



MOFs-derived porous Co-NC for rapid and high-capacity removal of nanoplastics

Kai Chen^{a,b}, Guanhong Lu^b, Xiaoyu Duan^b, Guanqing Song^{b,c}, Chi Song^{b,c}, Kaihuang Zhu^{a,b}, Yan Wang^b, Xiaofeng Xie^b, Jing Sun^{b,*}

^a School of Materials Science and Engineering, Shenyang University of Chemical Technology, Shenyang 110142, China

^b State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 585 Heshuo Road, Shanghai 201899, China

^c University of Chinese Academy of Sciences, 19 (A) Yuquan Road, Beijing 100049, China

ARTICLE INFO

Cintia Marangoni

Keywords:

Nanoplastics removal

Co-NC

MOFs

Magnetic extraction

ABSTRACT

Micro/Nano plastics (MPs/NPs), as an emerging pollutant, have been widely found in aquatic environments. They not only threaten the safety of water resources for human beings but also have adverse effects on the entire ecosystem. This article investigates the removal capacity of various porous carbon materials derived from MOFs for NPs, with Co-NC-800 exhibiting advantages such as rapid attachment to NPs with time less than 10 min, ultra-high adsorption capacity of $1057 \text{ mg} \cdot \text{g}^{-1}$, rapid magnetic extractability with time below 2 min, and reusability after five cycles with removal efficiency of 100 %. The zeta potential of aggregates (Co-NC after adsorbing NPs) positively correlated with removal efficiency at different pH with $R^2 = 0.9644$, indicating that electrostatic attraction plays a decisive role in adsorptions. The Pseudo-First-Order kinetic model fit well to demonstrate the ultra-fast NPs removal capacity of Co-NC-800. The Langmuir isotherm model was used to reflect the heterogeneous monolayer physical adsorption properties. The limited impact of competitive ions and successful removal of NPs in diverse water environments demonstrate the environmental suitability of Co-NC-800, meanwhile, its excellent reusability provide the possibility for its large-scale application.

1. Introduction

The extensive use of plastics and the deficient handling of plastic waste have led to a considerable build-up of plastic debris within global aquatic systems [1]. Plastic fragments undergo both physical disintegration and chemical degradation, culminating in the creation of MPs and NPs. MPs are categorized as plastic particles measuring less than 5 mm in diameter. While NPs are defined as plastic particles having a diameter of fewer than 1000 nm, based on their colloidal properties. NPs have a propensity to persist in natural environments for extended periods [2].

NPs can act as vectors for a range of pollutants, including heavy metals, antibiotics, and polycyclic aromatic hydrocarbons [3], facilitating their transit through the food chain and accumulation within various organisms [4]. Their ability to be taken up by cells and their similarity in size to cellular components can lead to bioaccumulation and subsequent biological toxicity [5]. Consequently, the removal of NPs from aqueous matrices is crucial to safeguarding both ecological

balance and human health.

Currently, research on the removal of MPs from water is not only limited in quantity but also most methods have inherent limitations. For instance, the water treatment method using Al and Fe-based salts for coagulation could eliminate $36.89 \pm 3.24 \%$ of MPs, but the required concentration greatly exceeds the safe limit of Al and Fe in drinking water [6]. Lares et al. [7] indicates that although a majority of MPs can be removed in the conventional activated sludge process and membrane bioreactors for wastewater treatment, the membrane bioreactors face a more severe challenge of membrane fouling during the treatment process. Additionally, the method of using electrospun polyacrylonitrile membranes for filtering NPs is not ideal in terms of cost-effectiveness [8]. In contrast, adsorption techniques represent a viable and effective strategy for the removal of a diversity of pollutants, notable for their low operational costs, high adsorption capacities and environmental compatibility. Researchers have introduced numerous innovative adsorbent materials, such as magnetite nanoparticles [9], MOFs [10], biochar [11], magnetic carbon nanotubes [12], activated carbon [13]

* Corresponding author.

E-mail address: jingsun@mail.sic.ac.cn (J. Sun).

<https://doi.org/10.1016/j.seppur.2025.132008>

Received 16 August 2024; Received in revised form 3 February 2025; Accepted 7 February 2025

Available online 15 February 2025

1383-5866/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

and sponge materials [14]. These adsorbents have recently attracted extensive attention. Wang et al. [15] modified biochar with Mg^{2+} and Zn^{2+} to produce porous carbon with high specific surface area ($265.47 \text{ m}^2/\text{g}$, $329.87 \text{ m}^2/\text{g}$) and large average pore diameter (3.83 nm), which exhibited excellent adsorption performance for polystyrene microplastics, reaching $374.57 \text{ mg}\cdot\text{g}^{-1}$. The enhanced adsorption of magnetic biochar is due to the synergistic effect of electrostatic interactions and van der Waals weak interactions. Experiments have shown that pH value is vital to the adsorption process, indicating that electrostatic interactions between magnetic biochar and pollutants are the primary adsorption mechanism.

Over the last two decades, numerous MOFs have been extensively researched for diverse applications, such as gas storage [16], adsorption separation [17], photocatalysis [18], ion exchange [19] and molecular recognition [20]. These applications rely on the reasonable structures of MOFs [21], uniform pore size distribution, rich Lewis acidic sites and high specific surface area [22]. MOFs exhibit attractive characteristics as a prospective adsorbent for eliminating NPs from water matrices.

Modak et al. [10] developed a Cr-MOF for eliminating polystyrene nano plastics with sizes of $50\text{--}70 \text{ nm}$, achieving a maximum adsorption capacity of up to $800 \text{ mg}\cdot\text{g}^{-1}$, with a decrease in adsorption efficiency of 20 % after four cycles. Cr-MOF exhibited a high specific surface area of $2281.8 \text{ m}^2/\text{g}$ and an average pore size of 2.91 nm . At pH values above 5, a direct proportionality between zeta potential and adsorption efficiency was observed, confirming that the primary driving force for adsorption is electrostatic interaction. Pedrero et al. [23] designed a mesoporous UiO-66 for the removal of 30 nm polystyrene NPs. Mesoporous UiO-66 modified with hexadecyl trimethyl ammonium bromide (CTAB) showed a mesoporous volume of $134 \text{ cm}^3/\text{g}$ and a zeta potential of $32.6 \pm 1.7 \text{ mV}$, with an adsorption efficiency of 40.5 % for NPs. The mesoporous UiO-66 modified with polyethylene oxide–polypropylene oxide–polyethylene oxide (P123) had a mesoporous volume of $683 \text{ cm}^3/\text{g}$ and a zeta potential of $10.5 \pm 2.2 \text{ mV}$, with an adsorption efficiency of 39.9 % for NPs. The comparison of these two materials demonstrated the irreplaceable role of mesoporous volume in the adsorption of nano plastics. The authors suggested that the expanded mesoporous volume provides sufficient active sites for the adsorption of NPs. Liu et al. [24] developed four Zr-MOFs materials for the adsorption of amoxicillin in wastewater and investigated the effects of functional groups on adsorption and the adsorption mechanism. UiO-66- NH_2 exhibited the highest adsorption capacity of $2.3 \pm 0.4 \text{ mg}\cdot\text{g}^{-1}$, and spectroscopic analysis and Materials Studio simulations revealed that UiO-66- NH_2 has different adsorption mechanisms for amoxicillin at various pH levels. Ahmadijokani et al. [25] utilized UiO-66 to adsorb four different dyes—methyl red (MR), methyl orange (MO), malachite green (MG), and methylene blue (MB)—from wastewater, with maximum adsorption capacities of 384, 454, 133 and $370 \text{ mg}\cdot\text{g}^{-1}$, respectively. Adsorption mechanism studies suggested that the adsorption of dyes on UiO-66 might be due to electrostatic interactions, π - π stacking, hydrogen bonding, and pore entrapment. The stability of UiO-66 in water was studied over a one-year period, and after retrieval, the crystal structure of UiO-66 remained unchanged, demonstrating its excellent water stability.

Although adsorbents have shown potential in removing MPs, challenges such as low adsorption capacity, slow adsorption rates, and the difficulty in recovering the adsorbents have yet to be addressed. Therefore, it is of great importance to design adsorbents that are both eco-friendly and efficient to remove NPs from water environments. Additionally, the adsorption mechanisms of most adsorbent materials for microplastics are not clear, and it is important to disclose the adsorption mechanisms of adsorbents for microplastics.

Therefore, this work designs a porous magnetic Co-NC derived from MOFs, which effectively addresses the issue of MOFs decomposing in aqueous solutions by thermally decomposing them into carbon materials at high temperatures, thus avoiding secondary pollution to the environment. Compared to other materials, Co-NC inherits the high specific

surface area and porous characteristics of the MOFs precursors, possessing more adsorption active sites, which can effectively increase the adsorption capacity for NPs. During the decomposition process, the volatilization of N and O elements promotes the formation of metal defects, which helps to create more acidic sites and increase the surface potential, thereby enhancing the adsorption capacity and rate for NPs. Bimetallic MOFs have better electron transfer properties, which may facilitate electrostatic adsorption between MOFs and NPs. The reduction of Co^{2+} to Co^0 during the pyrolysis process endows the material with a magnetism, allowing it to be completely removed by an external magnetic field without any negative impact on the environment. Unfortunately, the material designed in this study still has high energy consumption and pollution issues during the preparation and cycling process, such as the synthesis of MOFs needing to be completed in methanol, the pyrolysis requiring high-temperature calcination at 800°C in a nitrogen atmosphere, and the material needing to be washed in an alkaline aqueous environment under ultrasound for cyclic regeneration. The primary goals of this study are: i) Explore the ability of MOF derivatives to remove NPs. ii) Disclose the impact of various environmental factors on NPs removal and assess their environmental suitability. iii) Deeply explore the adsorption mechanism of Co-NC on NPs through systematic analytical methods.

