Adsorption of polycyclic aromatic hydrocarbons over CuZnFeAl–LDH modified by sodium dodecyl sulfate†

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Polycyclic aromatic hydrocarbons (PAHs) have received extensive attention due to being highly toxic, mutagenic, and carcinogenic organic pollutants. As a result, a series of adsorbents have been designed and developed to solve the problem. In this paper, CuZnFeAl–S has been explored as a highly efficient adsorbent for PAHs. First, CuZnFeAl–LDH was prepared using a coprecipitation method and then calcined at 500 °C to obtain CuZnFeAlO. Finally, CuZnFeAl–S was prepared by modifying CuZnFeAlO with sodium dodecyl sulfate (SDS). The physical and chemical properties of the adsorbents were characterized by XRD, N₂ adsorption–desorption, SEM, ICP, FT-IR, TG-DSC, and IGC; subsequently their adsorption performance was investigated. The results show that the surface properties of CuZnFeAl–S changed from hydrophilic to hydrophobic after SDS modification, which enhanced the adsorption of PAHs obviously. The removal of naphthalene and phenanthrene on CuZnFeAl–S reached 97.3% and 90.3%, respectively. And the adsorption process of naphthalene and phenanthrene conforms to Langmuir adsorption and Freundlich adsorption, respectively. Besides, the adsorption thermodynamics indicate that the adsorption of PAHs was a spontaneous exothermic reaction. The highly efficient PAH adsorption performance of CuZnFeAl–S is the synergistic result of various molecule interactions, such as hydrogen bonding, π–π interactions, and electrostatic attraction.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are typical persistent organic pollutants with high toxicity, mutagenicity, carcinogenicity and hydrophobicity. Sixteen PAHs have been identified as priority pollutants by the US Environmental Protection Agency on account of their threat to health and the environment. In recent years, many materials have been developed for the adsorption of PAHs, including layered double hydroxide (LDH), activated carbon, biochar, graphene and montmorillonite.

Hydrotalcite-like compounds (HTLcs) are typical alkali metal adsorbents with a common type of layered material consisting of positively charged lamellae and exchangeable interlayer anions. HTLcs are widely used in the field of adsorption because of their large specific surface area and adjustable laminate, which are easy to modify. Composite metal oxide, obtained after calcination at 250–500 °C, possesses a unique “memory effect.” Layered double oxide has a large specific surface area and thermodynamic stability. The topological effect of cationic laminates can accommodate high molecular weight organic/inorganic anions between the layers. HTLcs modified by a surfactant enhance hydrophobicity, making them suitable for the adsorption of substances, such as organic pollutants in the environment. Huang et al. evaluated the effect of Ni–Fe LDH catalyzing bisphenol A under optimized conditions, and finally achieved 56% and 68% removal of TOC and COD. Dai et al. applied CuNiAl–LDH in the reaction of hydroxylation of phenol, and the conversion of phenol could reach 62.8% under the optimal reaction conditions. Kuang et al. found that activated carbon modified by sodium dodecyl sulfate (SDS) can significantly improve the adsorption performance of methylene blue, and the modified activated carbon is twice as good as the activated carbon. The high adsorption capacity can be attributed to the hydrophobic group of the surfactant, which is expected to bind to the hydrophobic surface of activated carbon. Demissie et al. studied adsorbents based on fresh agglomerates of Al₉₀ nanoclusters modified with SDS (SDS–PAC₉₀) to simultaneously remove multiple synthetic dyes and suspensions from water. Under optimal conditions, the dye removal extent is over 95%, and the turbidity removal extent is over 98%. In addition, the surface properties of materials are generally reflected by...
specific surface area and surface dispersion components, and IGC can reflect the surface properties parameters of materials.\textsuperscript{18} IGC provides a value of $\gamma_s$\textsuperscript{a}, which is similar to the measured value of the contact angle, but can more accurately reflect wettability.\textsuperscript{19} The specific composition of surface energy is related to the sites and functional groups of polar molecules, so it is considered that the surface wettability can be modified.\textsuperscript{20} The smaller the surface dispersion component is, the better the stability of the material is. When the material is used as an adsorbent, it is more conducive to adsorb some other substances.

