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From Waste to Waste Treatment: Mesoporous Magnetic NiFe₂O₄/ZnCuCr-Layered Double Hydroxide Composite for Wastewater Treatment

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Abstract:

Mesoporous magnetic NiFe₂O₄/ZnCuCr-LDH composite is synthesized by an environmental-friendly hydrothermal process from saccharin wastewater to achieve the goal of “treating the wastes with wastes”. During this process, all waste iron-catalyst and 82% of COD are removed from the wastewater. The composite is characterized by FT-IR, XRD, SEM, XPS, BET and VSM analyses and its potential for wastewater treatment is evaluated by Congo Red (CR) adsorption. An over 97% removal efficiency is achieved with an initial CR concentration ranging from 100 ~ 450 mg/L. The adsorption kinetic is investigated and it is found that the experimental data agrees well with the pseudo-second-order kinetic model, intra-particle diffusion and Langmuir adsorption isotherm model. Adsorption isotherm indicates a spontaneous and endothermic adsorption type. The adsorption mechanism is also explored and the important roles of electrostatic attraction and anion exchange are demonstrated.

Key words: Wastewater; NiFe₂O₄; LDH; Adsorption; Congo red

1. Introduction

Industrial effluents such as saccharin wastewater, electroplating wastewater, heavy metal wastewater discharged into the environment has become a global concern due to freshwater crisis^[2]. Saccharin wastewater is one of the wastewater that are the most difficult to be disposed. Saccharin is featured with its complex composition, high colority, high COD_{Cr}, high BOD₅, high salinity and low pH^[3]. Among all dyes in saccharin wastewater, more than 70% are azo compounds which contain one or more azo bonds as the chromophore group^[4; 5] designed to be resistant to light, weather, water, detergent and biodegradation in aerobic conditions and are remarkably steady. Therefore, it is necessary to be treated ahead of its discharge to the environment. To remove heavy metal ions and impurities, various treatment techniques^[6] such as adsorption^[7], chemical precipitation, ion exchange^[8], membrane filtration^[9; 10], coagulation^[11], photocatalysis^[12] and biological oxidation^[13] have been investigated. So far, adsorption is accepted as an effective and environment-friendly method for

heavy metal wastewater treatment. Many traditional adsorbents such as activated carbon^[14], clay^[15], silicon nanomaterial^[16], and metal oxides^[17] have been studied. However, it's still a challenge to develop adsorbents with a low cost, high recyclability and easy separation ability.

Recently, magnetic nanoparticles such as magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and spinel ferrite have attracted considerable attention in wastewater treatment due to their high surface-to-volume and magnetic properties^[18]. In particular, heavy metal ions in wastewater can be employed as the raw materials to synthesize spinel ferrite. Chen et al.^[19] reported that heavy metals from electroplating wastewater (EPW) and pickling waste liquor (PWL) fix into stable components of ferrite lattice. Among various spinel ferrite, NiFe_2O_4 nanoparticles are particularly attractive because of their high saturation magnetization, easy separation ability and good performance in scavenging hazardous pollutants^[20].

Another method in the synthesis of solid phase to simultaneously scavenging the ions in wastewater is the preparation of layered double hydroxides [LDHs]^[21]. LDHs with their high surface area, high porosity and good anion exchange property have exerted some promising applications in adsorption. Pollutant anions can be scavenged in the synthesis of LDHs, because anions could intercalate between the layers^[26]. Furthermore, the photo-decomposition of organic compounds is facilitated with LDHs composing of various metals such as Zn, Ni, and Cr. The hydrothermal method and co-precipitation^[28] are the popular methods used for the preparation of LDHs, but when organic guest species with a low affinity to LDHs are intercalated into the interlayers, the ion exchange and co-precipitation methods are not applicable any more, the hydrothermal method is usually used. This method has been shown to be highly effective, because only the desired organic anions can occupy the interlayer space in LDHs under the hydrothermal condition in addition to the insoluble magnesium and aluminium hydroxides resourced from their precursors. Lei et al.^[29] have demonstrated that Ni/Mg/Al LDH prepared by hydrothermal method exhibited excellent adsorption performances.

Therefore, a high potential is expected for the adsorption in wastewater treatment if we can combine the easy separation ability of ferrites and the high adsorbability of LDHs to develop magnetic composites^[30] to control both the material microstructure and their macro-appearance in the co-existence of various complex components in wastewater. Herein, in this work, we investigate a facile process to prepare $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ composites via the hydrothermal method from saccharin wastewater to achieve the goal of "treating the wastes with wastes". The wastewater treatment potential is studied by using a simulated Congo Red (CR) adsorption with different contact times, adsorbent dosages, pHs and CR initial concentrations. The experimental adsorption data is also compared with various models to explore the adsorption mechanism.

2. Experimental section

2.1 Materials

Saccharin wastewater was provided by a local saccharin manufacturer in Tianjin in

China, containing 44.8 g Fe/L. The chemicals in analytical grade including NiSO₄, Cu(NO₃)₂, Zn(NO₃)₂, Cr(NO₃)₃, NaOH and NaClO₃ were purchased from Tianjin Fuchen Chemical Reagent Co., Ltd. Congo red (C₂₈H₃₁ClN₂O₃) was provided by Tianjin Fengchuan Chemical Technology Co. Ltd. 1 g/L CR solution was prepared by dissolving 1.0000 g CR in 1 L deionized water, and other concentrations of CR was obtained by diluting.

2.2 Methods

2.2.1 Synthesis of NiFe₂O₄ nanoparticles

0.012 mol NaClO₃ was added into 25 ml saccharin wastewater to oxidize Fe²⁺ into Fe³⁺ (0.02 mol) followed by 0.01 mol NiSO₄. The pH value was adjusted to 9.0 by adding NaOH under vigorous stirring for 30 min. After then, the above alkali solution was transferred into a 100 mL Teflon lined stainless steel autoclave. The autoclave was sealed and heated at 150 °C for 12 hours, then cooled down to room temperature in air. The obtained NiFe₂O₄ product was filtered and washed with deionized water and absolute ethanol several times, and dried at 60 °C overnight.

2.2.2 Synthesis of NiFe₂O₄/ZnCuCr-LDH composite

The molar ratio of Zn²⁺, Cr³⁺ and Cu²⁺ was 2:1:9. All the chemicals were dissolved in 25 mL of deionized water. NaOH solution was used to adjust the pH to 5.5 under vigorous stirring. Then the obtained NiFe₂O₄ powder was dispersed into the above solution at a molar ratio of NiFe₂O₄/LDH of 0.3 and ultrasonically treated for 15 minutes at room temperature in air. After then, the suspension was transferred into the stainless steel autoclave with Teflon liner. The hydrothermal treatment was conducted at 150 °C for 12 hours. Subsequently, the as-prepared NiFe₂O₄/ZnCuCr-LDH composite was dried at 60 °C overnight. In comparison, pure ZnCuCr-LDH was also prepared in the similar way without NiFe₂O₄ addition as the bench sample.