2. Experimental preparation

2.1. Chemicals and materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 99 %), cobaltous nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 99.9 %), 2-methylimidazole (2-Meim, $\text{C}_4\text{H}_6\text{N}_2$, 98 %), methanol (MeOH , CH_3OH , 99.5 %), calcium chloride (CaCl_2 , 99 %), polystyrene nanoplastics (PSNPs, 5 %w/v) with diameter of $0.5\text{--}1.0 \mu\text{m}$, magnesium chloride hexahydrate ($\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, 98 %), were acquired from Adamas Corporation (Shanghai, China). Sodium hydroxide (NaOH), sodium phosphate tribasic anhydrous (Na_3PO_4), potassium chloride (KCl) sodium nitrate (NaNO_3) were obtained from China Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid (HCl , 36–38 %), sodium chloride (NaCl , 99.5 %) and sodium sulfate (Na_2SO_4 , 99.5 %) were bought from Shanghai General reagent Technology Co., Ltd. Deionized water (DI , H_2O) was sourced from the Milli-Q system, produced by Shanghai Tongdi Scientific Instruments Co., Ltd. All chemicals employed in the study were of analytical purity.

2.2. Sample preparation

2.2.1. Synthesis of ZIF-67

Solution A is prepared by dissolving 30 mmol of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 100 ml of MeOH, while solution B is prepared by dissolving 26.33 mmol of 2-Meim in 100 ml of MeOH. Under rapid stirring at room temperature, solution A is added evenly and slowly to solution B and the rotation speed is adjusted to 500 rpm after complete addition. After 24 h, the obtained suspension was centrifuged at a speed of 8000 rpm for 10 min. Subsequently, it was washed thrice with MeOH before being dried for 12 h at 80°C to yield ZIF-67.

2.2.2. Synthesis of Zn: Co = 1: 1 – ZIF

Solution A is prepared by dissolving 15 mmol of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 15 mmol of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 100 ml of MeOH, while solution B is prepared by dissolving 26.33 mmol of 2-Meim in 100 ml of MeOH. The other steps are the same as the synthesis of ZIF-67. The obtained sample is Zn: Co = 1: 1-ZIF.

2.2.3. Synthesis of Zn: Co = 1: 2 – ZIF

Solution A is prepared by dissolving 10 mmol of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and 20 mmol of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 100 ml of MeOH, while solution B is prepared by dissolving 26.33 mmol of 2-Meim in 100 ml of MeOH. The other steps are the same as the synthesis of ZIF-67. The obtained sample

is Zn: Co = 1: 2-ZIF.

2.2.4. Preparation of MOF derivatives

The ZIF-67, Zn: Co = 1: 1-ZIF, Zn: Co = 1: 2-ZIF obtained was calcined in a tubular furnace in nitrogen atmosphere at different temperatures (700, 800, 900 °C) for 2 h. The heating rate was 5 °C·min⁻¹. After being cooled naturally, the adsorbent was labeled as Co-NC-(700, 800, 900), Zn: Co = 1: 1-NC-(700, 800, 900), Zn: Co = 1: 2-NC-(700, 800, 900) respectively.

2.3. Material characterization

The surface morphology, crystallinity, thermal stability, structural defect content, and specific surface area of Co-NC-(700, 800, 900) were characterized. To further comprehend the adsorption mechanism of Co-NC on NPs, the surface morphology, functional groups, saturation magnetization strength, zeta potential, surface element valence, relative content of Co-NC before and after NPs adsorption were characterized and characterization methods were provided in [Supplementary information \(SI\)](#).

2.4. Characterization of NPs suspension concentration

The absorbance of polystyrene (PS) NPs suspension was measured by UV-vis spectrophotometer (PerkinElmer Lambda 1050+, USA) in the range of 280–800 nm. The maximum absorbance peak of PSNPs suspension was measured at a wavelength of 346 nm ([Fig. S1a](#)). By measuring the absorbance peaks of NPs suspension at different concentrations at 346 nm, the concentration-absorbance curve of NPs suspension was obtained ([Fig. S1b](#)). The absorbance of the supernatant after adsorption was measured at 346 nm, and the remaining NPs concentration in the supernatant after adsorption was calculated based on the concentration-absorbance curve formula of NPs [26].

2.5. Preliminary experiments

The preliminary adsorption experiments were conducted on nine samples to verify their suitability for removing NPs. To achieve the purpose, 3 mg adsorbent and 10 ml of 10 mg·L⁻¹ NPs suspension were selected for the experiment. They were mixed in a deionized water environment (pH = 6 ± 0.5) and oscillated on a vortex oscillator for 5 min. The adsorbent could be completely removed within 2 min using a magnet. The results of the experiment are presented in [Fig. S2a](#), the adsorption efficiency of Zn: Co = 1: 2-NC-800, Zn: Co = 1: 2-NC-900, Co-NC-800 and Co-NC-900 reached 100 %. Subsequently, these four adsorbents were selected again to adsorb NP at higher concentrations. Using 2 mg adsorbent, adsorption experiments were conducted on 20 ml NPs suspensions with a concentration of 10 mg·L⁻¹ under the same environmental conditions. Zn: Co = 1: 2-NC-800, Zn: Co = 1: 2-NC-900, Co-NC-800 and Co-NC-900 showed adsorption efficiencies of 89.49 %, 77.06 %, 96.37 % and 81.12 % respectively. Therefore, Co-NC-800 was identified as the most promising adsorbent for further testing and the Co-NC mentioned in the article collectively refers to Co-NC-800. Zeta potential of various materials as shown in [Fig. S3](#). Finally, 2 mg Co-NC was placed in 20 ml NPs suspension (40 mg·L⁻¹) and shaken for 10 min using a vortex oscillator. The PSNPs before and after being adsorbed by Co-NC are shown in [Fig. S4a–b](#).

2.6. Batch experiments

After synthesizing, characterizing, and selecting MOF derivative materials, Co-NC (2 mg) was placed in a reagent bottle containing 20 ml of a 40 mg·L⁻¹ NPs suspension and oscillated in a vortex oscillator at 25 °C. Samples were extracted at time of 2, 5, 8, 10 and 12 min, respectively and then separated by magnet. The concentration of remaining NPs in suspension was analyzed using a UV-vis

spectrophotometer to determine the suitable equilibrium time. In addition, the effect of distinct concentrations of NPs suspension on the removal efficiency of Co-NC was analyzed for NPs suspension in the range of 30 mg·L⁻¹ to 200 mg·L⁻¹. 0.1 M HCl or NaOH was applied to alter the pH of the NPs suspension to the expected value (3–11) while keeping other factors constant. The impact of different pH conditions on the capability of Co-NC in removing NPs was evaluated. The adsorption process is influenced by different environmental conditions, hence, it is imperative to delineate the impacts of diverse competitive ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻, PO₄³⁻ and NO₃⁻) on the removal of NPs. Lastly, to ascertain the practical application performance of the material, the tap water from the Shanghai Institute of Ceramics laboratory and the river water from Pingcheng Road in Jiading District, Shanghai were collected, and the Bohai Sea water from Huludao City, Liaoning Province was purchased for NPs adsorption experiments. Unless otherwise specified, all experiments were conducted under the condition of pH = 6 ± 0.5 and 25 °C.

The calculation formula for the adsorption capacity (Q_e) of Co-NC is as follows:

$$Q_e = (C_0 - C_t) \frac{V}{m}$$

The adsorption efficiency (R_e) is:

$$R_e = \frac{C_0 - C_{t*}}{C_0} 100\%$$

C₀ and C_t signify the concentration of NPs suspension at the initial and contact time t, respectively. V (mL) is the volume of NPs suspension; m (mg) is the amount of adsorbent used. To comprehensively understand the interaction between NPs and Co-NC, kinetics and adsorption isotherm models were established for fitting [27,28]. The SI provides a concise overview of the models.

2.7. Reusability of Co-NC in removing NPs

We conducted recycling experiments on Co-NC to confirm its large-scale and economic applicability [29]. The Co-NC adsorbed NPs are placed in alkaline water with pH = 11, and sonicated to wash and regenerate the Co-NC. Further research was conducted on the adsorption performance of regenerated Co-NC on NPs, and five cycles were conducted to test their reusability.

3. Results and discussion

3.1. Characterization of NPs and Co-NC

The microscopic morphology of ZIF-67, NPs, Co-NC calcinated at different temperatures, and Co-NC after adsorption were analyzed using scanning electron microscope (SEM). As shown in [Fig. 1a–f](#), ZIF-67 has a regular dodecahedral structure [30]. Co-NC after pyrolysis slightly contracted each other inward at the edges compared to ZIF-67, maintaining the morphological characteristics of ZIF-67. As the carbonization temperature increased, the structure of Co-NC continued to concave inward, resulting in a smaller particle size. Upon reaching 900 °C, particle breakage occurred, and adjacent particles agglomerated [31]. This further indicates that as the temperature increased, the dodecahedral structure of ZIF-67 was gradually destroyed, and lattice distortion became severe. NPs exhibit uniform spherical particles with a diameter of around 500 nm as shown in [Fig. 1e](#). After adsorbing NPs, uniform spherical NPs were connected on the surface of Co-NC.