The purpose of this study was to investigate the adsorption of PAHs from an aqueous solution using CuZnFeAl-LDH and its modified materials. The successful modification of CuZnFeAl-LDH benefits from the memory properties of the material. The LDH intercalated with SDS can effectively increase the layer spacing, change the surface properties of the adsorption material, change its surface from hydrophilic to hydrophobic, and enhance the adsorption effect of hydrophobic organic compounds.\textsuperscript{21} The solubility of low molecular weight PAHs in water is much greater than that of high molecular weight PAHs,\textsuperscript{22} so low molecular weight bicyclic naphthalene and tricyclic phenanthrene were selected as model compounds to explore the adsorption effect of modified LDH. LDH intercalated with SDS was investigated considering the reaction kinetics and adsorption equilibrium.

2. Experimental methods

2.1 Preparation and modification of adsorbents

CuZnFeAl-LDH was prepared using the coprecipitation method. First, solution A contained 150 mL of 0.012 mol L\textsuperscript{–1} Cu(NO\textsubscript{3})\textsubscript{2}, 0.048 mol L\textsuperscript{–1} Zn(NO\textsubscript{3})\textsubscript{2}, 0.010 mol L\textsuperscript{–1} Fe(NO\textsubscript{3})\textsubscript{3} and 0.010 mol L\textsuperscript{–1} Al(NO\textsubscript{3})\textsubscript{3}. Solution B contained 150 mL of 0.15 mol L\textsuperscript{–1} NaOH and 0.10 mol L\textsuperscript{–1} Na\textsubscript{2}CO\textsubscript{3}. At 60 °C, solution A and solution B were dropped into the reaction flask and maintained at pH 9–10. The reaction was allowed to proceed for 6 h, followed washing with deionized water until neutral and drying for 8 h at 60 °C. The resultant adsorbent was recorded as CuZnFeAl-LDH.

CuZnFeAl-LDH was calcined for 6 h at 500 °C to obtain CuZnFeAlO. 0.5 mol L\textsuperscript{–1} SDS and CuZnFeAlO were added into a 100 mL three-necked flask stirring 24 h, following filtering and washing to obtain CuZnFeAl-S.

2.2 Characterizations

XRD analysis was performed on a Bruker D8 Advance powder X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm) at 40 kV and 200 mA, a scanning rate of 20° min\textsuperscript{–1} and 2θ ranging from 0° to 80°. Brunauer–Emmett–Teller (BET) and nitrogen physical adsorption–desorption parameters of the sample were determined by nitrogen adsorption data obtained with a Micromeritics ASAP 2020 analyzer, and the pretreatment was degassing for 2 h at 200 °C. The metal content in the sample was determined using inductively coupled plasma atomic emission spectrometry on a PerkinElmer ICP-OES optima 3000 instrument. The morphologies of the adsorbents were observed by SEM using Hitachi S-4800 instruments. Fourier transform infrared (FT-IR) spectra were obtained on a nexus 870 FT-IR spectrometer. An STA 499 F3-type synchronous thermal analyzer was used to determine the thermal stability of the sample. The measurement range was from 60 to 800 °C, rising at a rate of 10 °C min\textsuperscript{–1}. Inverse gas chromatography (IGC, GC-9860) technology was used to measure the surface dispersion energy component ($\gamma_s$\textsuperscript{a}).

2.3 Adsorption tests

A certain amount of adsorbents was added to a 1000 mL beaker, solution containing 500 mL of solution at certain concentrations of naphthalene and phenanthrene. Samples were taken every 5 minute and were extracted with equal volumes of cyclohexane and dichloromethane. The supernatant was analyzed using gas chromatography with an external standard method. The column was an Rt-x 1701. The analysis conditions for naphthalene are as follows: the initial temperature was 50 °C, which was applied for 1 min. Then, the temperature was increased to 180 °C at 20 °C min\textsuperscript{–1} for 2 min. The gasification chamber temperature was 120 °C and the detector temperature was 205 °C. The analysis conditions for phenanthrene: the inlet temperature was set to 260 °C, and the initial column temperature was set to 80 °C. After 1 min, the temperature was increased to 200 °C at 20 °C min\textsuperscript{–1}, where it was maintained for 2 min.

