

Research Article

Fuhua Wei*, Yan Wang, Qinhui Ren, Qin Zhang, Hongliang Chen, and Zhao Liang*

Preparation of Co/Cr-MOFs for efficient removal of fleroxacin and Rhodamine B

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Abstract: Cr/Co-MOFs were synthesized via a solvothermal method using chromium acetate and cobalt chloride hexahydrate as metal ions, and trimeric acid as the organic ligand. The structures of Cr/Co-MOFs were characterized using Fourier infrared spectroscopy, X-ray diffraction, and scanning electron microscopy techniques. These Cr/Co-MOFs were used for removing organic contaminants in wastewater treatment. Fleroxacin and Rhodamine B (RhB) were specifically selected as target molecules in this study to evaluate the removal efficiency based on the mass of Co/Cr-MOFs, concentrations of organic contaminants, and adsorption time. Experimental findings indicated that at a Co/Cr-MOFs dosage of 100 mg, with initial concentrations of Fleroxacin (30 ppm) and RhB (20 ppm), removal efficiencies achieved were 95% and 99%, respectively. Within a timeframe of 5 h, Co/Cr-MOFs attained adsorption capacities amounting to $269.6 \text{ mg} \cdot \text{g}^{-1}$ for fleroxacin and $289.5 \text{ mg} \cdot \text{g}^{-1}$ for RhB. The interaction between Co/Cr-MOFs and fleroxacin, as well as RhB, is primarily attributed to factors such as pore size, hydrogen bonding, electrostatic charge, and π - π interactions. Moreover, theoretical analysis corroborated these experimental results by demonstrating conformity between the adsorption process and both second-order kinetic model equations alongside Langmuir isotherm model equations. Collectively, the experimental data combined with theoretical investigations underscore the practical significance associated with employing Co/Cr-MOFs for effective eradication of organic pollutants.

Keywords: metal-organic frameworks, antibiotic, dye, wastewater treatment, organic pollutant

1 Introduction

Water pollution poses a serious threat to human health and has a detrimental impact on the environment [1]. Therefore, controlling and treating water pollution are of paramount importance and urgency. Numerous sources contribute to water pollution, including various substances. Among them, emerging organic pollutants have been found to contaminate water supplies, such as pharmaceuticals, cosmetics, as well as industrial pollutants like dyes and pigments [2,3]. Despite their low concentrations, most emerging organic pollutants exhibit considerable resistance to removal through conventional water purification methods due to their physical and chemical properties such as high water solubility [4]. Dyes are used for various purposes, such as artistic endeavors and preservation efforts, in order to introduce color into materials. They provide long-lasting coloring for fabric and fiber surfaces while displaying resistance against exposure to light and detergents [5–7]. In contrast, pigments used in plastics, fibers, and polymer materials remain insoluble within the medium they are applied to [8]. Consequently, wastewater from dye processing companies is discharged into the environment after the dyeing process, leading to water resource pollution. Research suggests that the release of colored wastewater disrupts oxygen dispersion and self-purification mechanisms within aquatic systems [9–11]. The presence of a visible colored layer forms on the water surface when mixed with a water source due to its lower density compared to water. This layer hinders sunlight penetration through the water surface, impeding photosynthesis and respiration processes of underwater organisms [12,13]. The emergence of another group of pollutants in water has been attributed to the commercialization and usage of antibiotics for treating bacterial infections. Approximately 90% of antibiotic active components enter the environment through excretion via urine and feces [14]. Antibiotic contamination poses a global challenge due to potential health issues associated with excessive exposure, which can lead to antibiotic resistance [15]. Research reports have indicated that urban surface water sources, groundwater reservoirs, drinking water supplies,

* **Corresponding author: Fuhua Wei**, College of Chemistry and Chemical Engineering, Anshun University, Anshun, 561000, Guizhou, China, e-mail: wfh.1981@163.com

* **Corresponding author: Zhao Liang**, Institute of Micro/Nano Materials and Devices, Ningbo University of Technology, Ningbo, 315211, China, e-mail: walleliang@163.com

Yan Wang, Qinhui Ren, Qin Zhang, Hongliang Chen: College of Chemistry and Chemical Engineering, Anshun University, Anshun, 561000, Guizhou, China

and wastewater are all contaminated by antibiotics [16]. Therefore, effective strategies need to be implemented for eliminating antibiotics from natural aquatic environments.

A variety of methods is available for removing pollutants from wastewater, including membrane filtration [17], biological treatment [18], adsorption [19], electrochemical treatment [20], advanced oxidation technology [21], among others. However, traditional approaches such as coagulation and filtration have certain drawbacks such as high maintenance costs and operational inconvenience [22]. In contrast, adsorption-based techniques offer potential advantages in terms of cost-effectiveness, energy efficiency, and solution efficacy for pollutant remediation [23]. Recently developed highly efficient adsorbents address these limitations while also meeting the criteria of environmental sustainability and economic viability. One promising class of materials is metal-organic frameworks (MOFs), which possess a large specific surface area [24] and a tunable pore structure that makes them versatile for applications in storage [25,26], sensing [27], separation processes [28], biomedicine [29], and catalysis [30,31]. Among the reported MOFs used for environmental antibiotic treatment, norfloxacin and doxycycline hydrochloride were effectively removed using Zr-MOFs synthesized with 2,5-dihydroxy terephthalic acid and 2-amino-terephthalic acid, respectively. The adsorption capacities of these MOFs reached 134.5 and 148.7 mg·g⁻¹ [32,33]. Additionally, a bimetallic MOF material Cu/Co-MOFs was utilized to remove doxycycline hydrochloride with a maximum adsorption capacity of 268.5 mg·g⁻¹ [34].

Due to the limited removal efficiency of monomer MOFs, precise control over the structure and function of bimetallic MOFs can be achieved by modifying metal nodes and organic ligands to meet diverse application requirements. Moreover, bimetallic MOFs demonstrate a synergistic effect in pollutant removal, thereby enhancing the effectiveness of MOF-based pollutant elimination.

The objective of this study was to create functional materials and utilize them for the degradation of organic pollutants, with a specific focus on fleroxacin and Rhodamine B (RhB). To achieve this, Cr/Co-MOFs was synthesized by combining cobalt chloride hexahydrate and chromium acetate as metal precursors, along with 1,3,5-benzoic acid as the organic linker. Subsequently, these Cr/Co-MOFs were employed for effectively eliminating organic pollutants.