As shown in [Fig. 2a](#), ZIF-67 with a dodecahedral structure shows major diffraction peaks at 7.4°, 10.4°, 12.8°, 18.1°, 16.5°, 22.2°, 24.4°, 25.7°, and 26.8°, which closely align with the standard ZIF-67 diffraction peaks reported in the literature [32]. [Fig. 2b](#) shows XRD data of Co-NC obtained after pyrolysis at 700 °C, 800 °C and 900 °C for 2 h under N₂

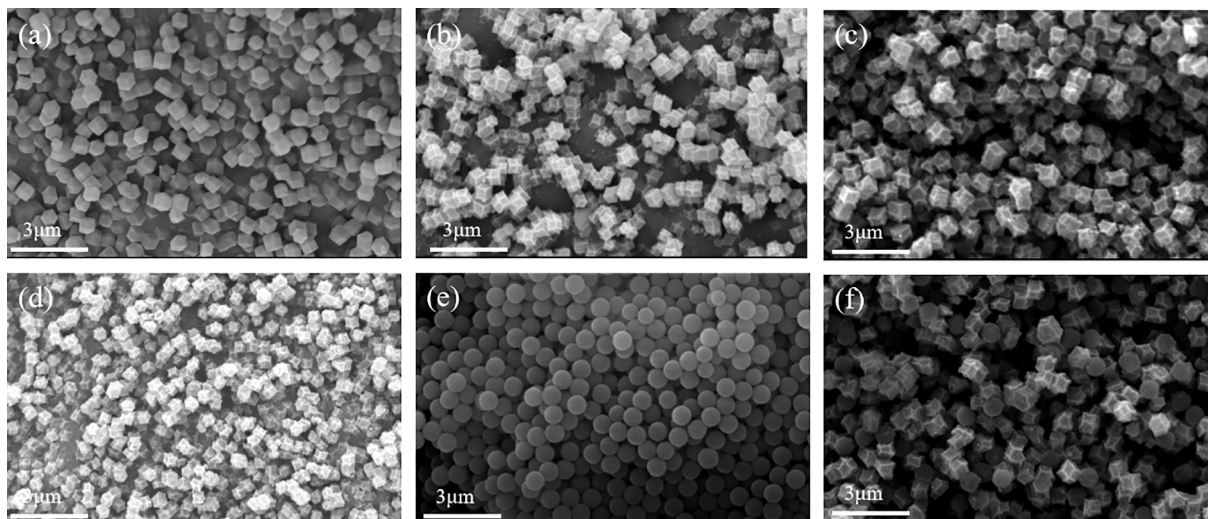


Fig. 1. SEM of (a) ZIF-67, (b) Co-NC-700, (c) Co-NC-800, (d) Co-NC-900, (e) PSNPs, (f) Co-NC-800 after adsorption.

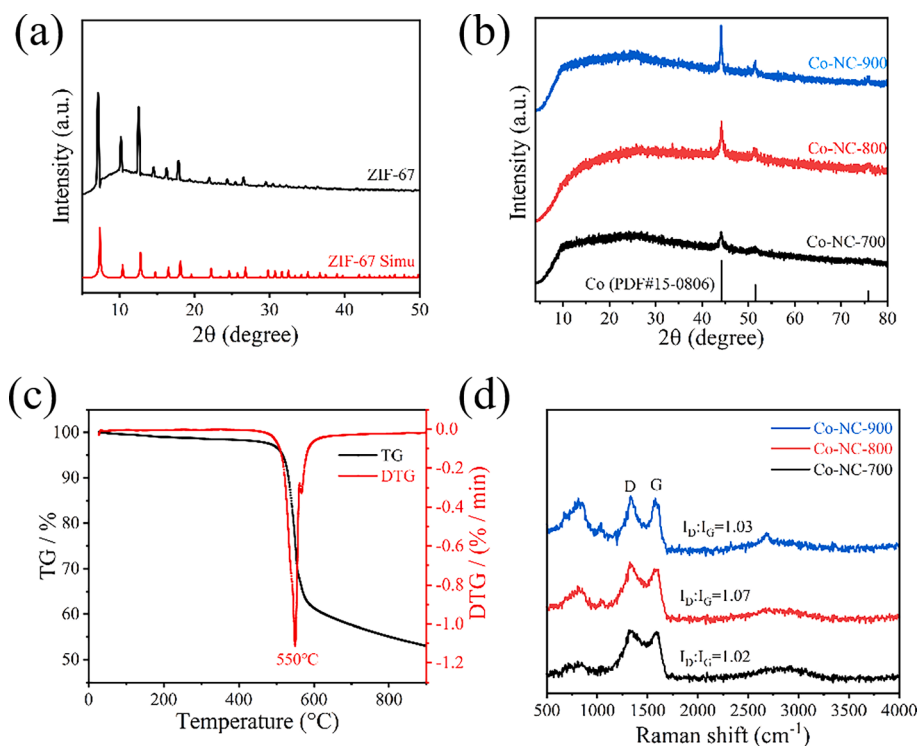


Fig. 2. Characteristics of the adsorbent. (a, b) XRD pattern, (c) Thermogravimetric analysis curve of ZIF-67, (d) Raman spectra.

atmosphere, the diffraction peaks correspond well to the (111), (200) and (220) crystal planes of zero valent cobalt at 44.2° , 51.5° and 75.8° . As the temperature increased, the peak intensity of the Co element increased, indicating that the carbonization temperature will not change the crystal morphology of the product, but altered the crystallinity of the crystal.

To study the pyrolysis behavior of ZIF-67, the thermogravimetric analysis curve of ZIF-67 was measured under an N_2 atmosphere, as shown in Fig. 2c. ZIF-67 loses 3.3 % weight in the first stage below $500^\circ C$ as a result of the elimination of surface-adsorbed water, interparticle water molecules, and methanol solvent. The second weight loss (33.7 %) of ZIF-67 from $500^\circ C$ to $580^\circ C$ was ascribed to the structural collapse of ZIF-67. The temperature rose from $600^\circ C$ to $900^\circ C$, ZIF-67 gradually carbonized and metal oxides and metal nitrides formed, with

evaporation of N, O element.

The degree of graphitization of different adsorbents was studied through Raman spectroscopy as shown in Fig. 2d. The D peak and G peak are both characteristic Raman peaks of carbon atomic crystals, with the D peak situated at 1350 cm^{-1} and the G peak at approximately 1580 cm^{-1} . The D peak is correlated with lattice defects within the carbon structure, whereas the G peak reflects the level of carbonization within the material. The ratio of the intensities of the D peak to the G peak, expressed as $I_D:I_G$, serves as a quantitative measure of the defect density within the carbon atomic crystal, with a higher ratio indicating a higher prevalence of defects [33].

The hysteresis loops of Co-NC before and after NPs adsorption are shown in Fig. 3a. The hysteresis loops exhibit an S-shaped curve with low remanence and coercivity. The results indicate that Co-NC exhibits

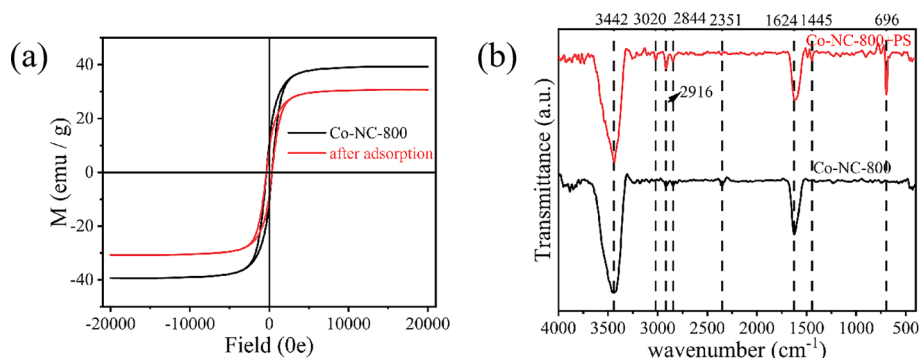


Fig. 3. (a) The hysteresis loop of Co-NC-800 and after adsorption NPs, (b) The FTIR spectra of Co-NC-800 and after adsorption NPs.

soft magnetic properties. Soft magnetic materials are essential in magnetic separation due to they can be reused multiple times and still retain strong adsorption capacity after desorption [34]. The magnetization intensity of Co-NC decreases upon NPs adsorption, suggesting a strong interaction between Co-NC and NPs [34].

Fig. 3b is a clear visual representation of the FTIR spectra of Co-NC before and after NPs adsorption. The broad peak located between 1515 cm^{-1} – 1700 cm^{-1} is attributed to the skeletal vibration of the imidazole pentagonal ring, the characteristic peak of 2531 cm^{-1} can be ascribed to the stretching vibration of $\text{C}=\text{N}$, and the broad peak at 3310 cm^{-1} – 3655 cm^{-1} is attributed to the bending vibration of $\text{N}-\text{H}$ or intramolecular hydrogen bonding [35]. After adsorbing NPs, significant changes occurred in the spectral peaks. Firstly, the newly appeared peaks at 2844 cm^{-1} , 2916 cm^{-1} and 3020 cm^{-1} in the spectrum can be attributed to the stretching vibrations of symmetric stretching and asymmetric vibrations of $\text{C}-\text{H}$ and aromatic $\text{C}-\text{H}$, respectively [36], the peak at 1445 cm^{-1} represents the stretching vibration of the benzene ring of NPs, and the peak at 696 cm^{-1} represents the stretching vibration of $\text{C}-\text{H}$ outside the benzene ring of NPs [37]. These new peaks confirm the successful adsorption of NPs by Co-NC [29]. Secondly, the absorption peak of imidazole pentagonal ring of NPs shifts from 1624 cm^{-1} to the right with a slight decrease in peak intensity. There are two possible explanations, one reason for the red shift is the π - π stacking between the pentagonal ring in Co-NC and the benzene ring in NPs. Additionally, the $\text{C}=\text{C}$ bond in the benzene ring acts as an electron donor, interacting with the $\text{C}=\text{N}$ bond in the imidazole pentagonal ring through π - π electron donor-acceptor (π - π EDA) interactions, which results in changes in peak intensity. The decreased intensity at 2351 cm^{-1} is mainly attributed to the formation of π - π EDA interactions between $\text{C}=\text{N}$ and $\text{C}=\text{C}$ in the benzene ring [38,39].

The specific surface area and pore size distribution of ZIF-67 and Co-NC pyrolysis at different temperatures were evaluated based on N_2 adsorption-desorption isotherms. Detailed data is shown in Table 1 and Fig. 4a–b. As the pyrolysis temperature increases, the specific surface area of Co-NC decreases continuously, while the mesoporous content continues to increase. This can be attributed to the higher pyrolysis temperature leads to increased collapse of ZIF-67, resulting in a higher

mesoporous content, the expanded mesoporous surface area provides sufficient active sites conducive to the adsorption of microplastics.