The equation for calculating the removal (Rem):

$$\text{Rem} = \frac{c_0 - c_t}{c_0} \times 100\%$$

The equation for calculating the adsorption capacity:

$$q_t = \frac{c_0 - c_t}{m} V$$

$c_0$: initial concentration of solution (mg L\textsuperscript{–1}), $c_t$: concentration of solution at adsorption time $t$ (mg L\textsuperscript{–1}), $m$: mass of adsorbent (mg), $V$: volume of solution (L)

2.4 Adsorption kinetics

To investigate the adsorption kinetics of naphthalene and phenanthrene solutions on the adsorbent CuZnFeAl-S, a pseudo-first-order kinetic model (3) was used to fit and analyze the kinetic data.

$$k = \frac{[\ln q_e - \ln(q_e - q_t)]}{t}$$

$q_t$ is the adsorption capacity at time $t$ in the solution (mg g\textsuperscript{–1}), $q_e$ is the adsorption capacity at adsorption equilibrium (mg g\textsuperscript{–1}), $t$ is the adsorption time, and $k$ is the adsorption kinetic constant.

$$q_e = \frac{Q_{\text{max}}bcx}{1 + bce}$$

$$q_e = K_t \times e^{-ct}$$

$c_e$ is the concentration in the solution at adsorption equilibrium (mg L\textsuperscript{–1}), $K_t$, $n$ is the Freundlich constant, $Q_{\text{max}}$ is the maximum
adsorption capacity (mg g⁻¹), and b is the Langmuir constant related to adsorption capacity (L mg⁻¹).

2.5 Adsorption thermodynamics

The relationship between adsorption temperature and capacity was explored. The thermodynamic parameters ΔG, ΔH and ΔS were obtained using the following eqn (6)–(8).

\[
K_D = \frac{q_d}{c_e}
\]  
\[
\Delta G = -RT \ln K_D
\]  
\[
\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

\(q_d\) is the equilibrium adsorption capacity of the adsorbent (mg g⁻¹), \(c_e\) is the equilibrium concentration (mg L⁻¹), \(R\) is the gas molar constant, and \(T\) is the reaction temperature (K).

2.6 IGC analysis

Using \(N_2\) as the carrier gas, \(n\)-alkanes (\(n\)-hexane, \(n\)-heptane, \(n\)-octane and \(n\)-nonane) were used to determine hydroxalite and surface dispersion components under a series of surface coverages. The carrier gas flow was 30 mL min⁻¹, the detector temperature was 200 °C, the vaporization chamber temperature was 120 °C and the column temperature range was 80–110 °C. Preparation of the chromatographic column: a stainless steel column was selected as the chromatographic column, with a length of 15 cm and an inner diameter of 0.2 cm. The chromatographic column was cleaned with acetone, filled with CuZnFeAl–LDH, CuZnFeAlO and CuZnFeAl–S after drying, and aged with \(N_2\) for 2 h at 180 °C.

The IGC technique involves the passage of several solvent probes with different properties under infinite dilution on a steel column containing the material to be measured. The time required for different probes to pass through the chromatographic column is directly related to the surface characteristics of the material.

\[
V_a = F \frac{P_0 - P_w}{P_w} (t_i - t_0) J \frac{T}{T_C}
\]

\[
RT \ln(V_a) = (\gamma_a^d)^{0.5} N \alpha (\gamma_l^d)^{0.5} + C
\]

\(t_i\) is the retention time of probe molecule, \(t_0\) is the air retention time, \(T\) is the column temperature, \(F\) is the carrier gas flow rate, \(J\) is the James–Martin pressure correction factor, \(T_C\) is the indoor ambient temperature, \(R\) is the ideal gas constant, and \(C\) is the constant related to the stationary phase, \(\gamma_a^d\) is the dispersive component of solid surface energy, \(\gamma_l^d\) is the dispersive component of liquid surface energy, and \(N\) is Avogadro constant, \(\alpha\) is the cross-sectional area of the probe molecule.

