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Theoretical and experimental investigation on rapid and efficient adsorption characteristics of microplastics by magnetic sponge carbon



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- A magnetic sponge carbon (MSC) is prepared by one-step pyrolysis method.
- FeMSC is saturated in 10 min and has an adsorption capacity of up to 369 mg/g.
- MSC has an excellent anti-interference ability under different conditions.
- Magnetism can not only enhance MPs adsorption, but also facilitate the separation.
- DFT calculation shows that Fe-doping can form chemisorption to enhance adsorption.

A R T I C L E I N F O

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Keywords: Magnetic sponge carbon Microplastics adsorption Anti-interference Mechanism Theoretical calculation



ABSTRACT

Microplastic pollution control has always been a thorny problem all over the world. Magnetic porous carbon materials have shown a good development prospect in microplastic adsorption due to their excellent adsorption performance and easy magnetic separation from water. However, the adsorption capacity and rate of magnetic porous carbon on microplastics are still not high, and the adsorption mechanism is not fully revealed, which hinders its further development. In this study, magnetic sponge carbon was prepared using glucosamine hydrochloride as the carbon source, melamine as the foaming agent, iron nitrate and cobalt nitrate as the magnetizing agents. Among them, Fe-doped magnetic sponge carbon (FeMSC) exhibited excellent adsorption performance for microplastics due to its sponge-like morphology (fluffy), strong magnetic properties (42 emu/g) and high Fe-loading (8.37 Atomic%). FeMSC could adsorb to saturation within 10 min, and the adsorption capacity of polystyrene (PS) reached as high as 369.07 mg/g in 200 mg/L microplastic solution, which was almost the fastest adsorption rate and highest adsorption capacity reported so far in the same condition. The performance of the material against external interference was also tested. FeMSC performed well in a wide pH range and different water quality, except in the strong alkaline condition. This is because the surface of microplastics and adsorbents will have many negative charges under strong alkalinity, significantly weakening the adsorption. Furthermore, theoretical calculations were innovatively used to reveal the adsorption mechanism at the molecular level. It was found that Fe-doping could form chemisorption between PS and the adsorbent, thereby significantly increasing the adsorption energy between the adsorbent and PS. The magnetic sponge carbon prepared in this study has excellent adsorption performance for microplastics and can be easily separated from water, which is a promising microplastic adsorbent.

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1. Introduction

Microplastics (MPs) are new global pollutants that are ubiquitous in soil (Nizzetto et al., 2016), water (Alimi et al., 2018), and the atmosphere (Revell et al., 2021), which have attracted worldwide attention since this concept was introduced in 2004 (Thompson et al., 2004). MPs have the characteristics of complex morphology, good stability, long residence time and good adsorption performance (Andrady, 2011). Although many MPs are not toxic, their excellent adsorption properties determine that they will adsorb a large number of toxic substances, which will bring greater harm to the environment (Hirai et al., 2011). In recent years, many studies have shown that MPs in water have a negative impact on marine ecosystems, lakes, rivers, reservoirs, and even polar glaciers (Horton et al., 2017; Kokalj et al., 2018; Lebreton et al., 2017; Lei et al., 2018). As one of the largest gathering places of MPs, a large number of microplastics flow into the ocean every year. It is easy for marine organisms to ingest MPs, which migrate and accumulate within the body, posing a significant threat to the health of marine organisms (Kokalj et al., 2018; Lei et al., 2018). In addition to marine ecosystems, lakes are also short-term gathering places for MPs (Horton et al., 2017). As the main transport channel for all kinds of MPs into lakes and oceans, rivers also enrich more microplastics (Lebreton et al., 2017). Lakes and rivers, as important drinking water sources, also bring many microplastics into drinking water. A study has shown that MPs have been found in human blood vessels for the first time, and the content of polystyrene (PS) accounts for 36 % of the total (Leslie et al., 2022). It is estimated that each person will consume about 0-4700 MPs particles from drinking water every year (Zhang et al., 2020). Although there is no research report indicating the specific impact of MPs on the human body, many researchers generally believe that MPs pose a potential threat to the human body (Wright and Kelly, 2017). Therefore, the detection and control of MPs in water are imperative. At present, the common technologies for removing MPs from water include flocculation sedimentation, filtration, adsorption and flotation (Andersen et al., 2021; Bannick et al., 2019; Chen et al., 2022; Ren et al., 2021). Adsorption technology is considered one of the most promising control measures for MPs in water due to its low cost, good removal performance, and low implementation difficulty (Chen et al., 2022).