2.3 Adsorption tests

The wastewater treatment performance of the NiFe₂O₄/ZnCuCr-LDH was evaluated by the CR adsorption on a water bath thermostatic oscillator at a constant shaking speed of 130 rpm in conical flasks. Adsorption procedure for single-factor experiments was performed by varying the contact time (0 ~ 720 min), adsorbent dosage (5 ~ 17.5 g/L), initial pH value (2 ~ 9) and initial CR concentration (100 ~ 450 mg/L). The initial pH of the dye solution was adjusted by 0.1 mol/L nitric acid and 0.1 mol/L sodium hydroxide. The solution volume in conical flask was 20 mL and the temperature of each experiment was 298 K. After adsorption, the residual CR was determined by a UV-vis spectrophotometer at 497.2 nm after the separation of adsorbent by a magnet. The removal efficiency (R, %) and the amount of CR adsorbed per unit mass of the adsorbents (q, mg/g) were evaluated from Eq. (1) and Eq. (2).

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_e)V}{m} \times 100\% \quad (2)$$

where C_0 and C_t (mg/L) are the concentrations of CR in the solution at the initial time and final time, respectively; V (mL) is the initial volume of the CR solution, and m (g) is the mass of the adsorbent.

The same experimental process was conducted to the kinetic and isotherm experiments. In the adsorption kinetics, the aqueous samples were taken at desired time points (5, 10, 15, 20, 25, 30, 40, 60, 120, 240 and 480 min). Adsorption isotherm was studied at different temperatures (293, 298, 303, 308 K). The residual concentrations of CR were measured using the same method as the above UV-vis analysis.

2.4 Characterizations

Powder X-ray diffraction (XRD) patterns of the NiFe_2O_4 , ZnCuCr-LDH , $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ were recorded using a Bruker D8 Advanced XRD diffractometer at $\text{Cu K}\alpha$ radiation ($\lambda=0.15418 \text{ \AA}$) at 40 kV and 40 mA with a scanning rate of 5° min^{-1} between 5 and 80° . The Fourier transfer infrared (FT-IR) spectra were recorded by a FT-IR spectrometer (SENSOR 27, Bruker, Germany) with KBr pellets in the range of $4000 - 400 \text{ cm}^{-1}$. A scanning electron microscope (SEM) (FEI Quanta 450 FEG FESEM) was used to study the surface morphology of NiFe_2O_4 , ZnZrCr-LDH and $\text{NiFe}_2\text{O}_4/\text{ZnZrCr-LDH}$ s. N_2 adsorption-desorption isotherms were measured by using a Micromeritics analyser (America ASAP 2420). The specific surface areas were evaluated using Brunauer-Emmett-Teller (BET) method based on the adsorption isotherm. X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific) was utilized to evaluate the surface chemical structure of the ZnCuCr-LDH nanoparticles. The radiation source was $\text{Al K}\alpha$ (at pressure of 10^{-9} mbar) and the shift of binding energies (BE) was calibrated with respect to the reference peak of carbon at binding energy of 284.6 eV . Magnetic curves were recorded by a Vibrating sample magnetometer (740, LAKESHORE, America). The (dye) concentrations were determined photometrically on UV-Vis spectrophotometer (Lambda 25, Perkin Elmer, America).

3. Results and Discussion

3.1 Characterizations

Fig. S4 shows the magnetization curves of $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ and pure NiFe_2O_4 . The saturated magnetization(M_s) of pure NiFe_2O_4 is 35.48 emu/g and the composite containing 30% NiFe_2O_4 exhibits a ferromagnetic behavior with the values of M_s of 10.82 emu/g . As shown in the inset of Fig. S4, $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ can be separated quickly from the suspension solution with the volume concentration of 25 g/L after being magnetized by an external magnet in 12 seconds. Magnetic separation is particularly fulfilling because it conquers many of the problems which present in filtration, centrifugation or gravitational separation of nano-materials. It

requires less energy to attain a satisfied separation, in addition, it enhances the reusability of metal resources recovered from the wastewater.

Fig. 1 shows the SEM images of pure ZnCuCr-LDH and NiFe₂O₄/ZnCuCr-LDH composite. The pure ZnCuCr-LDH are small platelets with a smooth surface and size of ca. 1 μm (Fig. 1a). After been prepared to the NiFe₂O₄/ZnCuCr-LDH composite (Fig. 1b), some particles can be clearly seen on the surface, indicating the successful adhesion of NiFe₂O₄ nanoparticles to the layer-like LDHs.

Fig. 1. SEM images of ZnCuCr-LDH (a) and NiFe₂O₄/ZnCuCr-LDH (b)

To confirm the crystal structure of the as-prepared materials, the XRD patterns of the prepared ZnCuCr-LDH, NiFe₂O₄/ZnCuCr-LDH and NiFe₂O₄ are displayed in Fig. 2. The diffraction peaks of NiFe₂O₄ /ZnCuCr-LDH at $2\theta = 10, 20, 33$ and 59° can be assigned to (003), (006), (012) and (110) crystal facets of ZnCuCr-LDH^[32], another set of diffraction signals approximately at $2\theta = 30, 35, 43, 57$ and 63° are assigned to (220), (311), (400), (440), (511) and (422) of single phase cubic spinel structure of NiFe₂O₄^[33]. This demonstrates both NiFe₂O₄ and ZnCuCr-LDH phases in the composite. Furthermore, after the surface decoration with NiFe₂O₄ nanoparticles, the regularity of LDH will be decreased, which is also confirmed by the broaden peaks and the reduced intensity of (003) and (006) peaks. The interlayer space (d_{003}) of pure LDH increased from 0.887 to 0.897 nm for the NiFe₂O₄/ZnCuCr-LDH composite. The reason is that LDH layer board is influenced by NiFe₂O₄ magnetic materials. SEM and XRD analyses prove the successful synthesis of the NiFe₂O₄/ZnCuCr-LDH composite and the surface modification of ZnCuCr-LDH by NiFe₂O₄ nanoparticles.