3. Results and discussion

3.1 Structural characterizations

The XRD patterns of the adsorbents are shown in Fig. 1. Characteristic peaks appear in the (003), (006), (009), (015), (018), (110) and (113) planes, confirming the formation of the hydrotalcite layered structure (JCPDS 089-0460). The spacing of the CuZnFeAl–LDH (003) plane (\(d_{003}\)) is about 0.76 nm, which is consistent with the ionic radius of \(\text{CO}_3^{2-}\). This result indicates that carbonate acts as the main anion between the layers due to the presence of \(\text{Na}_2\text{CO}_3\) in the synthesis. After calcination at 500 °C, the peak of CuZnFeAlO appeared at \(2\theta = 56.62°\) is that of spinel \(\text{ZnFe}_2\text{O}_4\) (JCPDS no. 22-1012). Besides, the characteristic peak at \(2\theta = 31.70°, 47.46°, 62.54°\) and 68.06°, corresponding to the hexagonal planar \(\text{ZnO}\) (JCPDS no. 36-1451). Furthermore, characteristic peaks corresponding to CuO were also found. It is worth noticing that no diffraction peaks assigned to \(\text{Al}_2\text{O}_3\) can be observed, which means that the \(\text{Al}_2\text{O}_3\) phase is amorphous. After Sds intercalation of CuZnFeAl–LDH, the (003) peak shifted to a smaller angle. The layer spacing of layered materials can be calculated using the Bragg equation. The crystal plane spacing \(d_{003}\) of CuZnFeAl–S increases to 2.63 nm, indicating that DS⁻ has been successfully inserted into the interlayer. The chain length of the Sds molecule is 2.08 nm, and the angle of Sds insertion into the LDH interlayer calculated using trigonometry is 65°.

Fig. 2 shows that CuZnFeAl–LDH presents a flake structure, which is relatively regular and has less surface impurities, which is consistent with the characterization results of XRD, indicating that LDH was successfully synthesized. After calcining, CuZnFeAlO (Fig. 2(b)) did not show a fixed morphology because the laminate collapsed and the particle size decreased during roasting, resulting in partial agglomeration. Fig. 2(c) shows the CuZnFeAl–S obtained after intercalation modification, the layered structure and the carbon on the surfactant are connected to form a fluffy structure.

Fig. 3 shows the \(N_2\) adsorption–desorption isotherms of the adsorbents, and the type IV isotherm with an \(H_3\) hysteresis loop under relative pressures of 0.4–1.0, which indicates that the material is a mesoporous structure. Table 1 shows the specific surface area and element analysis data of the three adsorbents. The ICP results showed that the metal element content of the
adsorbents before and after modification was close to the theoretical value. The specific surface area test results show that the specific surface area and pore volume of the CuZnFeAlO obtained after calcination increase significantly. This may be due to the collapse of part of the laminate during the calcination process, the decrease of the grain size, however the increase of the specific surface area and pore volume, which are consistent with the SEM. However, the specific surface area of CuZnFeAl-S is between CuZnFeAl-LDH and CuZnFeAlO, which may be caused by the use of SDS intercalation to cause part of the surface pores of CuZnFeAlO to be blocked by SDS.