Over the years, the development of MPs adsorption materials has been remarkably rapid. MPs adsorbents mainly include porous carbon materials (Wang et al., 2021), sponges/aerogels (Sun et al., 2020), metal hydroxides (Peng et al., 2022), zeolites (Zhao et al., 2022) and metal organic frameworks (MOFs) (Chen et al., 2020). Magnetic carbon materials have been widely used in removing MPs in recent years due to their high adsorption efficiency and the advantages of magnetic separation. The iron-modified magnetic biochar prepared by Singh et al. (2021) showed excellent adsorption performance on three kinds of nanoplastics (NPs), with an adsorption capacity of up to 290 mg/g. A similar Mg/Zn modified magnetic biochar also has good adsorption performance on MPs, with a maximum adsorption capacity of 226 mg/g (Wang et al., 2021). However, it takes 60 min to reach saturation adsorption, which will hinder its further application. In addition to magnetic biochar, magnetic carbon nanotubes also have good adsorption properties for MPs. The commercial carbon nanotube modified by FeCl₃·6H₂O also has an adsorption capacity of up to 1650 mg/g in 5 g/L MPs solution (Tang et al., 2021). Nevertheless, like the magnetic biochar above, the adsorption rate of magnetic carbon nanotubes is very low, and it takes 300 min to saturate. Therefore, it is necessary to develop further magnetic carbon materials with better MPs adsorption performance, especially magnetic carbon materials with excellent MPs adsorption kinetic characteristics.

A clear adsorption mechanism between adsorbent and MPs is essential for designing and modifying subsequent adsorbents. However, the adsorption mechanism between magnetic carbon materials and MPs has yet to be clearly proposed. Singh et al. (2021) found that the adsorption mechanism between magnetic biochar and PS was mainly electrostatic interaction through Zeta potential, and also, there was surface complexation through FTIR characterization. Wang et al. (2021) further proposed that this surface complexation is mainly formed by forming the chemical bond of metal-O-PS between magnetic biochar and PS. Tang et al. (2021) also pointed out that in addition to the above interactions, adsorption mechanisms such as π - π interaction and hydrogen bond interaction exist. Although so many mechanisms have been proposed, most are general or just reasonable speculation based on experiments, lacking theoretical support. Therefore, it is very meaningful to systematically and deeply reveal the adsorption mechanism between MPs and adsorbents.

In this study, a kind of magnetic sponge carbon material was prepared using glucosamine hydrochloride as a carbon source and melamine as a foaming agent. The physicochemical properties of the materials were studied in detail by Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) spectrum, Vibrating Sample Magnetometer (VSM), X-ray Photoelectron Spectroscopy (XPS), Zeta potential and other characterization methods. Then, a series of adsorption experiments were carried out with fluorescence technology as the detection method and PS as the representative of MPs. In order to test the adsorption performance of the material in the actual water, different pH water and different actual water were selected for testing. The recycling characteristics of the materials were also studied by multiple washing and desorption with ethanol. Furthermore, the adsorption mechanism between magnetic sponge carbon material and MPs was innovatively analyzed by establishing a reasonable theoretical model at the atomic level. In short, a new preparation method of magnetic carbon materials with fast and efficient adsorption of MPs was proposed, and the systemic and thorough mechanism for MPs adsorption was revealed. It has a certain value for the design and development of MPs adsorbents.

2. Material and methods

2.1. Materials

Fe(NO₃)₃·9H₂O (AR, 98.5 %), Co(NO₃)₂·6H₂O (AR, 99.0 %), Melamine (99 %) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Glucosamine hydrochloride (GAH, AR, 98.0 %) was purchased from Shanghai Dibo Biotechnology Co., Ltd. Commercial activated carbon (AC) was obtained from China Everbright Environment Co., Ltd. Green fluorescence PS microspheres (1 %, 1 μ m, Excitation wavelength 488 nm, Emission wavelength 523 nm) were obtained from Feynman Nanomaterials Technology Co., Ltd.