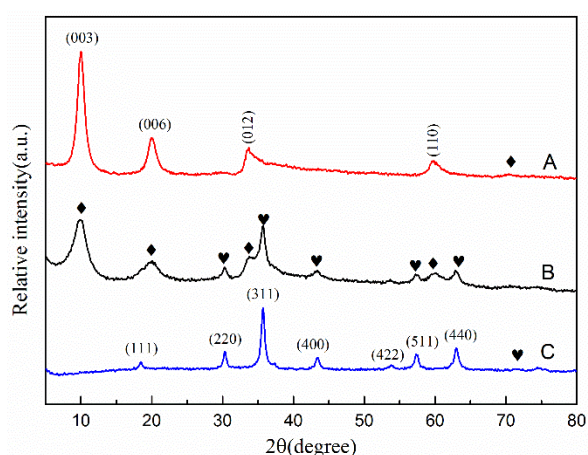


Fig. 2. XRD patterns of (A) ZnCuCr-LDH, (B) NiFe₂O₄/ZnCuCr-LDH, (C) NiFe₂O₄

To check the influence of the surface modification, the IR analysis of the NiFe₂O₄, NiFe₂O₄/ZnCuCr-LDH and ZnCuCr-LDH materials were conducted with KBr pellets in the range between 4000 - 400 cm⁻¹ (Fig. S1). A strong and broad absorption band at 3417 cm⁻¹ is indexed to the stretching vibrations of HOH and water molecules in the

interlayer space. The weak absorption band at 1625 cm^{-1} is resulted from the bending vibrations of OH. In particular, the absorption bands at 1384 cm^{-1} and 833 cm^{-1} are assigned to the vibrations of interlayer nitrate ion^[31]. Besides, three adsorption bands below 700 cm^{-1} are attributed to the lattice vibration modes of the M–H vibration centered at about 600 cm^{-1} and the M–OH vibration at about 568 cm^{-1} and 507 cm^{-1} in the brucite-like layers. Compared to NiFe_2O_4 and LDH, the absorption bands around 571 cm^{-1} , 511 cm^{-1} and 625 cm^{-1} are red-shifted for the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ composite. This is ascribed to the enhanced bond strength of the M–O–M formed from M–O in NiFe_2O_4 and M–OH in ZnCuCr-LDH.

Fig. S2 exhibits the XPS spectra of the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ composite. The survey XPS spectra confirms the elements of Ni, Fe, O, Zn, Cu, Cr and C. Compared to the pure NiFe_2O_4 and the pure LDH, generate displacement is found to the peaks of every elements for $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ ^[34] and the comparison are showed in Fig. S3b, c, d, e, f, g. This shift results from the electronic coupling effect between NiFe_2O_4 and LDH which finally accelerates the electron-hole separation process.

A nitrogen adsorption-desorption measurement was conducted to characterize the specific surface area and internal pore superstructure of the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ composite and the results are shown in Fig. S3 and Table S1. The N_2 adsorption-desorption isotherm is classified as the type IV with the distinct hysteresis loop in the relative pressure range of 0.6-1.0, which is a characteristic feature of mesoporous materials. The BET surface area, pore diameters and pore volume are obtained as $72.64\text{ m}^2/\text{g}$, 7.43 nm and $0.13\text{ cm}^3/\text{g}$, respectively.

3.2 Adsorption studies

3.2.1 Effect of contact time on CR adsorption

The effect of contact time on CR adsorption using the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ composite was studied within $0 \sim 720\text{ min}$ (Fig. 3). This experiment was conducted with an initial CR concentration of 200 mg/L and an adsorbent dosage of 10g/L . The adsorption of CR is rapid and about 77 % of CR is uptake within the initial 15 minutes resulting from abundant adsorption sites of the porous composite. Then the adsorption slows down due to the most of adsorption sites are occupied with time lapse^[35]. The adsorption reaches equilibrium in 240 min, indicating that a complete adsorption occurred within 240 min and a maximum removal efficiency of 89 %. Thus subsequent adsorption experiments were conducted with the contact time of 240 min.

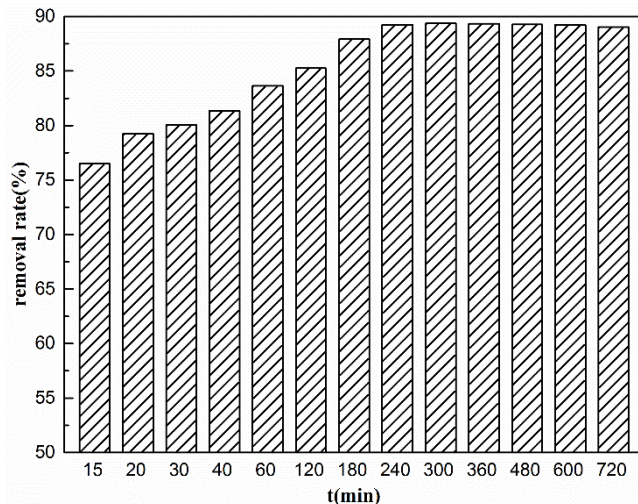


Fig. 3. Effect of contact time on CR adsorption using NiFe₂O₄/ZnCuCr-LDH

3.2.2 Effect of adsorbent dosage on CR adsorption

Fig.4 displays the removal rate of CR with the NiFe₂O₄/ZnCuCr-LDH dosage between 5 and 17.5 g/L at an initial CR concentration of 200 mg/L, and an optimal adsorbent dose of 12.5 g/L is obtained with a removal efficiency of 99%. By increasing the adsorbent dose, a higher removal rate is expected, but this is only noticed for low doses. This phenomenon could be explained by the more active sites with an increasing adsorbent dosage. However, when the addition of adsorbent reaches a very high value, e.g. 15 or 17.5 g/L, the over-added adsorbent can then not fully contact with adsorbate, a removal rate invariable is then observed^[36].

Fig. 4. Effect of the adsorbent dosage on CR adsorption using NiFe₂O₄/ZnCuCr-LDH

3.2.3 Effect of pH on CR adsorption

In the process of adsorption, the pH is a key factor that can significantly influence not only the surface charge of the adsorbent but also the structure of dye molecules. The initial CR concentration was 200 mg/L and the adsorbent dosage was 12.5 g/L in these experiments, and the pH ranged from 2.0 to 10.0 was adjusted by 0.1 mol/L HNO₃ and NaOH. The corresponding results are presented in Fig. 5. The maximal removal efficiency of 99% is achieved at the pH of 3.0. When pH > 5, the adsorption capacity decreases due to the adsorption competition on the active sites between OH⁻ groups and anionic ions of CR. At a low pH, the partially dissolution of the LDH leads to a low adsorption capacity^[37].