The constituents and chemical state of Co-NC, as well as the interaction between the Co-NC and NPs, were analyzed using X-ray photoelectron spectroscopy (XPS) to delve deeper into the adsorption mechanism. Fig. 5a displays the complete spectrum of Co-NC encompassing both the pre-adsorption and post-adsorption states. The measured spectrum of Co-NC consists of C, O, N, and Co. C 1s dissociated into three types of peaks at 289.3, 285.5, and 284.7 eV (Fig. 5b), corresponding to $\text{O}-\text{C}=\text{O}$, $\text{C}-\text{O}$, and $\text{C}-\text{C}$ [40,41]. After the adsorption of NPs, the binding energy of C 1s increased, and the relative content of $\text{C}-\text{C}$ increased from 36.26 % to 44.79 % (Table S2), once again proving the successful adsorption of NPs onto Co-NC. In addition, Fig. 5c shows the peak of O 1s is deconvoluted into two different peaks at 534.0 and 532.1 eV, being consistent with $\text{C}-\text{O}$ and $\text{C}=\text{O}$, respectively. After adsorbing NPs, the binding energy of O in $\text{C}-\text{O}$ increased from 534.0 eV to 534.5 eV, with a slight decrease in relative content (Table S3). The main reason is that O atoms in Co-NC act as electron acceptors during the adsorption process and undergo π - π EDA interaction with NPs [42]. As shown in Fig. 5d, six peaks were detected in the spectrum of Co, with peaks at approximately 778.5 and 793.2 eV attributed to Co^0 , 780.3 and 795.3 eV connected to Co^{2+} , the peaks observed at 785 and 801.7 eV are satellite peaks of Co (Table S4). After the adsorption of NPs, the binding energy of Co^{2+} increased from 780.3 eV to 780.6 eV, which may be due to the cation- π interaction between Co^{2+} and the benzene ring in NPs [43,44]. Fig. 5e shows N is convoluted into four peaks at 399, 400.9, 402.1, and 405.9 eV, representing pyridine N, pyrrole N, Co-N, and nitrogen oxides, respectively [45]. After adsorption, the binding energy of Co-N increased from 402.1 eV to 403.2 eV, once again confirming the cation- π interaction between Co^{2+} and the benzene ring in NPs.

3.2. Impact of various environmental parameters

Various environmental factors can substantially influence the adsorption capacity for NPs. To explore the catch applicability of Co-NC to NPs in actual water environment, further investigation was conducted to analyze the impact of different physicochemical properties (pH, ionic species) of water on the adsorption efficiency of Co-NC.

3.2.1. Impact of pH

Emerging research has validated that the role of solution pH in adsorption capacity is a pivotal factor that must be investigated to assess the environmental suitability and to understand the underlying mechanisms [10,29,46,47]. Fig. 6a shows the adsorption efficiency of Co-NC for NPs in the pH range of 3–11, as well as the zeta potentials of Co-NC and NPs, respectively. Co-NC shows a considerable adsorption capacity for NPs in both weakly acidic and neutral environments. As the pH value increases, the adsorption capacity continuously decreases, from 97.33 % to 54.42 %. This effect can be attributed to the presence of a positive charge on the surface of Co-NC in acidic environments, which strongly

Table 1

The physical properties of as-prepared samples.

Samples	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	Pore Volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Average pore size (nm)
ZIF-67	1923.890	0.702	1.459
Co-NC-700	435.194	0.284	2.580
Co-NC-800	327.469	0.240	2.864
Co-NC-900	290.460	0.198	2.722
Co-NC-800 after alkaline water rinse	373.236	0.258	2.768

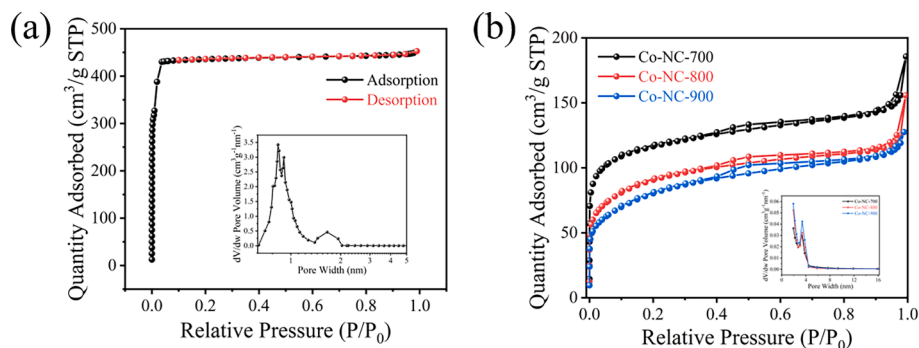


Fig. 4. N_2 adsorption-desorption isotherm and pore size distribution of (a) ZIF-67, (b) Co-NC- (700, 800, 900).

attracts negatively charged NPs. In alkaline conditions, the adsorption efficiency of Co-NC is reduced, likely as a result of the negative charge on the Co-NC surface that diminishes the electrostatic attraction between Co-NC and the NPs [48]. However, the Co-NC still exhibits an adsorption efficiency of over 50 %. This is due to the combined effect of uneven charge distribution on the surface of Co-NC and conjugation effect [49]. The high removal rate in weakly acidic and neutral aqueous environment demonstrates the effectiveness of Co-NC in adsorbing NPs.

It is important to further observe the removal efficiency at different pH and the zeta potential of the aggregates formed after adsorbing NPs (Fig. 6b). They are positively correlated, and the correlation R^2 reaches up to 0.9644, which is sufficient to demonstrate the dominant role of electrostatic force in the adsorption process [50].

3.2.2. Impact of competitive ions

As shown in Fig. 6c, the elimination of NPs may be influenced by various competitive ions [27]. Therefore, the effects of different cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (Cl^- , SO_4^{2-} , PO_4^{3-} and NO_3^-) on the adsorption of NPs were studied using chloride and sodium salts. The concentration of the salt mentioned above is 5 mM. The coexisting cations have a minimal impact on the removal efficiency of NPs, with Mg^{2+} exerting a greater influence (17.60 %). The presence of Ca^{2+} , Na^+ , and K^+ (8.92 ± 1 %) has minimal and equal effects on the removal efficiency of NPs, suggesting that the effects may be attributed to the presence of Cl^- . The degree of inhibition of coexisting anions on the removal capacity of NPs is: Cl^- (9.92 %) < NO_3^- (19.21 %) < PO_4^{3-} (27.14 %) < SO_4^{2-} (29.59 %). The appearance of PO_4^{3-} and SO_4^{2-} exhibits a significant antagonistic effect for removing NPs, primarily because of their relatively high charge density.

3.2.3. Adsorption of NPs from several aqueous environment

After determining the removal efficiency of NPs under different environmental conditions, various aqueous solution from tap water, river water and seawater was used to test the effectiveness of Co-NC for removing NPs in real environment, as shown in Fig. 6d.

The characteristics of various aqueous environment such as total organic carbon (TOC), total dissolved solids (TDS) and Zeta potential of Co-NC within them was listed in Table 2. The adsorption removal efficiency of NPs by Co-NC is 95.53 % in pure water, 55.82 % in sea water, 51.79 % in tap water and 31.39 % in river water. In four different water environments, variations in factors such as pH and conductivity led to changes in the zeta potential of Co-NC. The zeta potential decreased with increasing pH value. The conductivity of the water reflects the level of ionic strength, with higher conductivity indicating higher ionic strength. Higher ionic strength compressed the electric double layer of Co-NC, further reduced the zeta potential. The decrease in zeta potential caused the electrostatic attraction between Co-NC and NPs to be transformed into electrostatic repulsion, thus lowered the adsorption efficiency. Higher contents of TOC and TDS occupy more adsorption sites on the surface of Co-NC, leading to a decrease in the removal efficiency of

NPs. Moreover, the steric hindrance caused by the high content of TOC in river water further led to the decrease of the removal efficiency of NPs.

3.3. Adsorption kinetics, isotherms and thermodynamics

The effect of contact time on the removal efficiency of NPs by Co-NC was studied, and the kinetic parameters are shown in Fig. 7a and Table 3. The results clearly indicated that NPs were rapidly removed and reached equilibrium within 10 min of interacting with the Co-NC. In the early stage of response, the adsorption capacity of Co-NC rapidly increases, reaching $344.61 \text{ mg} \cdot \text{g}^{-1}$ within 2 min. In the following minutes, the adsorption rate decreases until saturation adsorption is reached. During the initial adsorption phase, the surface of Co-NC contains numerous adsorption sites and pores, and strong adsorption interactions occur between Co-NC and NPs. In addition, the initial high concentration of NPs results in strong adsorption driving force between NPs and Co-NC. With extended adsorption time, the adsorption rate continued to decline, which is because the adsorption sites of Co-NC reached saturation and can no longer adsorb NPs. To better understand the adsorption rate of Co-NC on NPs, kinetic models (pseudo-first and pseudo-second order) were used to analyze the adsorption behavior of Co-NC [51]. The adsorption kinetics parameters of NPs by Co-NC conform to a pseudo-first-order kinetic model, with a correlation coefficient $R^2 > 0.9999$.

To enhance comprehension of the adsorption mechanism, two classic nonlinear Langmuir and Freundlich isotherm models were employed in analyzing the equilibrium data. NPs suspensions with concentrations ranging from $30 \text{ mg} \cdot \text{L}^{-1}$ to $200 \text{ mg} \cdot \text{L}^{-1}$ were utilized, with a fixed Co-NC dose of 2 mg. The corresponding simulated curves are illustrated in Fig. 7b [52]. The parameters of isotherm models as listed in Table 4. The finding suggest that compared to the Freundlich model with a R^2 around 0.67646, the adsorption of Co-NC more closely follows the Langmuir model, with a R^2 around 0.84. This suggests that the adsorption of Co-NC is more likely to belong to heterogeneous monolayer adsorption.