2.2. Preparation of magnetic carbon materials

In this study, Fe-doped magnetic sponge carbon (FeMSC) was prepared using melamine as the foaming agent, GAH as the carbon source, and Fe (NO₃)₃·9H₂O as the magnetizing agent by our previously proposed onestep pyrolysis method (Lu et al., 2021). The specific preparation process is as follows: First, 40 g of melamine was magnetically stirred for 10 min until completely dispersed in 350 mL of deionized water. Then, 1 g GAH and 0.95 g Fe(NO₃)₃·9H₂O were added to the solution in turn and dried in a 90 °C oil bath with stirring until the water completely evaporated. The dried mixture material is ground and loaded into a crucible. In a muffle furnace under the N_2 atmosphere, the temperature was raised to 600 °C at 3 °C/min and held for 1 h. Subsequently, the temperature continued to rise to 900 °C at 3 °C/min and maintained for 1 h. Finally, the carbonized material was washed with deionized water for 12 h, filtered and dried to obtain the FeMSC. In the above preparation process, if the Fe(NO₃)₃·9H₂O is replaced with Co(NO₃)₂·6H₂O, the Co-doped MSC (CoMSC) can be obtained. In addition, the Fe-doped magnetic commercial activated carbon (FeMAC) was prepared as a comparison. First, 3 g AC and 3 g Fe(NO₃)₃·9H₂O were sequentially added to 100 mL of deionized water. The mixture was then dried by stirring in a 90 °C oil bath. The dried mixture was heated to 900 °C at 10 °C/min under the N2 atmosphere and held for 1 h. The magnetized material was washed with water, suction filtered and dried to obtain FeMAC.

2.3. Characterization of materials

The materials' surface topography and energy dispersion spectrum mapping were obtained using a ZEISS sigma 300 scanning electron microscope (SEM) at 3 kV and 15 kV. Gold was sprayed for 45 s with an Oxford Quorum SC7620 sputter coater to reduce the influence of magnetism. The N2 adsorption and desorption isotherms of magnetic materials at 77 K were measured using American Micromeritics ASAP 2460, which can be used to analyze the pore structure of the materials. All materials need to be degassed under 120 °C vacuum for 12 h before testing. The Fourier transform infrared (FTIR) spectra before and after adsorption of magnetic materials were obtained by Thermo Scientific Nicolet iS5. The hysteresis loops of the material were tested with a LakeShore 7404 vibrating sample magnetometer (VSM). X-ray photoelectron spectroscopy (XPS) was measured by Thermo Scientific K-Alpha at 12 kV. And narrow-spectrum scans were also performed for C, O, N, Fe, and Co. To study the effect of different pH on the adsorption performance, the Zeta potential of MPs and FeMSC at different pH was tested with Malvern Zetasizer Nano ZS90, and each sample was tested in triplicate.

2.4. Adsorption experiment of MPs

In a typical adsorption experiment, 20 mL of MPs with an initial concentration of 50 mg/L were prepared in a 50 mL centrifuge tube. 10 mg of magnetic carbon material was added to the above solution and adsorbed for 10 min on a flip mixing apparatus (Mixer-LM 1, LICHEN, China). The magnetic carbon material was then separated from the solution with a strong magnet. The intuitive adsorption and separation processes are shown in Fig. S1. The separated solution was used to measure the concentration using the quantitative analysis module of the fluorescence spectrometer (F97, Lengguang Technology, China). The calibration curve between fluorescence intensity and PS concentration on the fluorescence indexer is shown in Fig. S2, and the correlation R² is as high as 0.9997. Therefore, it is completely feasible to measure the concentration of PS by fluorescence intensity. It should be noted that since AC is non-magnetic, it is difficult to separate it from water, and the measured AC adsorption amount has a significant error. So apart from the adsorption capacity, other adsorption characteristics of AC have not been studied.

The adsorption experiments were carried out on different adsorbent dosages (5 mg, 10 mg, and 15 mg), different adsorption time (0.5 min, 1 min, 3 min, 5 min, 10 min, 15 min, and 20 min), different MPs concentration (25 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L), different pH (pH = 3, 5, 7, 9 and 11) and various water quality (deionized water, tap water, river water, lake water and seawater). In addition, the cyclic adsorption performance of the magnetic material was also investigated. Because the magnetic carbon material has weak adsorption to PS in ethanol (as seen in Section 3.3), the material was dried, re-adsorption was done using the method mentioned above.