2 Experiment

2.1 Experimental material

In the conducted experiment, ligands such as fleroxacin (98%, obtained from Shanghai Aladdin Biochemical

Technology Co., Ltd), RhB (analytical reagent (AR), provided by Shanghai McLean Biochemical Technology Co., Ltd), and 1,3,5-benzoic acid (98%, supplied by Shanghai Meryer Biochemical Technology Co., Ltd) were utilized. Metal sources including chromium acetate (AR, supplied by Shanghai Yien Chemical Technology Co., Ltd) and cobalt chloride hexahydrate (AR, obtained from Shanghai Aladdin Biochemical Technology Co., Ltd) were employed.

2.2 Preparation of Cr/Co-MOFs materials

The experimental procedure is illustrated in Figure 1. A total of 0.3000 g (0.0014 mol) of 1,3,5-benzoic acid, 0.3271 g (0.0014 mol) of chromium acetate, and 0.3397 g (0.0014 mol) of cobalt chloride hexahydrate were precisely weighed and placed in three separate small beakers with a capacity of 50 mL each, along with 10 mL of *N,N*-dimethylformamide (DMF) as the organic solvent. The mixture was completely dissolved using an ultrasonic cleaning machine before being transferred to a reaction kettle and subjected to constant temperature drying at 120°C for a duration of 12 h. After the reaction was complete, the mixture was cooled down to room temperature and filtered to obtain Cr/Co-MOFs product, which underwent three rounds of washing using DMF and distilled water separately. Following filtration, the resulting product was dried at 60°C for an additional period of 12 h in a drying oven to yield Cr/Co-MOFs.

2.3 Removal of fleroxacin and RhB by Cr/Co-MOFs materials

The adsorption performance of Cr/Co-MOF toward organic pollutants was investigated by selecting fleroxacin and RhB as target molecules at room temperature (approximately 15°C) and within a pH range of 6–8. Different quantities (20, 30, 50, 100 mg) of Cr/Co-MOFs were introduced into solutions containing varying concentrations (10, 30, 50 mg·L⁻¹) of fleroxacin. Similarly, various quantities (30, 50, 100 mg) of Cr/Co-MOFs were added to solutions with different concentrations (20, 30, 50 mg·L⁻¹) of RhB. The mixtures were gently stirred under ambient light conditions. At regular intervals of every half an hour, samples were collected and the concentrations of both fleroxacin and RhB in the solutions were analyzed using an ultraviolet spectrometer. The calculation formula used for analysis remained unchanged.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

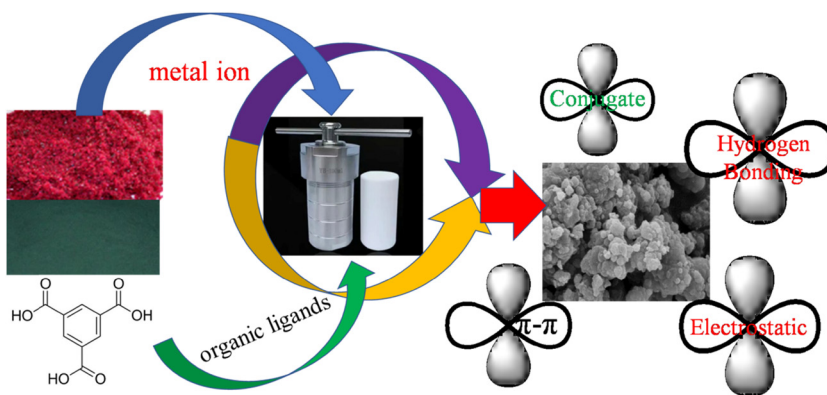


Figure 1: The experimental procedure.

$$\text{Removal rate (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

where C_0 denotes the initial concentration of feroxacin (RhB), C_e represents the concentration at adsorption equilibrium, C_t signifies the concentration at a specific time point t , V indicates the volume of the solution, and m corresponds to the mass of Cr/Co-MOFs.

3 Results and discussion

Based on the Fourier infrared spectroscopy (FT-IR) diagram (Figure 2), we observed two prominent bands at 1561 and 1374 cm^{-1} , indicating the equivalent state of the two carboxyl groups after delocalization. These bands are indicative of the reaction between metal ions and carboxyl groups. It is important to note that previous studies have

reported that the antisymmetric stretching vibration of carboxyl groups typically occurs within the range of 1,610–1,560 cm^{-1} , while symmetric stretching vibration appears within the range of 1,420–1,300 cm^{-1} [35,36]. The absorption peak at 1,105 cm^{-1} corresponds to C–O bond stretching vibration, whereas the peak at 722 and 765 cm^{-1} suggests substitution on benzene ring. Additionally, when analyzing the X-ray diffraction (XRD) pattern (Figure 3) and scanning electron microscopy (SEM) (Figure 4), we observed a well-defined morphology and structure with excellent dispersion in Co/Cr-MOFs. This high crystallinity can be attributed to weakened or even eliminated intermolecular interactions among organic ligands, which facilitates crystal growth in solvents.

The Thermogravimetry (TG) method is used to investigate the relationship between temperature and mass changes of a substance. As depicted in Figure 5, Co/Cr-MOFs can be divided into two distinct stages within the temperature

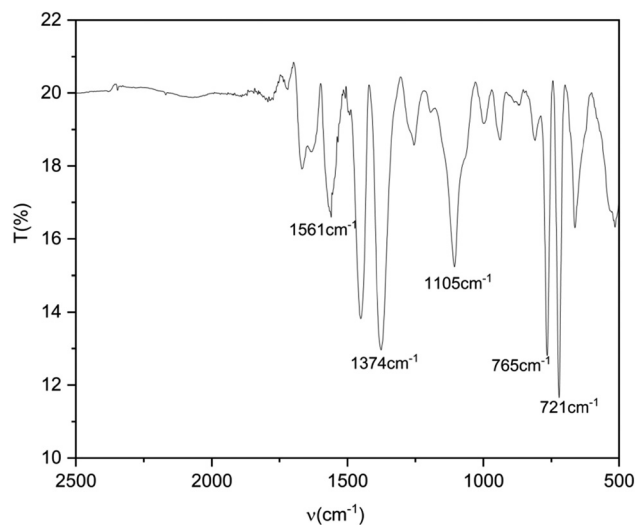


Figure 2: Infrared spectroscopy of Cr/Co-MOFs.

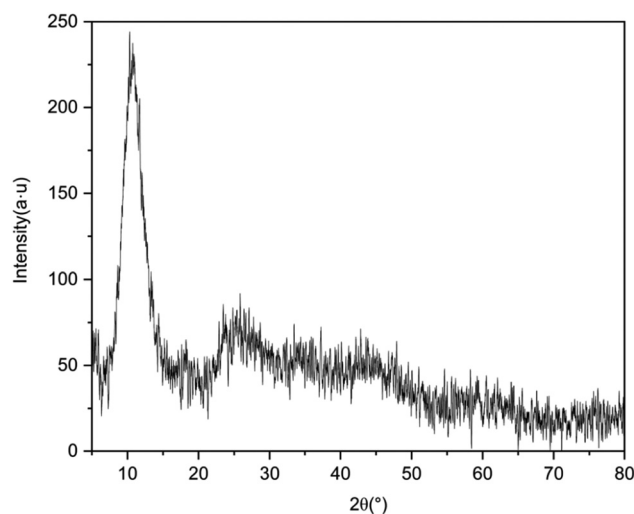


Figure 3: XRD analysis of Cr/Co-MOFs.