FT-IR spectra (Fig. 4) show two broad bands around 3460 and 1648 cm⁻¹, attributed to the stretching vibration and the bending vibration of interlayer water molecules, the spectral band of CuZnFeAlO is narrowed, indicating that part of the hydroxyl groups is effectively removed after calcination. The vibrational peak appearing around 1388 cm⁻¹ is caused by the asymmetric stretching vibration of carbonate. The peak intensity of CuZnFeAl-S is lower, indicating a lower content of interlayer pillar ions CO₃²⁻. The peaks at 2935 and 2857 cm⁻¹ are caused by the stretching vibration of the C–H bond in rₓCHₓ, the vibration peaks at 1233, 1060 and 983 cm⁻¹ are caused by –SO₃. The results show that SDS was successfully introduced into CuZnFeAlO, which indicates that SDS successfully entered the LDH interlayer. At the same time, these changes prove the geometric perturbation of functional groups (–SO₃). The existence of the S=O bond indicates that there is a hydrogen bond between LDH and the sulfate groups, which is electrostatically bound to the metal on the surface of LDH, i.e., S=O···H–O–M (M = Cu, Zn, Fe or Al).

After a series of probe molecules reached adsorption–desorption equilibrium on the surface of various hydrotalcites,

![Fig. 2 SEM patterns of adsorbents. (a) CuZnFeAl–LDH (b) CuZnFeAlO (c) CuZnFeAl–S.](image)

![Fig. 3 N₂ adsorption–desorption isotherms of different adsorbents.](image)

**Table 1** The specific surface area and element analysis of the adsorbent

| Samples                  | Cu/Zn/Fe/Al molar ratios | S BET/m² g⁻¹ | V T/cm³ g⁻¹ |
|--------------------------|--------------------------|--------------|-------------|
| CuZnFeAl–LDH             | 15.15/60.50/12.21/12.14  | 91           | 0.46        |
| CuZnFeAlO                | 14.86/61.49/11.89/11.76  | 125          | 0.87        |
| CuZnFeAl–S               | 15.02/60.53/12.27/12.18  | 103          | 0.52        |

*S BET-BET surface area, V T-total pore volume, P/P₀ = 0.990.*
and Gray, hydrophilic to hydrophobic. Meanwhile, according to Dorris probe molecules. SDS-modified talcite to the adsorption free energy. Surfactant modified LDH, the contribution of a single methylene on the surface of hydroxyl laminate and interlayer CO\(_2\) in LDH,\(^{39}\) including the second adsorption peak at 373 °C in the DSC diagram. These results are consistent with those of XRD and FT-IR, which indicates that carbonate is a compensating anion between the laminates. CuZnFeAl–LDH begins to decompose beyond 600 °C, the layered structure is completely destroyed and mixed oxides are formed. Fig. 6(c) shows the TG-DSC curve of CuZnFeAl–S. The interlayer organic combustion phenomenon occurred above 160 °C, which proved that the decomposition of LDH begins with the cleavage of the C–O bond. The thermal decomposition of surfactant anion intercalated CuZnFeAl–LDH involves the combustion of the organic phase and the release of heat. The thermal decomposition behavior is related to the properties of interlayer anions. In the range of 200–500 °C is the main weight-loss stage of the sample, which is mainly due to the removal of organic anions and the combustion of carbon chain. The endothermic peak appears in the range of 600–700 °C, which is due to the decomposition of sulfate formed by SDS decomposition. The introduction of surfactant leads to a decrease in thermal stability and more thermal weight loss.

3.2 Adsorption performance of adsorbents

Fig. 7(a) shows the relationship of the removal of 10 mg L\(^{-1}\) naphthalene solution with time by adsorbents. It is found that CuZnFeAl–LDH reached adsorption equilibrium in a short time, and the removal of naphthalene basically does not change after 2.0 h. At this time, the removal of naphthalene is 20.9%. CuZnFeAlO and CuZnFeAl–S reached adsorption equilibrium in about 5.5 h, and the removal of naphthalene was 90.1% and 94.2%, respectively. The specific binding sites of CuZnFeAl–S with anionic functional groups provide effective adsorption sites for target pollutants, which have the advantages of a large number of functional groups per unit mass of adsorbent and good dispersibility.