For details on the adsorption thermodynamics analysis, refer to the SI part.

3.4. Cycling stability

The ability of the adsorbent to be reused can mitigate costs in applications. Consequently, the effectiveness of Co-NC in adsorbing NPs was determined through a series of adsorption-desorption cycles. The Co-NC after adsorption were immersed in alkaline water at pH = 11 for 20 min under ultrasonication, followed by being washed with alkaline water for three times. The supernatant after each wash was tested for absorbance (Table S5) using a UV-vis spectrophotometer. After being washed, Co-NC particles were completely cleaned, dried, and subjected to adsorption experiments again. As depicted in Fig. 8a, the adsorption efficiency of NPs improved from 95.53 % to 100 % after cycling, and the

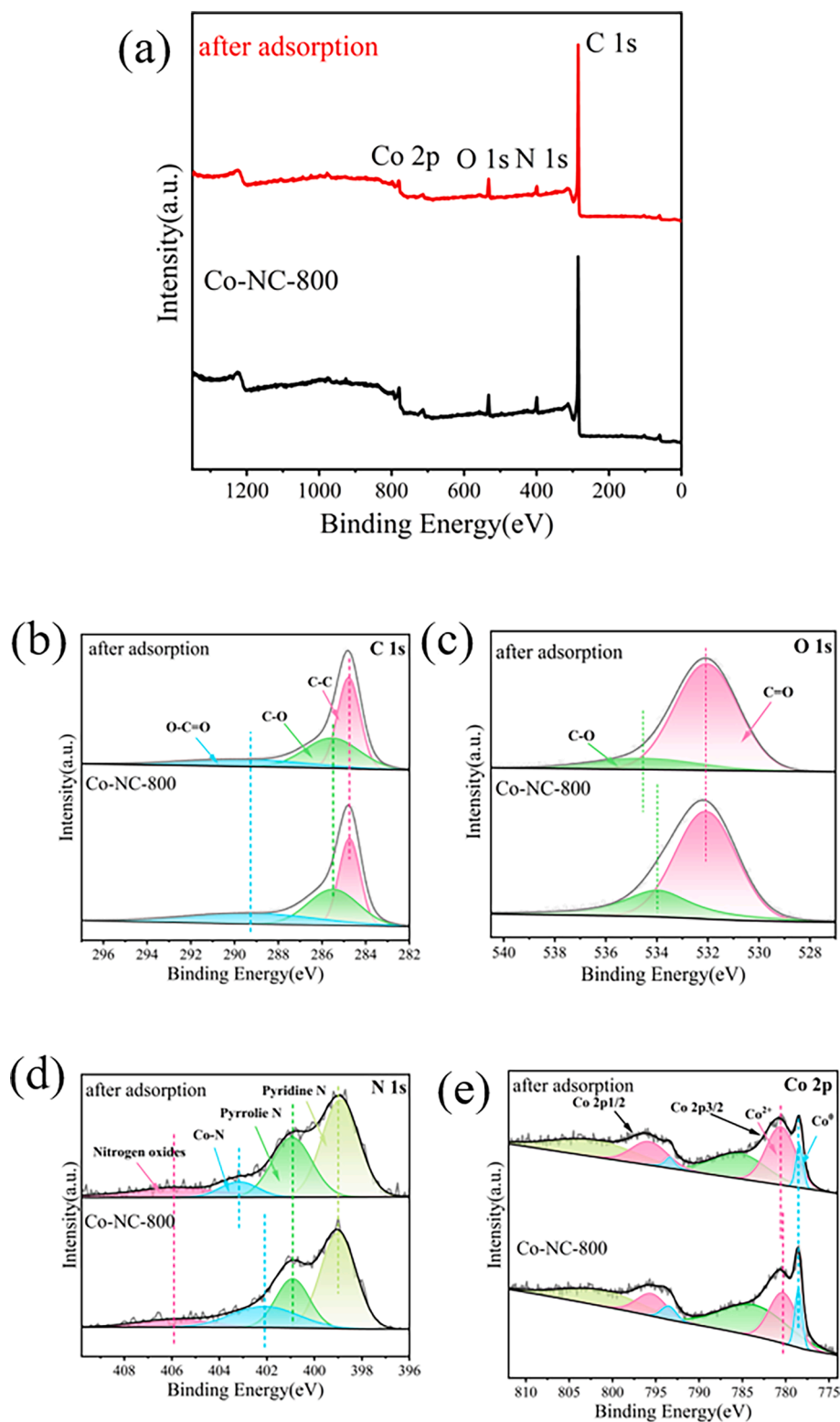


Fig. 5. XPS spectra of Co-NC-800 before and after adsorption NPs. (a) Full-spectrum diagram, (b) XPS spectra region of C 1 s, (c) O 1 s, (d) N 1 s, (e) Co 2p.

removal capacity of Co-NC remained at 100 % even in the fifth cycle. This may be attributed to the elimination of superficial unstable carbon from Co-NC by alkaline washing [31], resulting in an increase in surface area and the number of adsorption sites. The zeta potential of Co-NC is found to be 12.42 mV through measurements at this time. N₂ adsorption-desorption isotherm analysis was conducted on the desorbed Co-NC (Fig. 8b), indicating an increase in specific surface area and

mesopore content after alkaline washing (Table 1). In conclusion, the Co-NC exhibits excellent adsorption capacity and stability after cycle test and is capable of capturing and separating NPs from wastewater for multiple use.

We made a comprehensive comparison of NPs removal performance of various adsorbents from references as shown in Table 5 and sorted them in descending order based on the size of the NPs. Yan et al. [50]

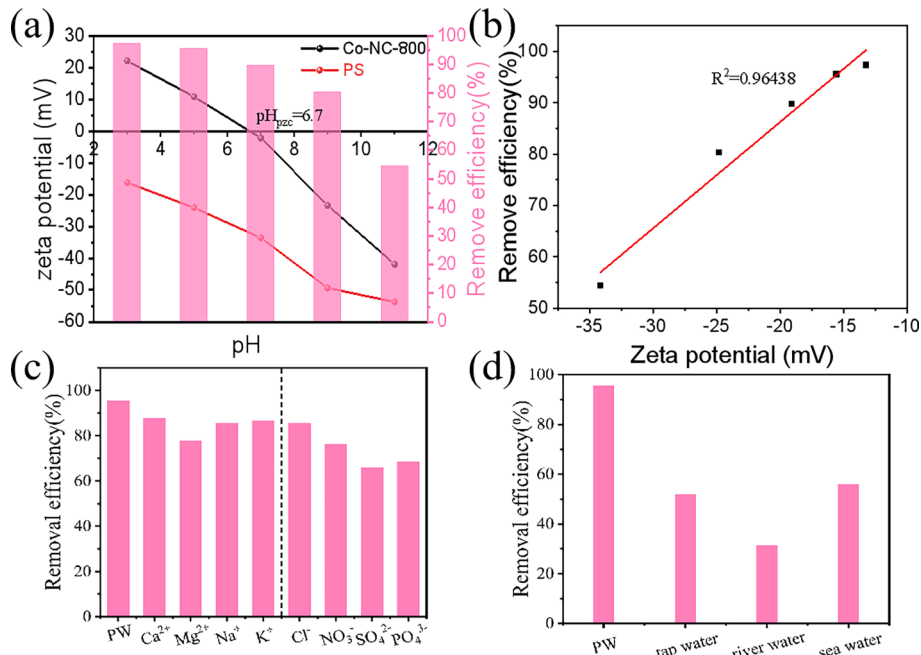


Fig. 6. (a) Effect of different pH conditions on the Co-NC-800 removal of NPs and zeta potential vs. pH, (b) Pearson correlation analysis of zeta potential of aggregation and NPs removal efficiency at different pH values. (c) Impact of different competitive ions on NPs removal, (d) Effect of different water resource on NPs removal.

Table 2
The properties of various aqueous environment and Zeta potential of dispersed Co-NC particles.

Various water substrates	Conductivity (mS·cm ⁻¹)	pH	TOC (mg·L ⁻¹)	TDS (mg·L ⁻¹)	Zeta potential of Co-NC (mV)	Removal efficiency
Pure water	0.0397	5.48	—	—	10.70	95.53 %
Tap water	0.0465	6.99	1.141	10	−9.86	51.79 %
River water	0.0463	7.17	6.851	11	−14.52	31.39 %
Sea water	0.2024	7.54	4.514	12	−6.65	55.82 %

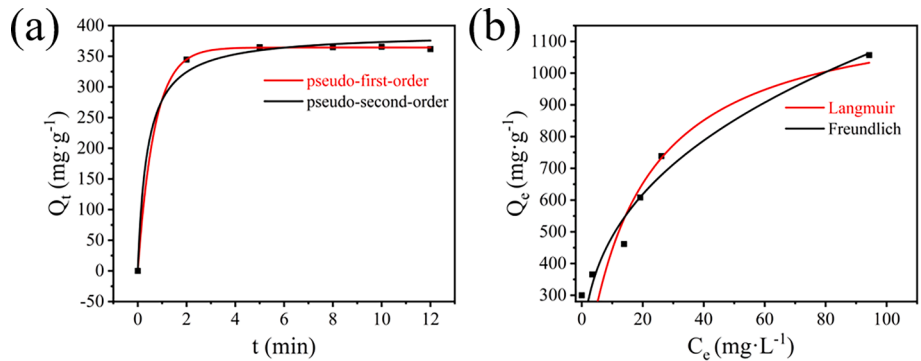


Fig. 7. Adsorption kinetics and isotherm fitting of Co-NC for NPs removal. (a) Adsorption kinetics, (b) Adsorption isotherm.

Table 3
The parameters of the Kinetics model.