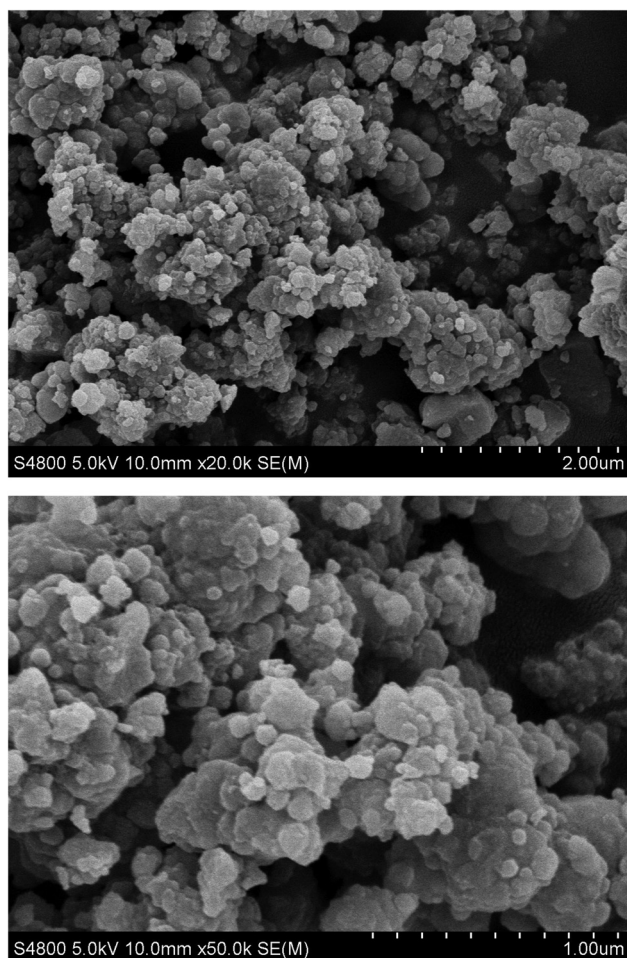


Figure 4: SEM analysis of Cr/Co-MOFs.

range of 800°C. In the initial stage, below 140°C, there is primarily evaporation of solvent molecules from the Co/Cr-MOFs

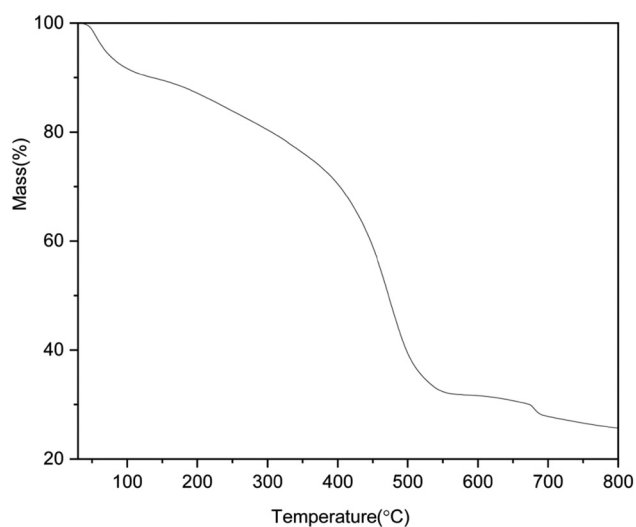


Figure 5: Thermogravimetric analysis of Cr/Co-MOFs.

sample, resulting in approximately a 10% reduction in weight. Subsequently, starting at around 350°C and continuing until about 560°C, there is significant collapse of the framework structure with complete degradation of its main constituents while retaining approximately 32% residual content. This figure illustrates that Co/Cr-MOFs exhibit exceptional stability prior to reaching temperatures above 350°C without any noticeable structural deterioration.

3.1 Adsorption of fleroxacin and RhB by Co/Cr-MOFs

In this study, the adsorption properties of Co/Cr-MOFs on organic pollutants were investigated with fleroxacin and RhB as individual target molecules. The experimental parameters, including the quantity of Co/Cr-MOFs, the

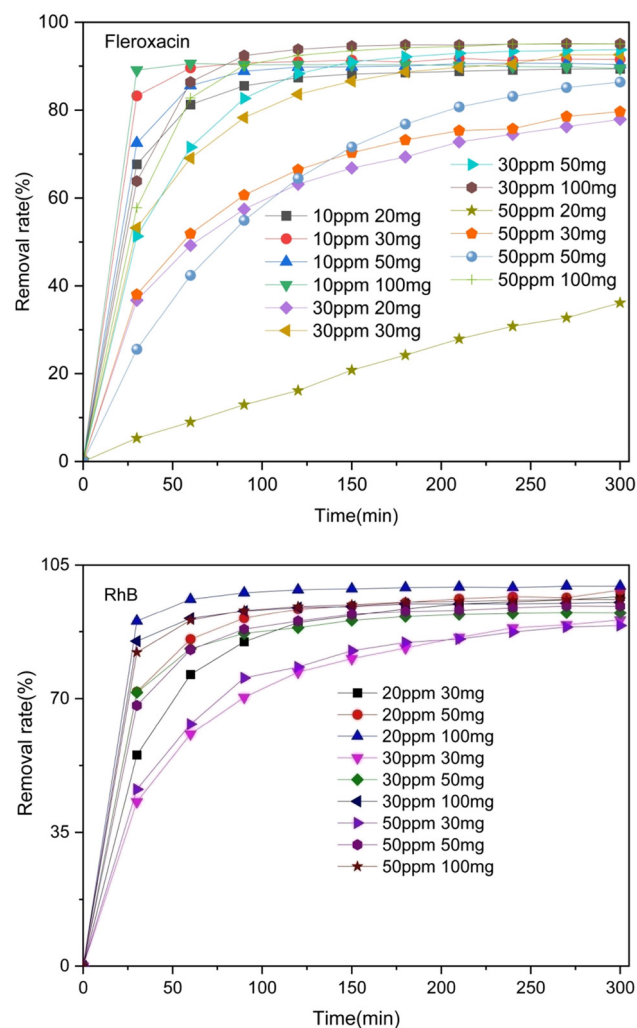


Figure 6: Reactivity of Co/Cr-MOFs toward the removal of organic pollutants.

concentration of organic pollutants, and the reaction duration, were systematically investigated. As shown in Figure 6, a removal rate of 95% was achieved for fleroxacin when using 100 mg of Co/Cr-MOFs with a concentration of 30 ppm. Similarly, a removal rate of 99% was obtained for RhB when using 100 mg of Co/Cr-MOFs with a concentration of 20 ppm. Furthermore, our experimental results indicate that increasing the amount of Co/Cr-MOFs resulted in higher removal rates for both compounds under constant concentrations. Conversely, keeping the amount constant while decreasing the concentrations led to an increasing trend in removal rate due to enhanced exposure and participation at active sites during adsorption processes. Additionally, decreased concentrations weakened competitive adsorption and allowed more molecules to be adsorbed at each active site.