Compared with CuZnFeAl–LDH, the removal of naphthalene by CuZnFeAl–S was increased by 4.5 times. CuZnFeAl–LDH with the special layered hydroxyl structure makes the hydroxylate have good hydrophilicity and is not easy to adsorb naphthalene in water. This phenomenon explains the change of surface properties from hydrophilic to hydrophobic, which increases its affinity for hydrophobic compounds such as PAHs.\(^{39}\) Fig. 7(b) shows the highest removal of phenanthrene in solution on CuZnFeAl–S is 84.5%, and the removal of phenanthrene in

| Adsorbent     | γ\(_d\) (mJ m\(^{-2}\)) | 383.15 K | 373.15 K | 363.15 K | 353.15 K |
|---------------|--------------------------|---------|---------|---------|---------|
| CuZnFeAl–S    | 15.87                    | 19.38   | 24.85   | 29.50   |
| CuZnFeAlO     | 28.43                    | 31.31   | 32.25   | 35.69   |
| CuZnFeAl–LDH  | 35.56                    | 34.29   | 37.09   | 39.16   |

Fig. 4 FT-IR spectra of adsorbents.
Fig. 5  Changes of $RT \ln V_n$ on adsorbent surface with the number of carbon atoms contained in $n$-alkanes at different temperatures. (a) CuZnFeAl–S (b) CuZnFeAlO (c) CuZnFeAl–LDH.

Fig. 6  TG-DSC patterns of adsorbents adsorbed before (a) CuZnFeAl–LDH (b) CuZnFeAlO (c) CuZnFeAl–S and adsorbed after (d) CuZnFeAl–LDH (e) CuZnFeAlO (f) CuZnFeAl–S.
solution on modified CuZnFeAl–S is 4.1 times higher than that of 20.7% before modification.

With the increase of adsorbent dosage, the removal of naphthalene in the solution also gradually increases (Fig. 8(a)). When the amount of adsorbent was 1.0 g L$^{-1}$, the amount of adsorbent continued to increase, and the change in the degree of naphthalene removal was not obvious. Simultaneously, the removal of naphthalene and phenanthrene can reach 97.3% and 90.3%, respectively. It can be seen that with the increase of the initial concentration of naphthalene and phenanthrene (from 10 mg L$^{-1}$ to 25 mg L$^{-1}$), the removal of naphthalene by the adsorbent gradually decreases, the removal of naphthalene decreases from 97.3% to 87.6% (Fig. 8(c)), and the removal of phenanthrene decreases from 90.3% to 75.6% (Fig. 8(d)).
3.3 Adsorption kinetics study

The adsorption of naphthalene (Fig. 9(a)) and phenanthrene (Fig. 9(c)) by adsorbents conforms to the first-order kinetic model. According to Table 3, the fitting of CuZnFeAl–S and CuZnFeAlO also conforms to the pseudo-first-order dynamic model. The adsorption kinetic constant $k$ of CuZnFeAl–S is the largest, indicating the fastest adsorption rate. The adsorption isotherms were processed by the Langmuir monolayer adsorption model and the Freundlich multilayer adsorption model. According to the results of the Langmuir single-layer adsorption model and Freundlich multilayer adsorption model in Fig. 9(b) and (d), the two adsorption models fit the experimental date. The adsorption process of naphthalene was consistent with Langmuir adsorption, and the maximum adsorption capacity of naphthalene was 23.55 mg g$^{-1}$. The adsorption process of phenanthrene was dominated by Freundlich adsorption, and the maximum adsorption capacity of phenanthrene was 25.36 mg g$^{-1}$. Enhancement of the adsorption performance on

| Adsorbent     | Naphthalene | Phenanthrene |
|---------------|-------------|--------------|
|               | Kinetic equation | $R^2$     | Kinetic equation | $R^2$     |
| CuZnFeAl–LDH  | $y = -0.38x + 0.30$ | 0.994      | $y = -0.42x + 1.31$ | 0.992      |
| CuZnFeAlO     | $y = -0.43x + 2.02$ | 0.991      | $y = -0.50x + 2.08$ | 0.991      |
| CuZnFeAl–S    | $y = -0.49x + 2.31$ | 0.990      | $y = -0.67x + 1.705$ | 0.981      |