Kinetic model (equation)	parameter	Value
Pseudo-first order $Q_t = Q_e(1 - e^{-k_1 t})$	k_1 (min ⁻¹)	1.4587
	Q_e (mg/g)	364.336
	R^2	0.9999
	k_2 (min ⁻¹)	0.00656
Pseudo-second order $Q_t = \frac{Q_e^2 k_2 t}{Q_e k_2 t + 1}$	Q_e (mg/g)	387.884
	R^2	0.94971

Table 4
The parameters of adsorption isotherms.

Isotherm model (equation)	Parameter	Value
Langmuir $Q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	K_L (L·mg ⁻¹)	0.05693
	R^2	0.84
	q_m (mg/g)	1225.248
	$K_F[(\text{mg} \cdot \text{g}^{-1})/(\text{mg} \cdot \text{L}^{-1})^{1/n}]$	217.1
Freundlich $Q_e = K_F C_e^n$	R^2	0.67646
	n	0.34932

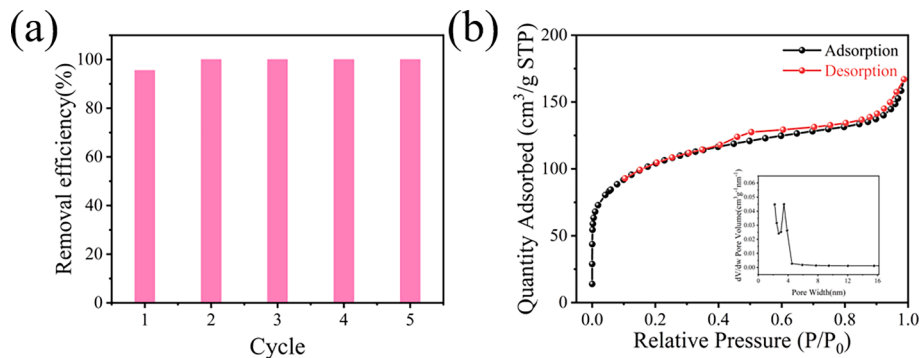


Fig. 8. (a) Reusability of Co-NC-800 for four cycles on NPs removal. (b) N₂ adsorption–desorption isotherm and pore size distribution of Co-NC-800 after washing with alkaline water (pH = 11).

Table 5
Comparison of NPs removal with various adsorbents.

Absorbent	Absorbent concentration (mg·L ⁻¹)	NPs concentration (mg·L ⁻¹)	R _{Abs/NPs}	MPs size (μm)	Adsorption time (min)	Remove efficiency	Cycles times	Cycles efficiency	Ref
ZIF-67	400	5	80	10	20	92.10 %	—	—	[26]
Fe@ZIF-8	500	25	20	1.1	5	81.2 ± 5.6 %	—	—	[53]
Magnetic biochar Zn-MBC Mg-MBC	1000	100	10	1	300	94.81 % 99.46 % 98.75 %	5	95.02 % 95.79 % 94.60 %	[15]
Sugarcane bagasse- derived biochar	1500	10	150	0.5	5	99 %	—	—	[11]
Co-NC	100	40	2.5	0.5	10	95.53	5	100 %	This work
Fe ₃ O ₄ nanoparticles	25	2	12.5	0.1 0.5 1	60	83.1 % 87.0 % 92.9 %	—	—	[50]
functional mesoporous biochar	400	20	20	0.1	720	100 %	5	89.70 %	[54]
CuNi@C	300	10	30	0.1	1440	99.18 %	4	75 %	[29]
Activated Carbon	5000	20	250	0.09	240	41 %	—	—	[52]
MIL-101(Cr)	100	5	20	0.08	225	100 %	4	68 ± 15 %	[10]
NMA	200	20	10	0.08	1440	94.10 %	4	89.80 %	[34]
Mesoporous UiO-66	2500	1000	2.5	0.03	10,080	100 %	—	—	[23]

“—” indicates that the data is not present in the literature.

investigated the impact of NP size on adsorption. The experimental results suggest that larger-sized NPs are more likely to be adsorbed, which may be attributed to the fact that larger-sized NPs tend to aggregate more readily. R_{Abs/NPs} represents the ratio of the concentration of the

adsorbent to the concentration of NPs, indicating the amount of adsorbent required for the adsorption of a unit mass of NPs. The lower the value of R_{Abs/NPs}, the better performance of the adsorbent. The lower R_{Abs/NPs} value means that a smaller amount of adsorbent is needed to

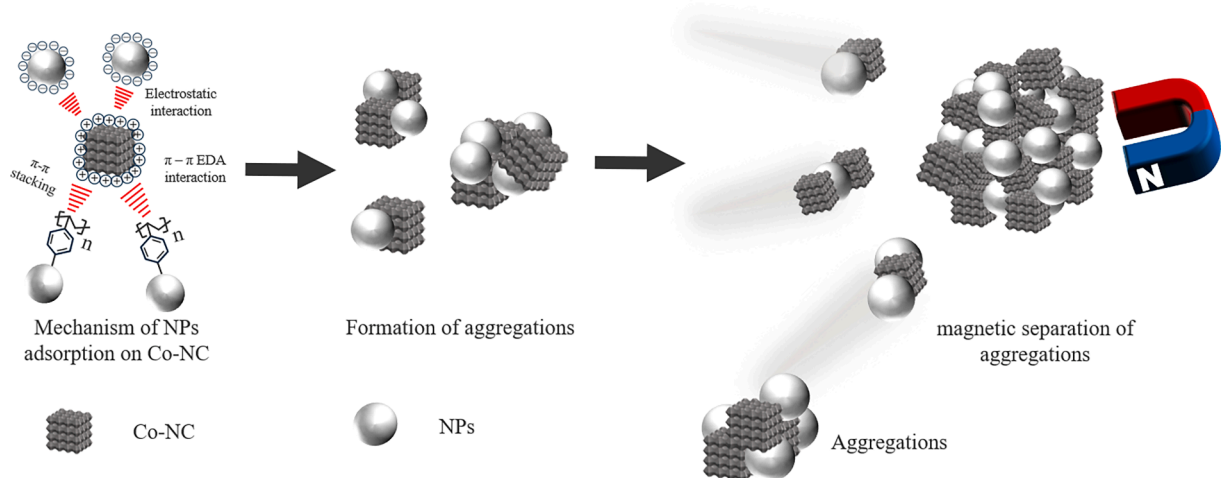


Fig. 9. The proposed NPs removal mechanisms by Co-NC in water.

effectively bind with the same amount of NPs. In the design and application of adsorbents, it is generally desired to have a lower $R_{\text{Abs/NPs}}$ value to reduce the amount of adsorbent used, lower the cost, minimize potential environmental impacts, and enhance the adsorption efficiency. In the reported references, $R_{\text{Abs/NPs}}$ usually between 10 and 250 and the adsorption process typically takes about 1 to 24 h. In our study, $R_{\text{Abs/NPs}}$ of Co-NC is only 2.5, with the adsorption time of 10 min, which fully demonstrated the rapid and efficient removal capacity of Co-NC for NPs.

3.5. Removal mechanism of NPs by Co-NC

Recent studies have indicated that capturing NPs primarily involves electrostatic interactions between the adsorbent and NPs, as illustrated in Fig. 9. Several key trends in different experimental stages in this study suggest the main forces driving the adsorption of NPs by Co-NC is electrostatic interactions. For instance, the significant impact of interfering ions and pH on NPs adsorption demonstrates a strong electrostatic attraction between them. Aggregates formed by Co-NC and NPs after adsorption at different pH show a strong positive correlation between their zeta potential and removal efficiency, with a high correlation coefficient R^2 of up to 0.96, indicating that electrostatic interactions are the main driving force for adsorption. At pH of 11, both the zeta potentials of Co-NC and NPs are below -40 mV, indicating a strong electrostatic repulsion between them, yet they still exhibit a high adsorption capacity of $200 \text{ mg} \cdot \text{g}^{-1}$. This confirms the involvement of other interaction in the NPs removal process. To further describe the interaction mechanisms between the Co-NC and NPs, FTIR and XPS spectral analyses of Co-NC before and after NPs adsorption provide key insights into weak interaction forces. The results indicate that the adsorption process involves weak interactions such as π - π stacking and π - π EDA [55].

4. Summary

In summary, Co-NC-800 was selected as the adsorbent, capable of achieving rapid and high-capacity removal of PSNPs in various water bodies within 10 min. After the adsorption process is completed, the Co-NC in the water can be completely removed in 2 min using an external magnetic field, avoiding secondary pollution to the water body. The adsorption efficiency was 95.53 % and the highest adsorption amount reached $1057 \text{ mg} \cdot \text{g}^{-1}$. Moreover, after being washed with alkaline water, the adsorption efficiency of Co-NC on NPs slightly increased. In the fifth cycle, the adsorption efficiency of Co-NC on NPs is 100 %. The correlation coefficient R^2 between the zeta potential of the aggregates generated after adsorption and removal efficiency was as high as 0.9644, indicating that the adsorption process is predominantly influenced by electrostatic interactions. Through FTIR and XPS analysis, the removal mechanism of Co-NC on NPs also includes weak interactions such as π - π stacking and π - π EDA. The adsorption efficiency exceeded 95 % for NPs removal in neutral and weak acidic conditions, yet it decreased to only 50 % under alkaline conditions. To explore the practical application of Co-NC, NPs adsorption experiments were conducted in different water bodies, the adsorption removal efficiency of NPs by Co-NC is 95.53 % in pure water, 55.82 % in sea water, 51.79 % in tap water and 31.39 % in river water. Therefore, low-cost and eco-friendly Co-NC has been proven to be a stable and effective adsorbent for NPs removal.

Author contributions

Kai Chen was the implementer of the experiments, including sample preparation, properties testing and manuscript writing. Jing Sun supervised this project. Guanhong Lu, Xiaoyu Duan, Guanhong Song, Chi Song, Kaihuang Zhu, Yan Wang, Xiaofeng Xie provided valuable comments. Jing Sun revised the manuscript. All authors have given approval to the final version of this manuscript.

