.1 XRD analysis

XRD patterns of different dyes adsorbed by SO$_3$-LDH are shown in Fig. 7a and Fig. 7b. The $d_{003}$ value is 8.654 Å for the sample of SO$_3$-LDH. After SO$_3$-LDH adsorbed by MO solutions of different concentration, the (003), (006) and (009) diffraction peaks all shift to the lower angles. As the increasing concentration of MO solution, the position offset of (003) reflection gradually decrease along with much larger $d_{003}$ value of 7.849 Å, 7.9045 Å, 7.923 Å and 7.998 Å for the samples of SO$_3$-LDH-100MO, SO$_3$-LDH-300MO, SO$_3$-LDH-500MO and SO$_3$-LDH-1000MO, and the intensities of (003) reflection gradually weakens. Meanwhile, four new peaks are observed at the position of 7.40°, 14.62°, 18.36° and 25.76° related to the intercalation of (006), (009) (015) and (012) basal reflection (Darmograi et al. 2015; Zhang et al. 2019a) as shown in Fig.7a, and a new strong peak appeared at 2θ positions of 3.56° corresponding to d-values of 24.78 Å attributed to the intercalation of (003) basal reflection by MO$^-$ anions in the low angle XRD patterns of Fig.7b, and its intensities progressively enhance, which indicates more and more MO$^-$ anions are inserted into the interlayers of hydrotalcite host with the increasing concentration of MO solution. For the sample of SO$_3$-LDH adsorbed by the 1000mg/L OII solution (SO$_3$-LDH-1000OII), the profiles of all diffraction peaks are similar to that of the SO$_3$-LDH-1000MO sample except the positions are close to the higher angle, and sulfonate anions of OII also inserted into the interlayers of (006) parallel crystal plane in LDH host structure, the intercalated peak of (006) basal plane is located at 7.901°, and the corresponding interlayer distance $(d_{006})$ is about 11.180 Å. After the SO$_3$-LDH adsorbed by 1000 mg/L CR solution (SO$_3$-LDH-1000CR),
the peak intensities of (003) and (006) basal reflection reduce, along with a new weak peak ascribed to
the intercalated peak of (006) basal plane appeared at the position of 8.13°, and the corresponding d_{006}
value is about 10.863 Å, which indicates sulfonate anions of CR also entered into the interlayer of (006)
parallel crystal plane.

3.5.2 FTIR analysis

FTIR spectroscopy was conducted to investigate the interaction between the SO₃⁻-LDH and the
dye molecules. In order to identify the adsorption mechanisms, the FTIR spectra of SO₃⁻-LDH adsorbed
by different dyes are shown in Fig.7c. As the increasing MO solution concentration from 100mg/L to
1000mg/L, the intensities of the adsorption bands at 1605 cm⁻¹ ascribed to aromatic C−C stretching
vibration, at 1520 cm⁻¹ assigned to N=N bands, at 1365 and 1119 cm⁻¹ attributed to the C−N bands, at
1421cm⁻¹, 1165 cm⁻¹ and 1036 cm⁻¹ related to the stretching vibrational mode of S=O in the sulfonate
group (−SO₃⁻), at 1007 cm⁻¹ related to the in-plane bending vibration of C−H, and at 946 cm⁻¹,
845 cm⁻¹, 819 cm⁻¹, 749 cm⁻¹ and 702 cm⁻¹ ascribed to the out-of-plane bending of C−H in aromatic
nucleus are remarkably enhanced. The strong peak around 1384 cm⁻¹ attributed to the antisymmetric
stretching mode of the NO₃⁻ anion (Kloprogge et al. 2005) are gradually weakened. The decrease of the
NO₃⁻ anions is related to the increase of MO molecules intercalated into the interlayer and absorbed on
the surface of SO₃⁻-LDH sheets. The increasing sulfonate along with decreasing nitrate shows that ion
exchange becomes more intense in the interlayers of SO₃⁻-LDH with the increase of MO solution
concentration. For the samples of SO₃⁻-LDH adsorbed by the 1000mg/L OII (SO₃⁻-LDH-1000 OII) and
1000mg/L CR solution (SO₃⁻-LDH-1000 OII), the intensities of all the adsorption bands of aromatic
C−C, N=N and C−N bands, S=O stretching vibration and the in-plane and the out-of-plane bending
vibration of C−H in aromatic nucleus are significantly increased, and the intensity of the adsorption
band of the antisymmetric stretching mode of the \( \text{NO}_3^- \) anion is dramatically decreased, which suggests that there is an obvious ion exchange between \( \text{NO}_3^- \) anion and sulfonate group (\( -\text{SO}_3^- \)). Therefore, the adsorption of OII, CR and MO is achieved through the ions exchange with the \( \text{NO}_3^- \) ions of the \( \text{SO}_3^-\text{-LDH} \).