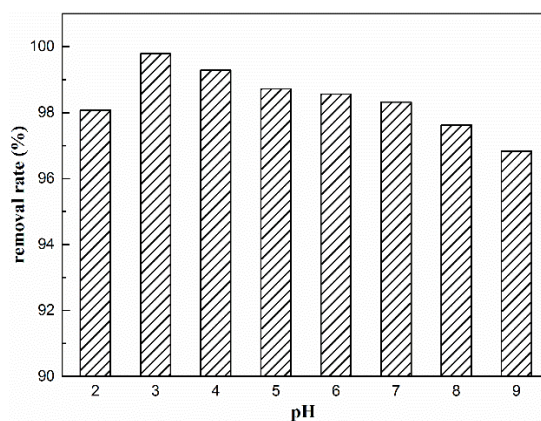


Fig. 5. Effect of pH on CR adsorption using NiFe₂O₄/ZnCuCr-LDH

3.2.3 Effect of initial CR concentration on CR adsorption

The experiments designed to evaluate the role of the initial CR concentration for the removal efficiency were conducted with the initial CR concentrations of 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/L, at the adsorbent dosage of 0.1 g/L and pH value of 3.0. Fig. 6a exhibits the effect of the initial CR concentration on CR removal. It can be seen that the removal efficiency of adsorbent is higher than 97% when the initial CR concentration rises from 100 to 450 mg/L. Fig. 6b shows that the amount of CR adsorption increases evidently with the increase of the initial CR concentration. This can be ascribed to the stronger driving force from the concentration gradient with an increased initial CR concentration to overcome the mass transfer resistance of the dye between the aqueous phase and solid phase. However, when the initial CR concentration continually increases to 500 mg/L, the removal efficiency decreased to 84 % with an also slightly smaller adsorption capacity. This can be explained by the fixed number of active sites with a specific amount of adsorbent. As the active sites are occupied, the adsorbent is insufficient to provide more active sites for CR.

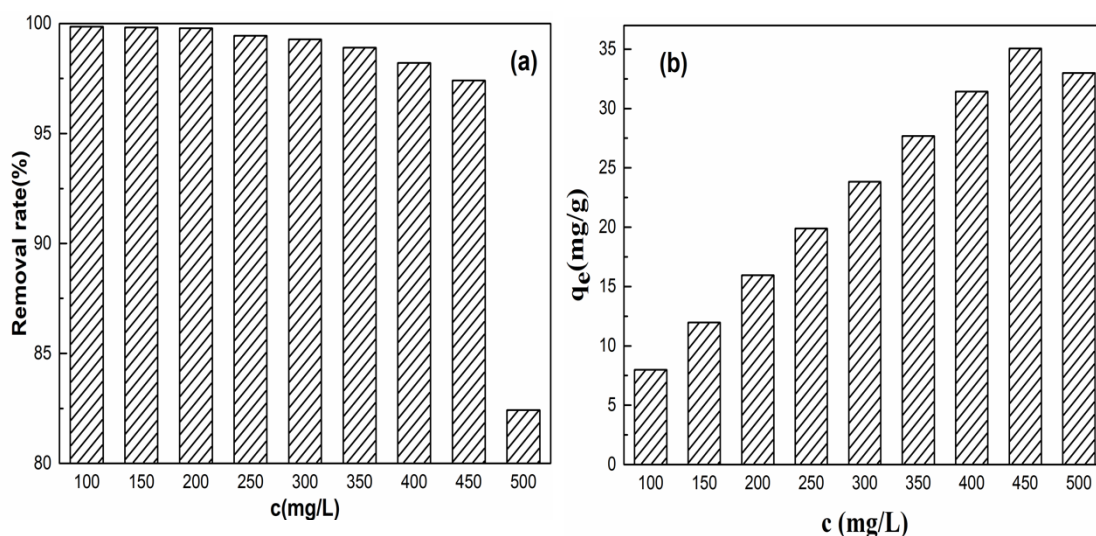


Fig. 6. Effect of the initial CR concentration on CR adsorption using NiFe₂O₄/ZnCuCr-LDH: (a) removal rate, (b) adsorption capacity

3.3 Adsorption kinetics

The adsorption kinetic parameters, which study the fast changing kinetic data to estimate adsorption rates and to determine possible controlling mechanism and potential rate-limiting steps, have a great practical value for technological applications. The models most widely used to study adsorption of dyes onto LDHs materials are pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models. The linear plots for CR adsorption onto NiFe₂O₄/ZnCuCr-LDH are displayed in Fig. 7 for four different models. The corresponding parameters are summarized in Table S2. Compared with the other three models, the pseudo-second-order model shows a much higher R² (> 0.999) and thus can be considered as the best model to describe the kinetic behavior of CR adsorption [38], indicating that the rate-controlling step involves with chemisorption or chemical bonding between the adsorbent active site and CR molecule. The slowest step determines the overall rate of the adsorption process, and this rate-limiting step can be identified by the diffusion process rather than the pseudo-second-order model. The diffusion process usually includes intra-particle diffusion, external transfer and so on. As shown in Table S2, intra-particle diffusion is more suitable to depict the diffusion behavior here. The plots of intra-particle diffusion shows multi-linearity with two stages (Fig .7c). The first stage is very steep which represents the adsorption on the external surface of NiFe₂O₄/ZnCuCr-LDH and is almost instantaneous. The second gentle incline indicated a comparatively slower adsorption when the adsorbate diffuses gradually into the interior surfaces of the particles and the adsorption changes to intra-particle diffusion controlled[38]. Due to the adsorption on the irregular and non-uniform sites on the steps and edges of the particles, the curves might appear multi-factor liner patterns.

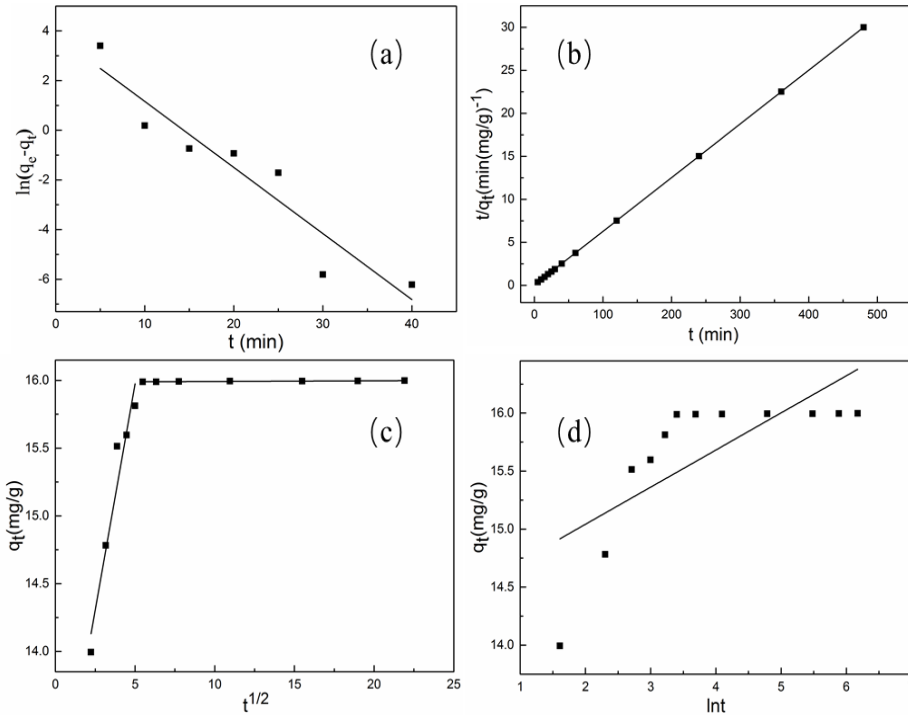


Fig 7. Kinetic models: (a) Pseudo-first-order, (b) Pseudo-second-order, (c) Intra-particle diffusion and (d) Elovich plot for adsorption of CR over NiFe₂O₄/ZnCuCr-LDH