3.2 Adsorption kinetics of fleroxacin and RhB by Co/Cr-MOFs

To further elucidate the mechanism underlying the elimination of fleroxacin and RhB by Co/Cr-MOFs, we employed two simulation models to gain a better understanding of the process. These models are based on different assumptions and formulas that accurately depict the changes in concentrations of fleroxacin and RhB during adsorption. The kinetic equation is presented as follows:

$$\ln C_t/C_0 = k_1 t \quad (3)$$

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

$$q_t = k_3 t^{1/2} \quad (5)$$

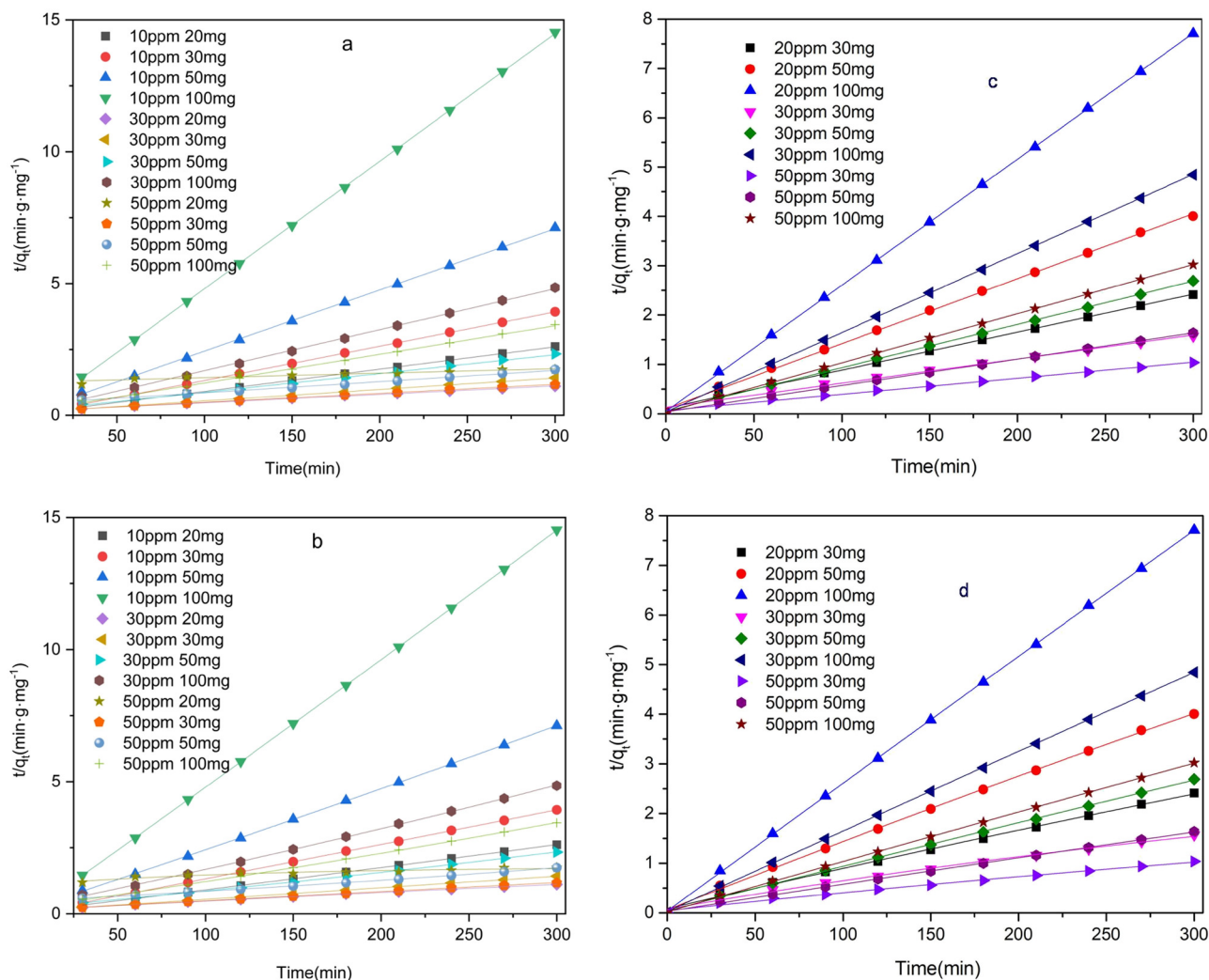


Figure 7: Pseudo-second-order kinetic model for the removal of organic pollutants using Co/Cr-MOFs: (a and b) fleroxacin; (c and d) RhB; (a and c) linear; (b and d) non-linear.

where the variables C_t , C_0 , k_1 , and k_2 , represent the levels of feroxacin and RhB at a given time point (t), the initial concentrations of feroxacin and RhB, the rate constants (expressed in minutes) for kinetic reactions, and the duration of the reaction (also expressed in minutes), respectively. The terms q_t and q_e refer to the concentrations (measured in $\text{mg}\cdot\text{g}^{-1}$) of the adsorbent material at a specific time point (t) and when equilibrium is reached.

As shown in Figures 7–9 and Tables 1–5, the second kinetics of feroxacin and RhB adsorption by Co/Cr-MOFs exhibit higher R^2 values compared to the first kinetics. This indicates a strong agreement between simulation and experiment. It suggests that the adsorption kinetics of feroxacin and RhB by Co/Cr-MOFs adhere to both linear and nonlinear aspects of the second kinetic model.

3.3 Investigation of the isothermal adsorption kinetics of feroxacin and RhB using Co/Cr-MOFs

The Langmuir and Freundlich isotherm models were employed to analyze the experimental results. As shown in Figure 10 and Table 6, when 100 mg of Co/Cr-MOFs was added to feroxacin at a concentration of 50 ppm, the analysis based on the Langmuir and Freundlich models yielded parameters presented in Table 5, resulting in R^2 values of 0.9749 and 0.3236, respectively. Similarly, for RhB at a concentration of 50 ppm with an addition of 30 mg Co/Cr-MOFs, both models provided parameters displayed in the table along with corresponding R^2 values of 0.9763 and 0.9874, respectively. These results indicate that Co/Cr-MOFs exhibit a preference for adhering to the Langmuir model when removing both feroxacin and RhB.