CRedit authorship contribution statement

Kai Chen: Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Guanhong Lu:** Investigation, Methodology. **Xiaoyu Duan:** Investigation. **Guanhong Song:** Methodology. **Chi Song:** Investigation. **Kaihuang Zhu:** Investigation. **Yan Wang:** Project administration, Investigation. **Xiaofeng Xie:** Investigation, Methodology. **Jing Sun:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (52072387).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2025.132008>.

Data availability

Data will be made available on request.

References

- [1] A.L. Andrady, Microplastics in the marine environment, *Mar. Pollut. Bull.* 62 (2011) 1596–1605, <https://doi.org/10.1016/j.marpolbul.2011.05.030>.
- [2] O.S. Alimi, J. Farner Budarz, L.M. Hernandez, N. Tufenkji, Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport, *Environ. Sci. Technol.* 52 (2018) 1704–1724, <https://doi.org/10.1021/acs.est.7b05559>.
- [3] Y. Tang, Y. Liu, Y. Chen, W. Zhang, J. Zhao, S. He, C. Yang, T. Zhang, C. Tang, C. Zhang, Z. Yang, A review: Research progress on microplastic pollutants in aquatic environments, *Sci. Total Environ.* 766 (2021) 142572, <https://doi.org/10.1016/j.scitotenv.2020.142572>.
- [4] R. Hurt, C.M. O'Reilly, W.L. Perry, Microplastic prevalence in two fish species in two U.S. reservoirs, *Limnol. Oceanogr. Lett.* 5 (2020) 147–153, <https://doi.org/10.1002/lol2.10140>.
- [5] L.M. Hernandez, E.G. Xu, H.C.E. Larsson, R. Tahara, V.B. Maisuria, N. Tufenkji, Plastic Teabags Release Billions of Microparticles and Nanoparticles into Tea, *Environ. Sci. Technol.* 53 (2019) 12300–12310, <https://doi.org/10.1021/acs.est.9b02540>.
- [6] B. Ma, W. Xue, C. Hu, H. Liu, J. Qu, L. Li, Characteristics of microplastic removal via coagulation and ultrafiltration during drinking water treatment, *Chem. Eng. J.* 359 (2019) 159–167, <https://doi.org/10.1016/j.cej.2018.11.155>.
- [7] M. Lares, Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology, *Water Res.* 133 (2018) 236–246, <https://doi.org/10.1016/j.watres.2018.01.049>.
- [8] R. Wang, L. Zhang, B. Chen, X. Zhu, Low-pressure driven electrospun membrane with tuned surface charge for efficient removal of polystyrene nanoplastics from water, *J. Membr. Sci.* 614 (2020) 118470, <https://doi.org/10.1016/j.memsci.2020.118470>.
- [9] X. Shi, X. Zhang, W. Gao, Y. Zhang, D. He, Removal of microplastics from water by magnetic nano-Fe₃O₄, *Sci. Total Environ.* 802 (2022) 149838, <https://doi.org/10.1016/j.scitotenv.2021.149838>.
- [10] S. Modak, M. Kasula, M.R. Esfahani, Nanoplastics Removal from Water using Metal–Organic Framework: Investigation of Adsorption Mechanisms, Kinetics, and Effective Environmental Parameters, *ACS Appl. Eng. Mater.* 1 (2023) 744–755, <https://doi.org/10.1021/acsaenm.2c00174>.
- [11] Z.A. Ganie, N. Khandelwal, E. Tiwari, N. Singh, G.K. Darbha, Biochar-facilitated remediation of nanoplastic contaminated water: Effect of pyrolysis temperature induced surface modifications, *J. Hazard. Mater.* 417 (2021) 126096, <https://doi.org/10.1016/j.jhazmat.2021.126096>.
- [12] Y. Tang, S. Zhang, Y. Su, D. Wu, Y. Zhao, B. Xie, Removal of microplastics from aqueous solutions by magnetic carbon nanotubes, *Chem. Eng. J.* 406 (2021) 126804, <https://doi.org/10.1016/j.cej.2020.126804>.
- [13] L. Ramirez Arenas, S. Ramseier Gentile, S. Zimmermann, S. Stoll, Nanoplastics adsorption and removal efficiency by granular activated carbon used in drinking