3.4 Adsorption isotherms

Adsorption isotherm is important both to design adsorption systems and to explain adsorption mechanism, because it describes how adsorbate interact with adsorbents. The experiments were performed by varying the initial CR concentration from 200 ~ 450 mg/L and the adsorption temperature from 20 to 35 °C. Fig 8 shows the adsorption capacity increases with the temperature, which indicates the adsorption reaction of CR onto NiFe₂O₄/ZnCuCr-LDH is an endothermic process.

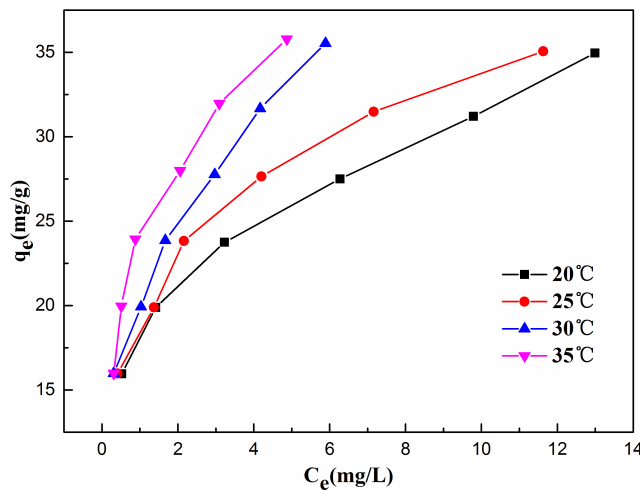


Fig 8. Adsorption isotherms of CR on NiFe₂O₄/ZnCuCr-LDH at different temperatures

The adsorption isotherm data were then fitted by four equilibrium models, i.e., Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models: and the liner plots aere showed in Fig. 9. The fitted parameters for the four models along with regression coefficients are listed in Table S3. Table S3 show the R² values calculated from Langmuir isotherms are all above 0.98 and the calculated q_{m,cal} (37.79 mg/g) is also very close to the experiment value (35.57 mg/g). Thus, Langmuir model is considered as the most suitable model to describe the adsorption behaviors of CR on NiFe₂O₄/ZnCuCr-LDH, which indicates a monolayer coverage of CR molecules on the adsorbent [39].

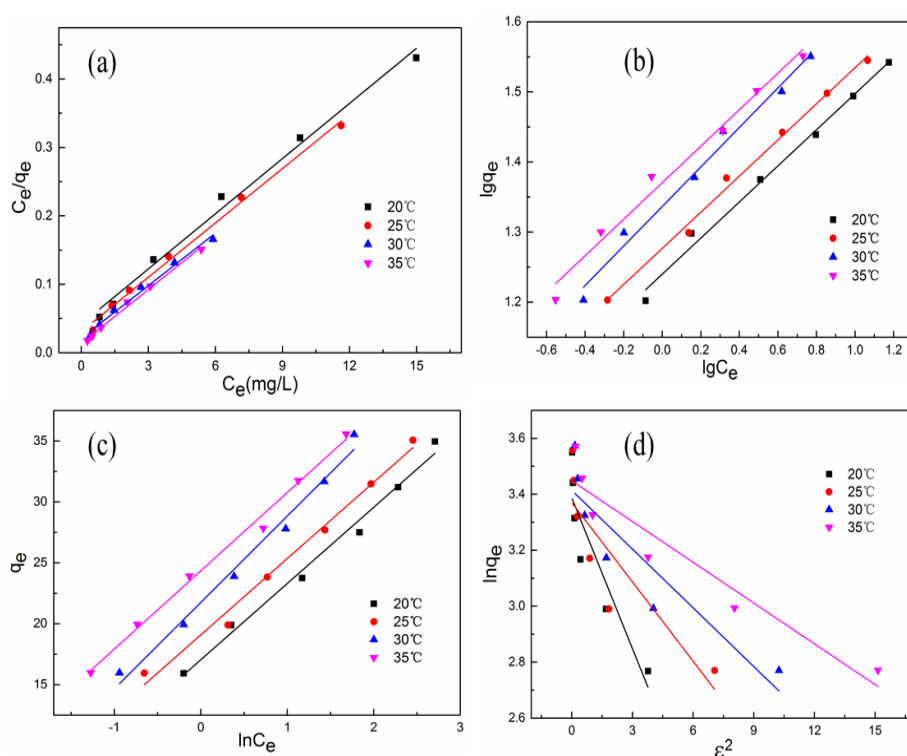


Fig 9. Plots of the Langmuir (a), Freundlich (b), Temkin (c) and D-R (d) isotherm models for the adsorption of CR on NiFe₂O₄/ZnCuCr-LDH

3.5 Adsorption thermodynamics

The temperature dependence of the adsorption in association with changes is provided by several thermodynamic parameters such as standard Gibbs energy (G^0), enthalpy (H^0) and entropy (S^0) of adsorption. The values of change in enthalpy (ΔH°) and entropy (ΔS°) were found using $1/T$ and $\ln(K)$ graphics, and the slope of the line is $(-\Delta H/R)$, and intercept is $(\Delta S/R)$, where K is the distribution coefficient ($K=q_e/C_e$), T (K) is the temperature, and R ($8.314 \text{ K} \cdot \text{mol}^{-1} \text{ K}^{-1}$) is the universal gas constant. The parameters are given in Table 2.

The negative values of ΔG^0 at different temperatures suggest the spontaneous

nature of CR adsorption on NiFe₂O₄/ZnCuCr-LDH. The value of ΔG^0 increases with the temperature, implying that the adsorption process is favorable at high temperature. The value of ΔH is 9.6946 KJ/mol which is much less than 40 KJ/mol, indicating the adsorption process is physical adsorption and endothermic. The positive value of ΔS^0 indicates an increase in randomness at the solid-solution interface during the adsorption process^[40].