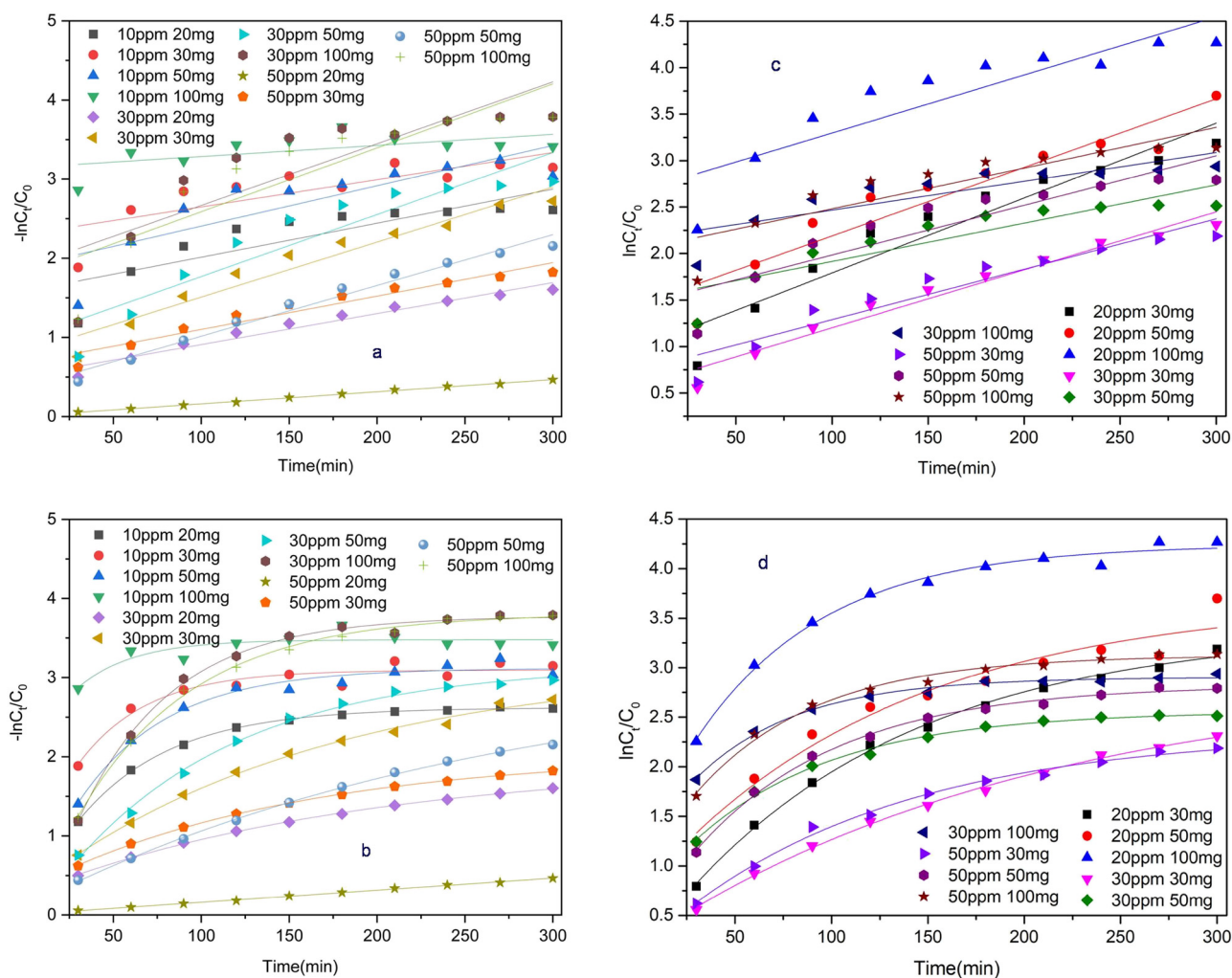


Figure 8: Pseudo-first-order kinetic model for the removal of organic pollutants using Co/Cr-MOFs: (a and b) feroxacin; (c and d) RhB; (a and c) linear; (b and d) non-linear.

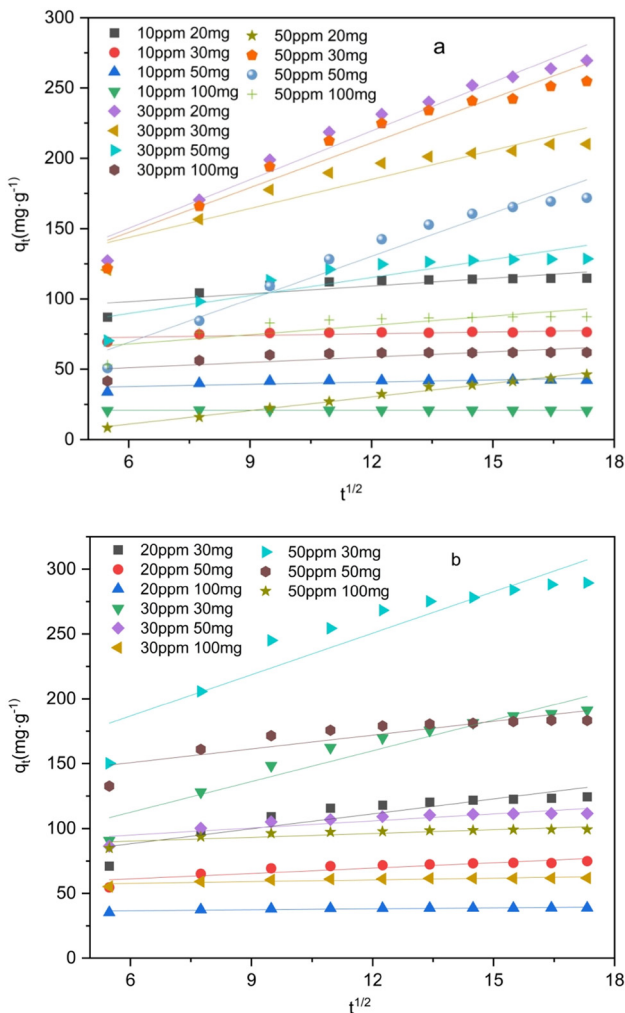


Figure 9: The intraparticle diffusion (IPD) kinetics model for the removal of organic pollutants using Co/Cr-MOFs: (a) fleroxacin; (b) RhB.