![Fig. 7. The XRD patterns (a, b) and FTIR spectra (c) of different dyes adsorbed by \( \text{SO}_3^-\text{-LDH} \)](image)

### 3.5.3 SEM analysis

SEM images of \( \text{SO}_3^-\text{-LDH} \) before and after adsorbed by MO are shown in Fig.8. After the \( \text{SO}_3^-\text{-LDH} \) adsorbed 100mg/L MO solution, the nanosheets of \( \text{SO}_3^-\text{-LDH}-100 \) become much tighter and larger (Fig.8b). After the \( \text{SO}_3^-\text{-LDH} \) adsorbed more MO\(^-\) anions, the LDH sheets in the sample of
SO$_3$-LDH-500 becomes loose (Fig.8c), and that of SO$_3$-LDH-1000 become much looser and smaller (Fig.8d).

Fig. 8. SEM images of SO$_3$-LDH before and after adsorbed different concentrations MO solutions: (a) 0 mg/L, (b) 100 mg/L, (c) 500 mg/L and (d) 1000 mg/L

3.5.4 Schematic illustration

The schematic illustration of the synthetic process of benzene sulfonate modified and unmodified hydrotalcites by one-pot hydrothermal method and the adsorption process of MO by SO$_3$-LDH were shown in Fig.9. Modified hydrotalcite (SO$_3$-LDH) was prepared using methyl orange as a soft template agent. Compared with unmodified hydrotalcite (NO$_3$-LDH), the insertion of benzene sulfonate anions into the hydrotalcite layer resulted in the increase of the interlayer Spacing from 8.269 Å to 8.654Å. The LDH host structure pre-intercalated by benzene sulfonate anions evolved into pillared layered materials, benzene sulfonate anions as a column expanded the interlayer spacing of (003) base plane, which facilitated the pollutant anions (MO, CR and OII) into the interlayer of SO$_3$-LDH and exchanged with NO$_3^-$ anion in the subsequent adsorption process. Theoretically, the dimension of MO$^-$ is
approximately 1.3 nm (Ling et al. 2016), and the thickness of one LDH sheet is about 0.48 nm. It is
easily calculated that a basal spacing of 1.78 nm and 3.08 nm would be observed for monolayer and
bilayer models (Xu et al. 2017) with perpendicular orientation of the MO in the interlayer space of
LDH. We can infer that a small amount of benzene sulfonate anions pre-inserted into the gallery of
hydrotalcite with a monolayer model in the process of hydrotalcite modification, and its inclination
angle is calculated to be about 29.1°. After the SO₃-LDH sample adsorbed MO molecules, dye
molecules intercalated again into the LDH host and successful exchange with NO₃⁻ anions (Darmograi
et al. 2015), the d₀₀₃ value increased to 24.78 Å. A large amount of MO⁻ anions were intercalated into
the gallery of SO₃-LDH with a bilayer model according to the Freundlich isotherm model, the tilting
angle increases to 53.6°. The adsorption capacity of MO by SO₃-LDH was significantly enhanced to
4200.8 mg/g, which was much higher than that of NO₃-LDH (2252.8 mg/g).

Fig.9. Schematic illustration of the synthetic process of LDH materials and adsorption process of MO
by SO₃-LDH

4 Conclusions

A benzene sulfonate modified ZnCr-layered double hydroxide (SO₃-LDH) was fabricated via a
facile one-pot hydrothermal technique. The pre-intercalated benzene sulfonate anions as the pillars expanded the interlayer gallery, which facilitated the pollutant anions (MO, CR and OII) into the interlayer of LDH in the subsequent adsorption process. The SO$_3$-LDH with good crystallinity exhibited super high adsorption capacity of 4200.8 mg/g, 1252.0 mg/g and 1670.6 mg/g for MO, CR and OII, much larger than NO$_3$-LDH. Therefore benzene sulfonate modification can greatly improve the adsorption property of hydrotalcite. The adsorption of the three dyes on the SO$_3$-LDH followed pseudo second-order kinetic model. The adsorption of OII and MO fitted the Freundlich adsorption isotherm model, while Langmuir isotherm model greatly predicted the CR adsorption process. The removal of these three dyes mainly depends on anionic exchange. SO$_3$-LDH has the advantages of fast adsorption rate and high adsorption capability, and can be used as a potential adsorbent for anionic dye wastewater.

Authors’ contributions JL: investigation, formal analysis, writing and editing, conduct experiment; YZ: conceptualization, methodology, supervision, writing and editing; QZ: funding acquisition; JS: conduct experiment; FD: conduct experiment. All authors read and approved the final manuscript.

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Figures

Figure 1

XRD patterns for the (a) NO3-LDH and (b) SO3-LDH
Figure 2

FT-IR spectra for (a) Modifier, (b) SO3-LDH and (c) NO3-LDH
Figure 3

SEM images of (a) NO3-LDH and (b) SO3-LDH
Figure 4

Adsorption of dyes by NO3-LDHs and SO3-LDH (a); Spectral scanning curve of (b) MO, (c) CR and (d) OII before and after SO3-LDH adsorption
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Figure 7

The XRD patterns (a, b) and FTIR spectra (c) of different dyes adsorbed by SO3-LDH
Figure 8

SEM images of SO3-LDH before and after adsorbed different concentrations MO solutions: (a) 0 mg/L, (b) 100 mg/L, (c) 500 mg/L and (d) 1000 mg/L
Figure 9

Schematic illustration of the synthetic process of LDH materials and adsorption process of MO by SO3-LDH

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