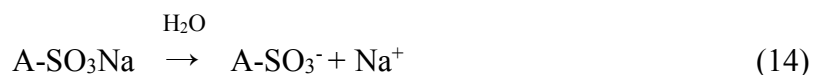
Table 2. Adsorption thermodynamic for the CR adsorption on the NiFe₂O₄/ZnCuCr-LDH

T(K)	ΔG^0 (kJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol·K)
293K	-3.8403		
298K	-4.0650		
303K	-4.1982	9.6946	46.0739
308K	-4.5584		

3.5 Adsorption mechanism

For a better understanding of the adsorption mechanism, XRD analysis was conducted to NiFe₂O₄/ZnCuCr-LDH after CR removal (Fig S5). Compared with the NiFe₂O₄/ZnCuCr-LDH, the peak intensities of the characteristic lines for LDH in LDH-CR are weakened, implying that the adsorption of CR over LDH impacts the crystallinity of LDH which drops from 75% to 60%. Fig S6 shows that the color of the adsorbent changes from brown to black after CR adsorption, further confirming the successful adsorption of CR onto LDH.

Fig.10 demonstrates the adsorption mechanism of CR on NiFe₂O₄/ZnCuCr-LDH. The adsorption of CR can be described as a three- step process, involving^[41]: firstly, CR is dissolved in the aqueous solution, and the sulphonate groups (A-SO₃Na) on the dye molecular are ionized to anions and cations (Eq 14); then the dye molecular anions are attracted to the surface of LDH through electrostatic forces; finally, the intercalation of NO₃⁻ anions is replaced by SO₃⁻ anions of CR via anion exchange^[42].



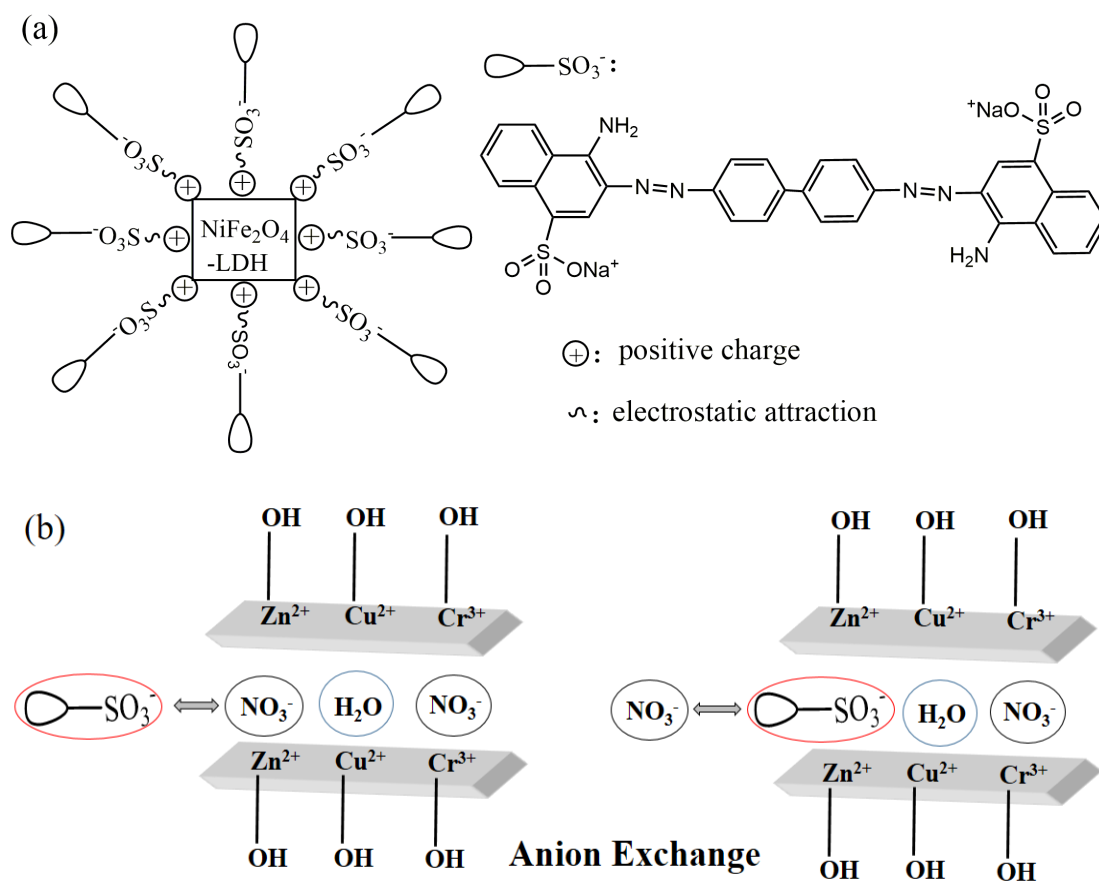


Fig.10 Schematic diagram of the adsorption mechanism of CR on NiFe₂O₄/ZnCuCr-LDH

4 Conclusions

In this work, we demonstrate a mesoporous magnet NiFe₂O₄/ZnCuCr-LDH composite prepared from saccharin wastewater by a facile hydrothermal method and its potential for practical adsorption application in wastewater treatment. During the process, about 82% COD of saccharin wastewater was removed and iron was fully re-utilized. The adsorption of CR on NiFe₂O₄/ZnCuCr-LDH was studied under different conditions by using single-factor experiments, which offered the optimal adsorption conditions (pH of 3 and adsorbent dose of 12.5 g/L). Under these conditions, the adsorbent exhibited a high removal efficiency more than 97% with a very wide initial CR concentration ranging from 150 ~ 450 mg/L. The adsorption kinetics study showed that the experimental data were in good agreement with pseudo-second-order kinetic model and Langmuir adsorption isotherm model with a high adsorption rate. Adsorption thermodynamic suggested that the adsorption process was endothermic and spontaneous in nature. The adsorption mechanism can be deduced that it was mainly electrostatic attraction and anion exchange. The simple synthesis and separation process, together with the excellent adsorption performance of the porous magnet composite, shows a good potential for this process to be used in practical wastewater treatment application.