3.4 Influence of pH on the adsorption behavior of fleroxacin and RhB onto Co/Cr-MOFs

The pH variations do not affect the adsorption of fleroxacin by Co/Cr-MOFs, as shown in Figure 11. However, the adsorption of RhB gradually decreases with increasing pH levels. This can be mainly attributed to structural changes in both fleroxacin and Rh.

3.5 Influence of temperature on the adsorption behavior of fleroxacin and RhB onto Co/Cr-MOFs

The adsorption capacity of Co/Cr-MOFs for fleroxacin and RhB gradually decreases as the temperature increases. This can be attributed to the increased molecular movement at higher temperatures, which leads to a greater chance of collisions with Co/Cr-MOFs and subsequent escape of more molecules, resulting in reduced adsorption. Additionally, elevated temperatures increase the internal energy of molecules, making it easier for them to detach from the surface of Co/Cr-MOFs and consequently reducing their adsorption capacity. To further investigate the influence of temperature, 100 mg of Co/Cr-MOFs were introduced into solutions with varying temperatures containing fleroxacin at a concentration of 50 ppm; similarly, 30 mg of Co/Cr-MOFs were added to solutions with different temperatures containing RhB at a concentration of 50 ppm. These experimental conditions were compared against

Table 1: Kinetic parameters for the adsorption of RhB over the Co/Cr-MOFs (linear)

| Concentration (ppm) (±5%) | Mass (mg) (±1%) | Pseudo-second-order (PSO) model | | Pseudo-first-order (PFO) model | | $q_{\text{max,exp}}$ (mg·g ⁻¹) |
|---------------------------|-----------------|--|--------|--------------------------------|--------|--|
| | | K_2 (g·mg ⁻¹ ·min ⁻¹) | R^2 | K_1 (L·min ⁻¹) | R^2 | |
| 20 | 30 | 0.02076 | 0.9960 | 0.43836 | 0.9062 | 124.5 |
| | 50 | 0.01714 | 0.9988 | 0.4425 | 0.8891 | 74.9 |
| | 100 | 0.00406 | 0.9999 | 0.75364 | 0.7673 | 38.9 |
| 30 | 30 | 0.02564 | 0.9880 | 0.10306 | 0.9611 | 191.2 |
| | 50 | 0.00464 | 0.9993 | 0.30631 | 0.7798 | 111.6 |
| | 100 | 0.00235 | 0.9999 | 0.27228 | 0.6899 | 61.9 |
| 50 | 30 | 0.007 | 0.9926 | 0.21495 | 0.8990 | 289.5 |
| | 50 | 0.00255 | 0.9989 | 0.46649 | 0.7971 | 183.3 |
| | 100 | 0.00173 | 0.9998 | 0.40744 | 0.7505 | 99.3 |

Table 2: Kinetic parameters for the adsorption of fleroxacin over the Co/Cr-MOFs (linear)

| Concentration (ppm) ($\pm 5\%$) | Mass (mg) ($\pm 1\%$) | PSO model | | PFO model | | $q_{\max, \exp}$ (mg·g ⁻¹) |
|-----------------------------------|-------------------------|--|--------|------------------------------|--------|--|
| | | K_2 (g·mg ⁻¹ ·min ⁻¹) | R^2 | K_1 (L·min ⁻¹) | R^2 | |
| 10 | 20 | 0.0084 | 0.9997 | 0.0043 | 0.6725 | 124.5 |
| | 30 | 0.0129 | 0.9999 | 0.0034 | 0.5910 | 74.9 |
| | 50 | 0.0232 | 0.9997 | 0.0051 | 0.6610 | 42.3 |
| | 100 | 0.0483 | 0.9999 | 0.0014 | 0.2774 | 38.9 |
| 30 | 20 | 0.0032 | 0.9989 | 0.0039 | 0.9570 | 191.2 |
| | 30 | 0.0043 | 0.9997 | 0.0069 | 0.9415 | 210.1 |
| | 50 | 0.0071 | 0.9980 | 0.0078 | 0.8481 | 111.6 |
| | 100 | 0.0155 | 0.9986 | 0.1178 | 0.6811 | 61.9 |
| 50 | 20 | 0.0016 | 0.8495 | 0.0015 | 0.9976 | 289.5 |
| | 30 | 0.0034 | 0.9995 | 0.0042 | 0.9328 | 183.3 |
| | 50 | 0.0042 | 0.9966 | 0.0064 | 0.9763 | 171.8 |
| | 100 | 0.0108 | 0.9982 | 0.0080 | 0.7590 | 99.3 |

Table 3: Kinetic parameters for the adsorption of fleroxacin over the Co/Cr-MOFs (nonlinear)

| Concentration (ppm) ($\pm 5\%$) | Mass (mg) ($\pm 1\%$) | PSO model | | PFO model | |
|-----------------------------------|-------------------------|--|--------|------------------------------|--------|
| | | K_2 (g·mg ⁻¹ ·min ⁻¹) | R^2 | K_1 (L·min ⁻¹) | R^2 |
| 10 | 20 | | 0.9999 | | 0.9989 |
| | 30 | | 0.9999 | | 0.9323 |
| | 50 | | 0.9999 | | 0.9754 |
| | 100 | | 0.9999 | | 0.7475 |
| 30 | 20 | | 0.9997 | | 0.9990 |
| | 30 | | 0.9997 | | 0.9939 |
| | 50 | | 0.9998 | | 0.9957 |
| | 100 | | 0.9995 | | 0.9954 |
| 50 | 20 | | 0.8909 | | 0.9973 |
| | 30 | | 0.9995 | | 0.9995 |
| | 50 | | 0.9998 | | 0.9989 |
| | 100 | | 0.9993 | | 0.9972 |

normal temperature conditions. The enthalpy change and entropy change were determined using the van't Hoff equation as follows:

$$\ln K_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

$$\Delta G^0 = -RT \ln K_0 \quad (7)$$

Table 4: Kinetic parameters for the adsorption of RhB over the Co/Cr-MOFs (nonlinear)

| Concentration (ppm) ($\pm 5\%$) | Mass (mg) ($\pm 1\%$) | PSO model | | PFO model | |
|-----------------------------------|-------------------------|--|--------|------------------------------|---------|
| | | K_2 (g·mg ⁻¹ ·min ⁻¹) | R^2 | K_1 (L·min ⁻¹) | R^2 |
| 20 | 30 | | 0.9962 | | 0.9963 |
| | 50 | | 0.9991 | | 0.9490 |
| | 100 | | 0.9999 | | 0.9886 |
| 30 | 30 | | 0.9921 | | 0.9972 |
| | 50 | | 0.9993 | | 0.9941 |
| | 100 | | 0.9999 | | 0.9916 |
| 50 | 30 | | 0.9939 | | 0.9934 |
| | 50 | | 0.9990 | | 0.9964 |
| | 100 | | 0.9998 | | 0.99012 |