- water treatment process, *Science of The Total Environment* 791 (2021) 148175, <https://doi.org/10.1016/j.scitotenv.2021.148175>.
- [14] X. Chen, H. Ma, X. Ji, R. Han, K. Pang, Z. Yang, Z. Liu, S. Peng, Engineering green MOF-based superhydrophobic sponge for efficiently synchronous removal of microplastics and pesticides from high-salinity water, *Water Res.* 243 (2023) 120314, <https://doi.org/10.1016/j.watres.2023.120314>.
 - [15] J. Wang, C. Sun, Q.-X. Huang, Y. Chi, J.-H. Yan, Adsorption and thermal degradation of microplastics from aqueous solutions by Mg/Zn modified magnetic biochars, *J. Hazard. Mater.* 419 (2021) 126486, <https://doi.org/10.1016/j.jhazmat.2021.126486>.
 - [16] Y.-P. Li, Y. Wang, Y.-Y. Xue, H.-P. Li, Q.-G. Zhai, S.-N. Li, Y.-C. Jiang, M.-C. Hu, X. Bu, Ultramicroporous Building Units as a Path to Bi-microporous Metal–Organic Frameworks with High Acetylene Storage and Separation Performance, *Angew. Chem. Int. Ed.* 58 (2019) 13590–13595, <https://doi.org/10.1002/anie.201908378>.
 - [17] C. Chen, D. Chen, S. Xie, H. Quan, X. Luo, L. Guo, Adsorption Behaviors of Organic Micropollutants on Zirconium Metal–Organic Framework UiO-66: Analysis of Surface Interactions, *ACS Appl. Mater. Interfaces* 9 (2017) 41043–41054, <https://doi.org/10.1021/acsami.7b13443>.
 - [18] J. Liu, R. Li, Y. Wang, Y. Wang, X. Zhang, C. Fan, The active roles of ZIF-8 on the enhanced visible photocatalytic activity of Ag/AgCl: Generation of superoxide radical and adsorption, *J. Alloy. Compd.* 693 (2017) 543–549, <https://doi.org/10.1016/j.jallcom.2016.09.201>.
 - [19] O.M. Yaghi, G. Li, H. Li, Selective binding and removal of guests in a microporous metal–organic framework, *Nature* 378 (1995) 703–706, <https://doi.org/10.1038/378703a0>.
 - [20] W.-T. Koo, J.-S. Jang, I.-D. Kim, Metal–Organic Frameworks for Chemiresistive Sensors, *Chem* 5 (2019) 1938–1963, <https://doi.org/10.1016/j.chempr.2019.04.013>.
 - [21] H. Deng, C.J. Doonan, H. Furukawa, R.B. Ferreira, J. Towne, C.B. Knobler, B. Wang, O.M. Yaghi, Multiple Functional Groups of Varying Ratios in Metal–Organic Frameworks, *Science* 327 (2010) 846–850, <https://doi.org/10.1126/science.1181761>.
 - [22] M. Sarker, I. Ahmed, S.H. Jung, Adsorptive removal of herbicides from water over nitrogen-doped carbon obtained from ionic liquid@ZIF-8, *Chem. Eng. J.* 323 (2017) 203–211, <https://doi.org/10.1016/j.cej.2017.04.103>.
 - [23] D. Pedrero, C. Edo, F. Fernández-Piñas, R. Rosal, S. Aguado, Efficient removal of nanoplastics from water using mesoporous metal organic frameworks, *Sep. Purif. Technol.* 333 (2024) 125816, <https://doi.org/10.1016/j.seppur.2023.125816>.
 - [24] L. Liu, W. Cui, C. Lu, A. Zain, W. Zhang, G. Shen, S. Hu, X. Qian, Analyzing the adsorptive behavior of Amoxicillin on four Zr-MOFs nanoparticles: Functional groups dependence of adsorption performance and mechanisms, *J. Environ. Manage.* 268 (2020) 110630, <https://doi.org/10.1016/j.jenvman.2020.110630>.
 - [25] F. Ahmadijokani, R. Mohammadkhani, S. Ahmadi-pouya, A. Shokrgozar, M. Rezakazemi, H. Molavi, T.M. Aminabhavi, M. Arjmand, Superior chemical stability of UiO-66 metal-organic frameworks (MOFs) for selective dye adsorption, *Chem. Eng. J.* 399 (2020) 125346, <https://doi.org/10.1016/j.cej.2020.125346>.
 - [26] H. Wan, J. Wang, X. Sheng, J. Yan, W. Zhang, Y. Xu, Removal of Polystyrene Microplastics from Aqueous Solution Using the Metal–Organic Framework Material of ZIF-67, *Toxics* 10 (2022) 70, <https://doi.org/10.3390/toxics10020070>.
 - [27] E. Tiwari, N. Singh, N. Khandelwal, F.A. Monikh, G.K. Darbha, Application of Zn/Al layered double hydroxides for the removal of nano-scale plastic debris from aqueous systems, *J. Hazard. Mater.* 397 (2020) 122769, <https://doi.org/10.1016/j.jhazmat.2020.122769>.
 - [28] N. Khandelwal, E. Tiwari, N. Singh, R. Marsac, T. Schäfer, F.A. Monikh, G. K. Darbha, Impact of long-term storage of various redox-sensitive supported nanocomposites on their application in removal of dyes from wastewater: Mechanisms delineation through spectroscopic investigations, *J. Hazard. Mater.* 401 (2021) 123375, <https://doi.org/10.1016/j.jhazmat.2020.123375>.
 - [29] G. Zhou, X. Huang, H. Xu, Q. Wang, M. Wang, Y. Wang, Q. Li, Y. Zhang, Q. Ye, J. Zhang, Removal of polystyrene nanoplastics from water by Cu Ni carbon material: The role of adsorption, *Sci. Total Environ.* 820 (2022) 153190, <https://doi.org/10.1016/j.scitotenv.2022.153190>.
 - [30] K. Im, J.-H. Jang, J. Heo, D. Kim, K.-S. Lee, H.-K. Lim, J. Kim, S.J. Yoo, Design of Co-NC as efficient electrocatalyst: The unique structure and active site for remarkable durability of proton exchange membrane fuel cells, *Appl Catal B* 308 (2022) 121220, <https://doi.org/10.1016/j.apcatb.2022.121220>.
 - [31] X. Li, Q. Jiang, S. Dou, L. Deng, J. Huo, S. Wang, ZIF-67-derived Co-NC@CoP-NC nanopolyhedra as an efficient bifunctional oxygen electrocatalyst, *J. Mater. Chem. A* 4 (2016) 15836–15840, <https://doi.org/10.1039/C6TA06434E>.
 - [32] C. Ma, Y. Wang, C. Zhang, Y. Huang, X. Zhang, J. Peng, C. Chai, M. Yuan, H. Ma, M. Zhai, ZIF-67 derived porous core-shell nanocomposites for high-efficiency electromagnetic absorption, *Appl. Surf. Sci.* 637 (2023) 157913, <https://doi.org/10.1016/j.apsusc.2023.157913>.
 - [33] L. Jin, X. Zhao, X. Qian, M. Dong, Nickel nanoparticles encapsulated in porous carbon and carbon nanotube hybrids from bimetallic metal-organic-frameworks for highly efficient adsorption of dyes, *J. Colloid Interface Sci.* 509 (2018) 245–253, <https://doi.org/10.1016/j.jcis.2017.09.002>.
 - [34] H. Zhao, X. Huang, L. Wang, X. Zhao, F. Yan, Y. Yang, G. Li, P. Gao, P. Ji, Removal of polystyrene nanoplastics from aqueous solutions using a novel magnetic material: Adsorbability, mechanism, and reusability, *Chem. Eng. J.* 430 (2022) 133122, <https://doi.org/10.1016/j.cej.2021.133122>.
 - [35] S. Li, Z. Li, B. Ke, Z. He, Y. Cui, Z. Pan, D. Li, S. Huang, C. Lai, J. Su, Magnetic multi-walled carbon nanotubes modified with polyaluminum chloride for removal of humic acid from aqueous solution, *J. Mol. Liq.* 279 (2019) 241–250, <https://doi.org/10.1016/j.molliq.2019.01.016>.
 - [36] A.D. Syakti, R. Bouhroum, N.V. Hidayati, C.J. Koenawan, A. Boulkamh, I. Sulisty, S. Lebarillier, S. Akhlus, P. Doumenq, P. Wong-Wah-Chung, Beach macro-litter monitoring and floating microplastic in a coastal area of Indonesia, *Mar. Pollut. Bull.* 122 (2017) 217–225, <https://doi.org/10.1016/j.marpolbul.2017.06.046>.
 - [37] N.A. Kumar, H.-J. Choi, Y.R. Shin, D.W. Chang, L. Dai, J.-B. Baek, Polyaniline-Grafted Reduced Graphene Oxide for Efficient Electrochemical Supercapacitors, *ACS Nano* 6 (2012) 1715–1723, <https://doi.org/10.1021/nn204688c>.
 - [38] X. Chen, H. Li, W. Liu, X. Zhang, Z. Wu, S. Bi, W. Zhang, H. Zhan, Effective removal of methyl orange and rhodamine B from aqueous solution using furfural industrial processing waste: Furfural residue as an eco-friendly biosorbent, *Colloids Surf A Physicochem Eng Asp* 583 (2019) 123976, <https://doi.org/10.1016/j.colsurfa.2019.123976>.
 - [39] X. Pan, M. Zhang, H. Liu, S. Ouyang, N. Ding, P. Zhang, Adsorption behavior and mechanism of acid orange 7 and methylene blue on self-assembled three-dimensional MgAl layered double hydroxide: Experimental and DFT investigation, *Appl. Surf. Sci.* 522 (2020) 146370, <https://doi.org/10.1016/j.apsusc.2020.146370>.
 - [40] R. Gurav, S.K. Bhatia, T.-R. Choi, H.J. Kim, Y.-K. Choi, H.-J. Lee, S. Ham, J.Y. Cho, S.H. Kim, S.H. Lee, J. Yun, Y.-H. Yang, Adsorptive removal of synthetic plastic components bisphenol-A and solvent black-3 dye from single and binary solutions using pristine pinecone biochar, *Chemosphere* 296 (2022) 134034, <https://doi.org/10.1016/j.chemosphere.2022.134034>.
 - [41] B. Chen, F. Long, S. Chen, Y. Cao, X. Pan, Magnetic chitosan biopolymer as a versatile adsorbent for simultaneous and synergistic removal of different sorts of dyestuffs from simulated wastewater, *Chem. Eng. J.* 385 (2020) 123926, <https://doi.org/10.1016/j.cej.2019.123926>.
 - [42] J. Tang, Y. Ma, S. Cui, Y. Ding, J. Zhu, X. Chen, Z. Zhang, Insights on ball milling enhanced iron magnesium layered double oxides bagasse biochar composite for ciprofloxacin adsorptive removal from water, *Bioresour. Technol.* 359 (2022) 127468, <https://doi.org/10.1016/j.biortech.2022.127468>.
 - [43] T. Gu, R. Sa, L. Zhang, D.-S. Li, R. Wang, Engineering interfacial coupling between Mo2C nanosheets and Co@NC polyhedron for boosting electrocatalytic water splitting and zinc-air batteries, *Appl Catal B* 296 (2021) 120360, <https://doi.org/10.1016/j.apcatb.2021.120360>.
 - [44] H. Zhu, Q. Jiao, R. Fu, P. Su, C. Yang, C. Feng, H. Li, D. Shi, Y. Zhao, Cu/NC@Co/NC composites derived from core-shell Cu-MOF@Co-MOF and their electromagnetic wave absorption properties, *J. Colloid Interface Sci.* 613 (2022) 182–193, <https://doi.org/10.1016/j.jcis.2021.11.166>.
 - [45] X.-W. Lv, X.-L. Liu, Y.-J. Suo, Y.-P. Liu, Z.-Y. Yuan, Identifying the Dominant Role of Pyridinic-N–Mo Bonding in Synergistic Electrocatalysis for Ambient Nitrogen Reduction, *ACS Nano* 15 (2021) 12109–12118, <https://doi.org/10.1021/acsnano.1c03465>.
 - [46] S. Yang, L. Peng, O.A. Syzgantseva, O. Trukhina, I. Kochetygov, A. Justin, D.T. Sun, H. Abedini, M.A. Syzgantseva, E. Oveis, G. Lu, W.L. Queen, Preparation of Highly Porous Metal–Organic Framework Beads for Metal Extraction from Liquid Streams, *J. Am. Chem. Soc.* 142 (2020) 13415–13425, <https://doi.org/10.1021/jacs.0c02371>.
 - [47] N. Singh, N. Khandelwal, Z.A. Ganie, E. Tiwari, G.K. Darbha, Eco-friendly magnetic biochar: An effective trap for nanoplastics of varying surface functionality and size in the aqueous environment, *Chem. Eng. J.* 418 (2021) 129405, <https://doi.org/10.1016/j.cej.2021.129405>.
 - [48] D. Zhou, A.A. Keller, Role of morphology in the aggregation kinetics of ZnO nanoparticles, *Water Res.* 44 (2010) 2948–2956, <https://doi.org/10.1016/j.watres.2010.02.025>.
 - [49] J. Ku, L. Zhang, W. Fu, S. Wang, W. Yin, H. Chen, Mechanistic study on calcium ion diffusion into fayalite: A step toward sustainable management of copper slag, *J. Hazard. Mater.* 410 (2021) 124630, <https://doi.org/10.1016/j.jhazmat.2020.124630>.
 - [50] R. Yan, S. Lin, W. Jiang, X. Yu, L. Zhang, W. Zhao, Q. Sui, Effect of aggregation behavior on microplastic removal by magnetic Fe₃O₄ nanoparticles, *Sci. Total Environ.* 898 (2023) 165431, <https://doi.org/10.1016/j.scitotenv.2023.165431>.
 - [51] É.C. Lima, M.A. Adebayo, F.M. Machado, Kinetic and Equilibrium Models of Adsorption, in: C.P. Bergmann, F.M. Machado (Eds.), *Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications*, Springer International Publishing, Cham, 2015, pp. 33–69, https://doi.org/10.1007/978-3-319-18875-1_3.
 - [52] L. Ramirez Arenas, S. Ramseier Gentile, S. Zimmermann, S. Stoll, Nanoplastics adsorption and removal efficiency by granular activated carbon used in drinking water treatment process, *Sci. Total Environ.* 791 (2021) 148175, <https://doi.org/10.1016/j.scitotenv.2021.148175>.
 - [53] F. Pasanen, R.O. Fuller, F. Maya, Fast and simultaneous removal of microplastics and plastic-derived endocrine disruptors using a magnetic ZIF-8 nanocomposite, *Chem. Eng. J.* 455 (2023) 140405, <https://doi.org/10.1016/j.cej.2022.140405>.
 - [54] N. Zhu, Q. Yan, Y. He, X. Wang, Z. Wei, D. Liang, H. Yue, Y. Yun, G. Li, N. Sang, Insights into the removal of polystyrene nanoplastics using the contaminated corn-cob-derived mesoporous biochar from mining area, *J. Hazard. Mater.* 433 (2022) 128756, <https://doi.org/10.1016/j.jhazmat.2022.128756>.
 - [55] N. Singh, E. Tiwari, N. Khandelwal, G.K. Darbha, Understanding the stability of nanoplastics in aqueous environments: effect of ionic strength, temperature, dissolved organic matter, clay, and heavy metals, *Environ. Sci.: Nano* 6 (2019) 2968–2976, <https://doi.org/10.1039/C9EN00557A>.