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Supporting information

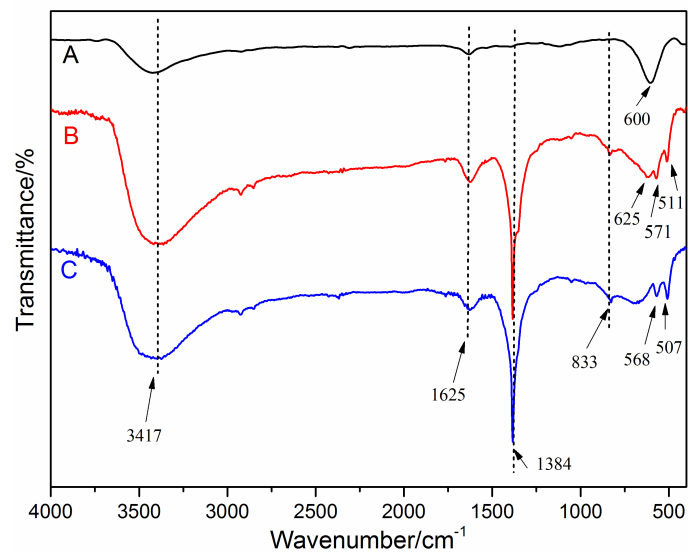


Fig.S1. IR spectra of (A) NiFe_2O_4 , (B) $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$, (C) ZnCuCr-LDH

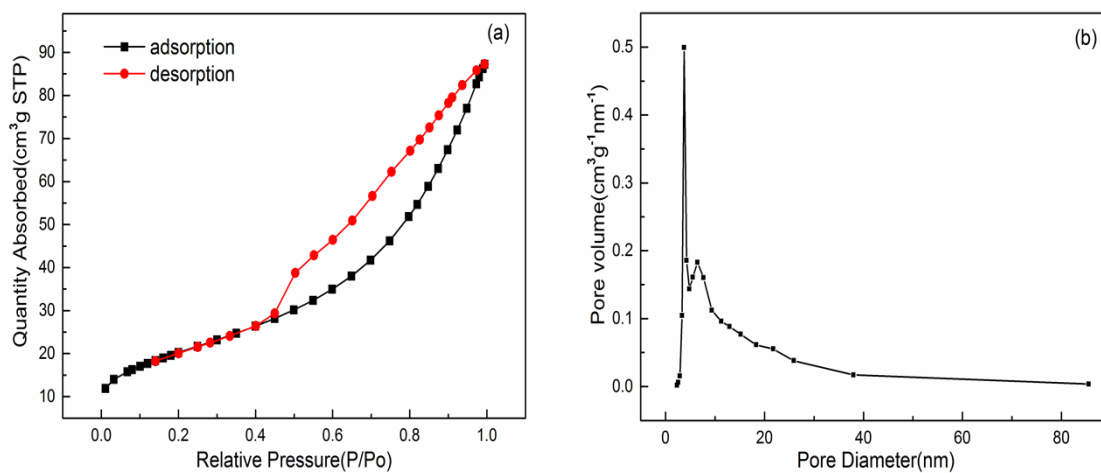
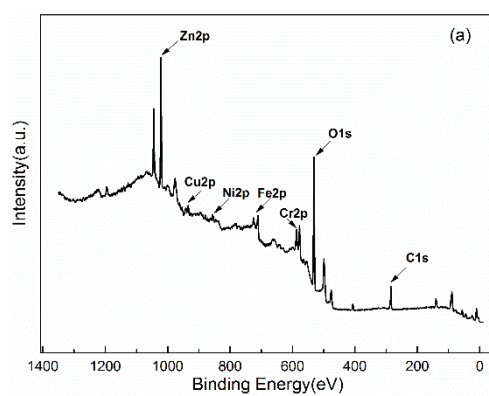


Fig.S2. (a) N_2 adsorption-desorption isotherm for $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$, (b) The pore size distribution curve for the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$.



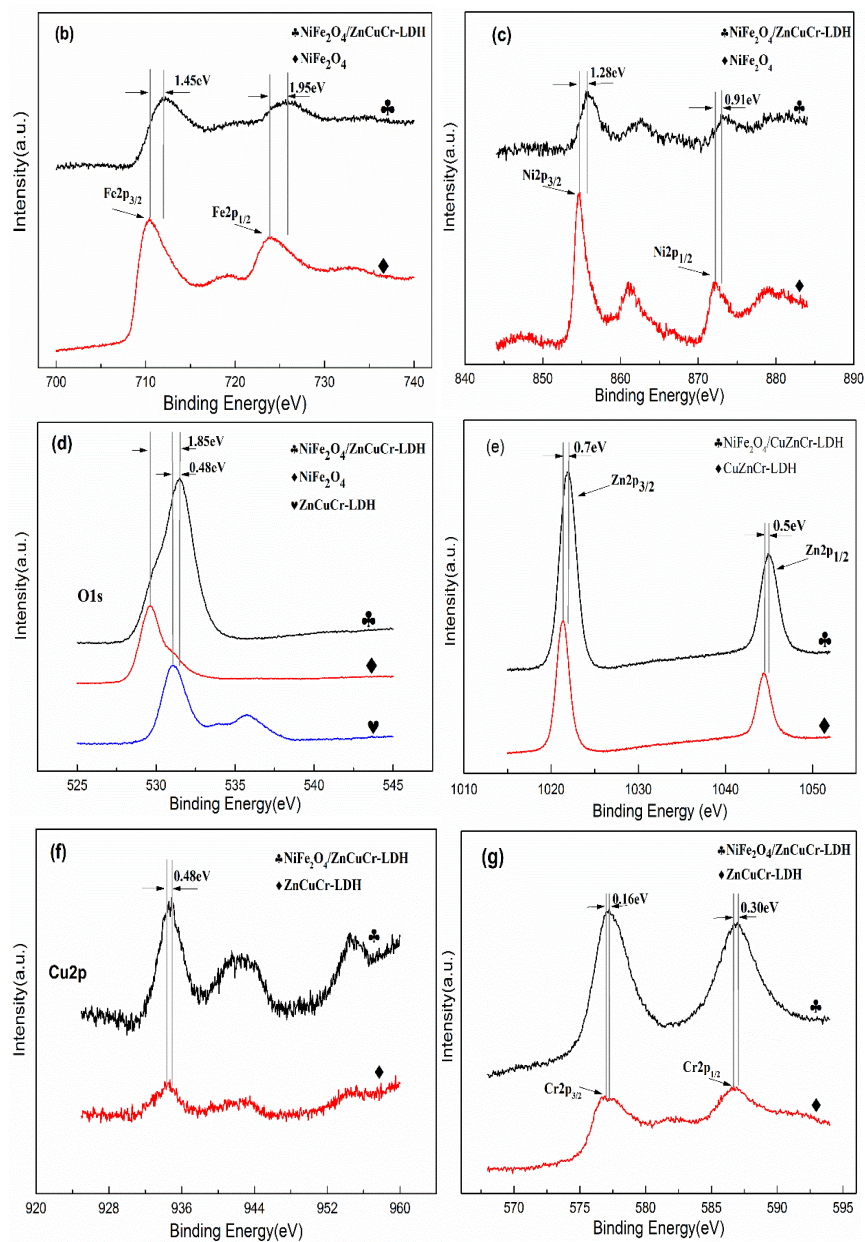


Fig. S3. (a) Survey XPS spectra of the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ composite, (b) Fe 2p XPS spectra, (c) Ni 2p XPS spectra, (d) O 1s XPS spectra, (e) Zn 2p XPS spectra, (f) Cu 2p XPS spectra and (g) Cr 2p XPS spectra.