Table 5: IPD kinetic parameters for the adsorption of RhB and fleroxacin over the Co/Cr-MOFs

| Fleroxacin | | | | RhB | | | |
|------------------------------|--------------------|--|---------|------------------------------|--------------------|--|---------|
| Concentration (ppm) (±5%) | Mass (mg) (±1%) | K_3 (g·mg ⁻¹ ·min ^{-0.5}) | R^2 | Concentration (ppm) (±5%) | Mass (mg) (±1%) | K_3 (g·mg ⁻¹ ·min ^{-0.5}) | R^2 |
| 10 | 20 | 1.85421 | 0.65133 | 20 | 30 | 3.83061 | 0.77507 |
| | 30 | 0.41626 | 0.51984 | | 50 | 1.38296 | 0.76014 |
| | 50 | 0.51866 | 0.54236 | | 100 | 0.23834 | 0.66434 |
| | 100 | 0.0008621 | 0.12387 | 30 | 30 | 7.90029 | 0.90911 |
| 30 | 20 | 11.52947 | 0.95393 | | 50 | 1.80934 | 0.76137 |
| | 30 | 6.88934 | 0.85795 | | 100 | 0.44795 | 0.70141 |
| | 50 | 4.29133 | 0.75248 | 50 | 30 | 10.65078 | 0.85003 |
| | 100 | 1.25441 | 0.53433 | | 50 | 3.54438 | 0.73096 |
| 50 | 20 | 3.22826 | 0.98994 | | 100 | 0.97485 | 0.70014 |
| | 30 | 10.58875 | 0.92429 | | | | |
| | 50 | 10.22471 | 0.9506 | | | | |
| | 100 | 2.20339 | 0.59957 | | | | |