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| Adsorbent     | Naphthalene | Phenanthrene |
|---------------|-------------|--------------|
|               | $Q_{max}$ (mg g$^{-1}$) | $b$ (L mg$^{-1}$) | $R^2$ | $K_f$ (g$^{1-n}$ g$^{-1}$ L$^{-n}$) | $n$ | $R^2$ |
| Naphthalene   | 23.55       | 1.25         | 0.996       | 12.15       | 2.45         | 0.992      |
| Phenanthrene  | 25.36       | 0.77         | 0.993       | 10.61       | 2.13         | 0.997      |
CuZnFeAl–S may be the synergistic effect of hydrogen bonding and electrostatic interactions exhibited by the surface interlayer adsorption process (Table 4).

3.4 Adsorption thermodynamics study

Fig. S1(a) and (b)† shows the adsorption performance of naphthalene and phenanthrene with temperature (from 293.15 K to 323.15 K), and Fig. S2(a) and (b)† describes the relationship between the equilibrium adsorption capacity and the equilibrium concentration on CuZnFeAl–S, respectively. As can be seen from Table 5, ∆G, ∆S and ∆H are negative, which indicates that the adsorption of naphthalene and phenanthrene on CuZnFeAl–S is a spontaneous exothermic reaction. As the temperature rises, entropy changes gradually slows down as ∆G decreases. ∆H is between −20 and 0 kJ mol⁻¹, manifesting that the adsorption is physical adsorption, which is consistent with the results of IGC. ∆S has a negative value, which reflects that the disorder degree of adsorbate at the interface between solid and liquid decreases in the process of adsorption. For the same adsorption material, the ∆H of naphthalene during adsorption is even smaller, implying that naphthalene is easier to adsorb on the surface of CuZnFeAl–S, which is consistent with the experimental results of adsorption kinetics, which further proves that CuZnFeAl–S has a strong adsorption capacity for naphthalene.

3.5 Mechanism research
Surfactant-intercalated CuZnFeAl–LDH has a layered structure, with the main laminate composed of metal and interlayer guest surfactant anions. They form a close structure through the interaction of covalent bonds and hydrogen bonds, the ordered aggregation of surfactants forms a hydrophobic region between the layers. The existence of this hydrophobic partition phase enables this material to partition and adsorb hydrophobic organics in water. High molecular weight organic anions can enter the interlayer of LDH, such as DS⁻ whose structure contains an –OSO₃⁻ bond.

Organic molecules are distributed into the organic phase formed between layers through the partition mechanism. Anionic surfactants intercalate into the interlayer to form a tightly packed hydrophobic microenvironment between the CuZnFeAl–LDH layers, which can significantly enhance the adsorption of PAHs. PAHs and surfactants can also increase the adsorption of PAHs on CuZnFeAl–S by hydrogen bonding, π–π interactions, and electrostatic attraction. Therefore, the adsorption of PAHs on CuZnFeAl–S is the result of comprehensive action.

4. Conclusions

The surface properties of the adsorbent CuZnFeAl–LDH were successfully changed from hydrophilic to hydrophobic by roasting and SDS intercalation, to increase the adsorption capacity for PAHs. Compared with CuZnFeAl–LDH, the adsorption of naphthalene and phenanthrene by CuZnFeAl–S was 4.5 and 4.1 times higher, respectively. The adsorption kinetics study showed that the adsorption of CuZnFeAl–S conformed to the pseudo-first-order kinetic equation. The results of adsorption thermodynamic experiments showed that the adsorption capacity increased with the increase in reaction temperature. The adsorption of PAHs and surfactants is the result of diverse factors.

Author Contributions

Boqing Liu and Jingjing Cao performed the experiments, analyzed the data and wrote the manuscript. Haiming He, Yu Shi performed the experiments. You Jiang analyzed the data, and wrote the manuscript. Shichang Yan and Songsong Xu provided helpful discussions. Jinhua Liang and Xiaoqian Ren performed the experiments. Boqing Liu and Jingjing Cao performed the experiments.

Conflicts of interest

The authors declare no competing financial interest.

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