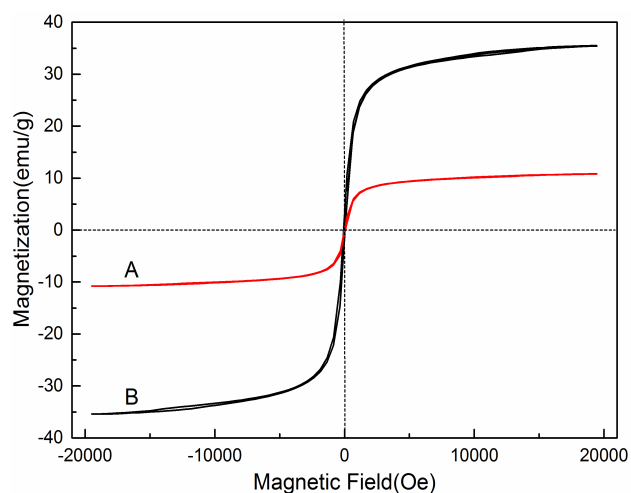


Fig. S4. Magnetization curves of $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ (A) and pure NiFe_2O_4 (B) (inset: separation of the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$ from the treated CR solution using an external magnetic field)

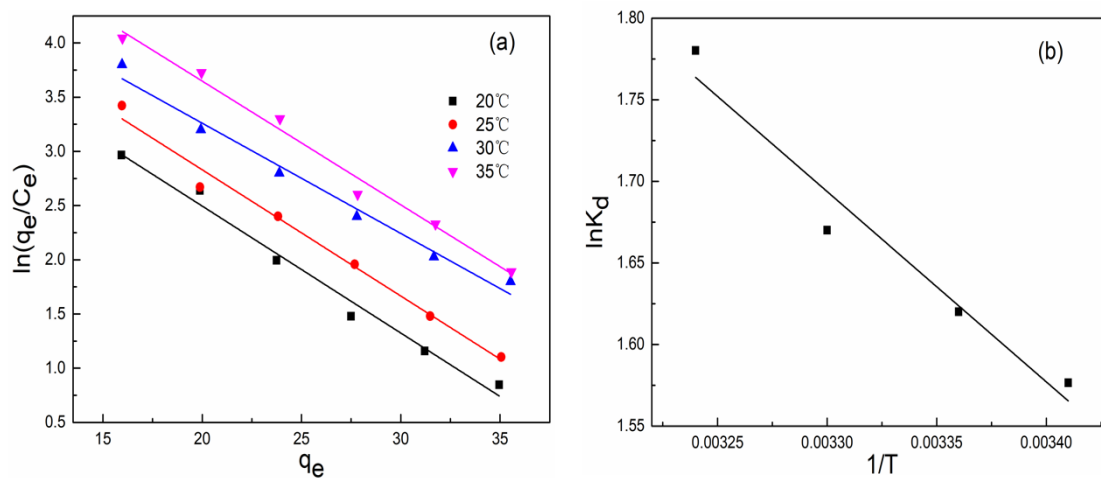


Fig. S5. (a) Plots of $\ln(q_e/C_e)$ as a function of for the CR adsorption on the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$. (b) Van't Hoff plot for the CR adsorption on the $\text{NiFe}_2\text{O}_4/\text{ZnCuCr-LDH}$

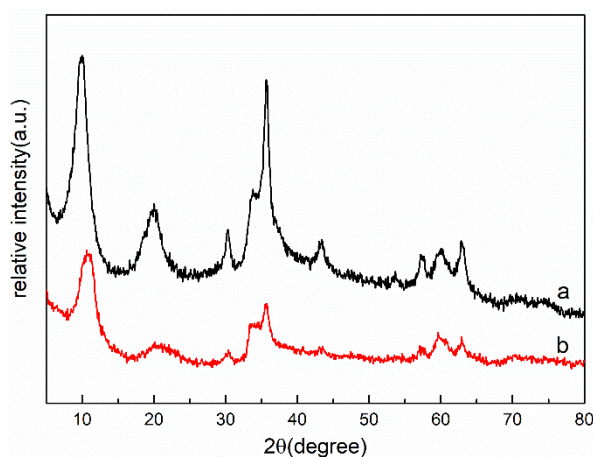


Fig. S6 XRD patterns of (a) ZnCuCr-LDH, (b) NiFe₂O₄/ZnCuCr-LDH



Fig. S7 Picture of NiFe₂O₄/ZnCuCr-LDH (NLDH) before and after CR removal

Table S1 BET surface area, pore volume, and pore diameter of different samples

Samples	BET surface area (m ² /g)	pore volume (cm ³ /g)	Pore diameter (nm)
NiFe ₂ O ₄ /ZnCuCr-LDH	72.64	0.13	7.43

Table S2. Pseudo-first-order, pseudo-second-order, Intra-particle diffusion and Elovich kinetic parameters for CR adsorption on NiFe₂O₄/ZnCuCr-LDH

Kinetic models	Pseudo-first-order		Pseudo-second-order		Intra-particle diffusion		Elovich	
	k ₁ (min ⁻¹)	R ²	k ₂ (g·mg ⁻¹ ·min ⁻¹)	R ²	k _i (mg·g ⁻¹ ·min ^{-0.5})	R ²	A	R ²
	0.2659	0.8816	0.0624	1.0000	0.6675	0.9216	0.3199	0.4987
					4.8671×10 ⁻⁴	0.9233		

Table S3. Adsorption isotherm parameters of Langmuir, Freundlich, Temkin and D-R models for the adsorption of CR on NiFe₂O₄/ZnCuCr-LDH

Model		T(°C)			
		20	25	30	35
Langmuir	K _L (L·mg ⁻¹)	0.6423	0.8560	1.2115	1.9444
	q _{max} (mg·g ⁻¹)	37.2301	37.7929	39.0625	38.0952
	R ²	0.9902	0.9944	0.9875	0.9931
Freundlich	K _F (mg ^{1-1/n} ·L ^{1/n} ·g ⁻¹)	17.3724	18.9095	21.6970	23.4596
	n	3.8852	3.8797	3.5491	3.8407

	R^2	0.9897	0.9933	0.9827	0.9796
Temkin	$A_T(\text{L}\cdot\text{mg}^{-1})$	15.2219	21.0537	21.4962	44.1751
	$B_T(\text{kJ}\cdot\text{mol}^{-1})$	0.3893	0.3956	0.3554	0.3985
	R^2	0.9858	0.9863	0.9829	0.9913
D-R	$q_{\text{max}}(\text{mg}\cdot\text{g}^{-1})$	29.5966	29.0977	30.4437	31.4453
	$\beta(\text{mol}^2\cdot\text{kJ}^{-2})$	0.1797	0.0945	0.0699	0.0486
	R^2	0.8028	0.6966	0.7916	0.8893