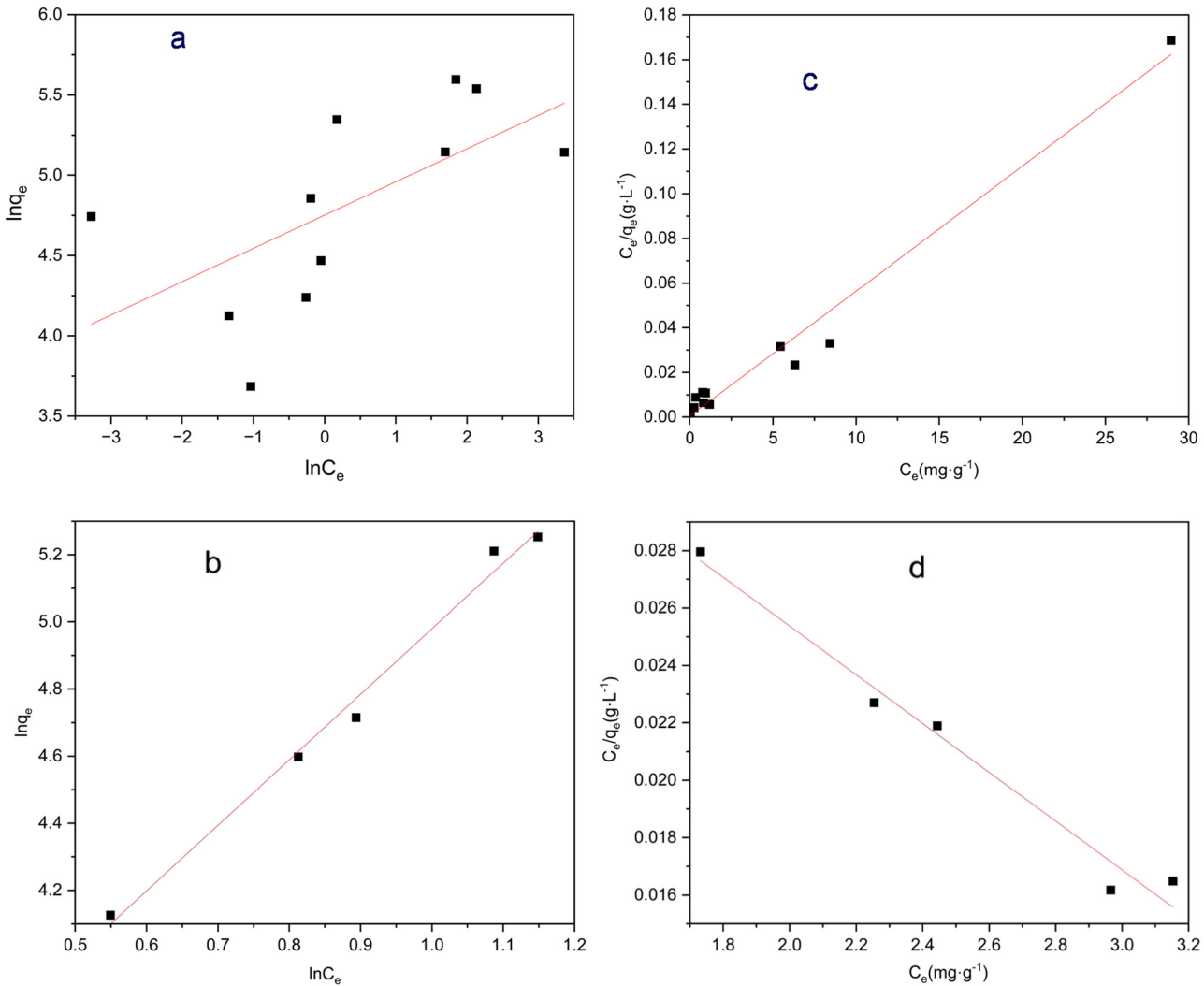


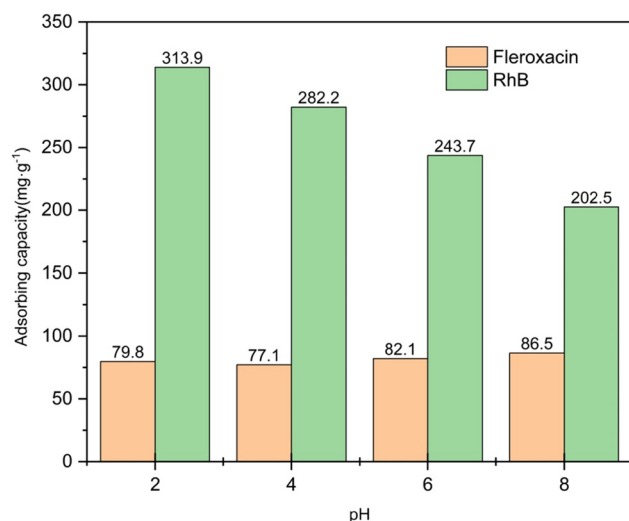
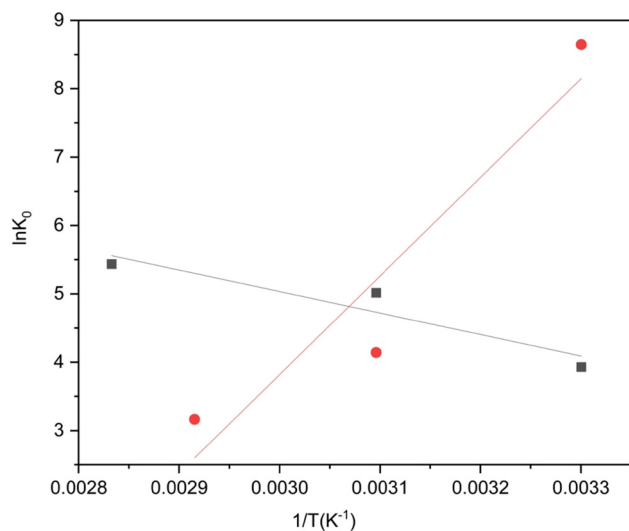
Figure 10: Isothermal modeling of organic pollutant removal by Co/Cr-MOFs: (a and c) fleroxacin; (b and d) RhB; (a and b) Freundlich isotherm; (c and d) Langmuir isotherm.

Table 6: Summary of Langmuir and Freundlich isotherm constants pollution by Co/Cr-MOFs

| Adsorbent | Langmuir isotherm | | Freundlich isotherm | |
|------------|-----------------------|--------|---------------------|--------|
| | K | R^2 | $1/n$ | R^2 |
| Fleroxacin | 5.59×10^{-6} | 0.9749 | 0.2072 | 0.3236 |
| RhB | -0.0085 | 0.9763 | 1.9528 | 0.9874 |

Table 7: Van't Hoff parameters of organic pollution adsorption onto Co/Cr-MOFs (20°C)

| Pollutant | ΔG° (kJ·mol ⁻¹) | ΔH° (-slope $\times R$) (kJ·mol ⁻¹) | S° (intercept $\times R$) (J·mol ⁻¹ ·K ⁻¹) |
|------------|---|--|--|
| Fleroxacin | -9.15 | 26.1 | 120.3 |
| RhB | -23.8 | -119.8 | -327.7 |

**Figure 11:** Influence of pH on the adsorption behavior of organic pollutants by Co/Cr-MOFs.**Figure 12:** Influence of temperature on the adsorption behavior of organic pollutants by Co/Cr-MOFs.

$$K_0 = \frac{q_e}{c_e} \quad (8)$$

Table 8: Comparative analysis of RhB adsorption using various adsorbents

| Adsorbent | q_{\max} | pH | Ref. |
|---|------------|------|-----------|
| <i>Azolla pinnata</i> | 199.7 | 3.6 | [39] |
| Zeolitic imidazolate frameworks | 85 | 10< | [40] |
| <i>Casuarina equisetifolia</i> cone powder | 49.5 | 2 | [41] |
| Bi ₂ O ₃ -bentonite nanocomposite | 69 | 3 | [42] |
| Dowex 5WX8 resin | 43.4 | 2.8 | [43] |
| Aleurites Moluccana waste seeds | 117 | 6 | [44] |
| Activated sugar-based carbon | 123.4 | 2–11 | [45] |
| <i>Casuarina equisetifolia</i> needles | 82.3 | 4.4 | [46] |
| Co/Cr-MOFs | 313.9 | 2 | This work |

The experimental results presented in Figure 12 and Table 7 reveal that the adsorption behavior of RhB on Co/Cr-MOFs is characterized by an exothermic nature and a non-spontaneous process. On the other hand, the adsorption of fleroxacin on Co/Cr-MOFs is found to be exothermic and spontaneous. The mechanism underlying this adsorption process involves a combination of physical and chemical processes, with an enthalpy change exceeding 84 kJ·mol⁻¹ primarily attributed to chemisorption. Physical adsorption is indicated for enthalpy changes below 84 kJ·mol⁻¹ [37,38]. Hence, it can be inferred that fleroxacin predominantly undergoes chemisorptive adsorption on Co/Cr-MOFs while RhB mainly experiences physical adsorption.

In brief, the adsorption capacity of Co/Cr-MOFs on organic pollutants was assessed by employing a kinetic model that incorporates the isothermal equation and van't Hoff equation, in conjunction with Table 8. The adsorption characteristics of Co/Cr-MOFs toward fleroxacin and RhB can be described as follows: First, based on our observations from adsorption and desorption experiments under an N₂ atmosphere, it is evident that Co/Cr-MOFs possess a significant specific surface area and pore size that enable simultaneous adsorption of both fleroxacin and RhB. Additionally, hydrogen bonding may also play a role in the interaction between Co/Cr-MOFs and these compounds. Furthermore, pH-dependent studies have revealed potential free groups on the surface of Co/Cr-MOFs that facilitate electrostatic interactions

with both compounds. Moreover, taking into account the presence of benzene rings in both fleroxacin and RhB as well as aromatic rings in Co/Cr-MOFs; π - π bond formation could further enhance their affinity for each other. As a result, all these factors collectively contribute to the exceptional adsorption performance demonstrated by Co/Cr-MOFs toward fleroxacin and RhB [47–50].

4 Conclusion

The Co/Cr-MOFs material was successfully synthesized using the solvothermal method, and its morphology and structure were characterized through XRD, SEM, FTIR, and TG techniques. Afterwards, we utilized the as-characterized Co/Cr-MOFs material to efficiently remove fleroxacin and RhB. Through systematic variations in the mass of Co/Cr-MOFs material, concentration of fleroxacin and RhB in solution, as well as pH conditions during adsorption experiments, the experimental findings clearly demonstrate that Co/Cr-MOFs exhibit impressive adsorption capacities toward fleroxacin ($269.6 \text{ mg}\cdot\text{g}^{-1}$) and RhB ($313.9 \text{ mg}\cdot\text{g}^{-1}$) within a 5-h timeframe. The Co/Cr-MOFs exhibited removal efficiencies of 95.1% and 99.5% for fleroxacin and RhB, within a duration of 5 h, respectively. Moreover, the analysis of kinetic modeling reveals excellent agreement with the pseudo-second order kinetics model for the adsorption of both target pollutants onto Co/Cr-MOFs. Additionally, the Langmuir and Freundlich isotherm analyses indicate multi-layer adsorption for fleroxacin, while single-layer adsorption occurs for RhB on the surface of Co/Cr-MOFs materials. These collective results strongly emphasize the promising potential of utilizing Co/Cr-MOFs materials for effectively removing fleroxacin and RhB contaminants in practical applications.

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