The calculation equations of adsorption efficiency (η_e , %) and adsorption capacity (q_c , mg/g) are as follows:

$$\eta_e = \frac{C_0 - C_1}{C_0} \times 100\%$$
 (1)

$$q_c = \frac{(C_0 - C_1) \cdot V}{m} \tag{2}$$

where C_0 (mg/L) and C_1 (mg/L) are the initial and post-adsorption concentrations of MPs, respectively. V (mL) is the volume of the MPs solution, and m (mg) is the mass of the magnetic carbon material.

2.5. Computational details

The adsorption mechanism was studied at the atomic and molecular level by taking Fe-doped carbon as an example. Referring to the research of Han et al. (2022), the FTIR and XPS characterization of this study, three carbon models were selected as shown in Fig. S3a–c, namely pristine carbon, Fe—O carbon, and Fe—N carbon. The PS model of Fig. S3d was used when calculating the adsorption of PS on carbon materials.

All structural optimizations, vibrational analyses, single-point calculations, etc., are performed on the quantum chemistry package ORCA (Neese, 2012, 2018). The version used in this study was ORCA 5.0 (Neese, 2022). To simulate a more realistic environment, the Solvation Model Based on Density (SMD) implicit solvent model was added to all calculations to account for solvent effects (Marenich et al., 2009). Structural optimization and vibration analysis of all models were performed at the r²SCAN-3c (Grimme et al., 2021) level, which is a combinatorial method with basis sets and DFT-D4 correction (Grimme et al., 2010). Single-point calculations use the higher-level RI-wB97M-V/def2-TZVP (Mardirossian and Head-Gordon, 2016; Weigend and Ahlrichs, 2005). The ORCA input generation, wavefunction analysis, etc., are done by Multiwfn3.8 (Lu and Chen, 2012). The interactions in adsorption, including covalent bonds, weak interactions, and other interactions, were investigated using the Interaction Region Indicator (IRI) method (Lu and Chen, 2021). All molecular structure maps, isosurface maps, and other images were rendered by tachyon in Visual Molecular Dynamics (VMD) software (Humphrey et al., 1996).

3. Results and discussion

3.1. Characterization results

The scanning electron microscope (SEM) images of the three magnetic carbon materials before and after adsorption of polystyrene (PS) are shown in Fig. 1a-f. At 10 k magnification, FeMAC (Fig. 1a) is heterogeneous on the whole, which is composed of different massive substances. Considering the synthesis process of the material, it is speculated that it may be made up of bulk activated carbon and iron oxide. Both FeMSC (Fig. 1b) and CoMSC (Fig. 1c) were fluffy and spongy. FeMSC carried some strip carbon fibers, and CoMSC carried many carbon nanoflowers. These two materials did not show obvious mixing characteristics like activated carbon and iron oxides, and it was speculated that metal oxides were bound to the MSC. Further magnify to 30 k times to observe the adsorption morphology of PS on carbon materials (Fig. 1d-f). PS was only accumulated and adsorbed on the surface of the FeMAC (Fig. 1d). The adsorption interaction is weak, so PS easily falls off the surface of the FeMAC, which explains the weak removal of PS by FeMAC. However, the adsorption of PS on FeMSC (Fig. 1e) and CoMSC (Fig. 1f) was more stable. This is because in addition to the van der Waals interaction on the carbon surface, there is also the visible wrapping and entanglement effect of strip carbon fibers and carbon nanoflowers, significantly enhancing PS adsorption interaction.

Energy dispersive X-ray spectroscopy (EDX) mapping can show the distribution and content of each element in the material. The EDX maps and line scan results of the three magnetic materials are shown in Fig. 1g–i. From the perspective of element distribution, iron (cyan) and oxygen (green) elements in FeMAC (Fig. 1g) are clustered (Spherical clusters with a diameter of about 550 nm) and distributed, and their positions are almost the same. This confirms the assumption that FeMAC in Fig. 1a is composed of bulk activated carbon and iron oxide. In contrast, FeMSC (Fig. 1h) and CoMSC (Fig. 1i) have relatively uniform distribution of the three elements, indicating that the metal oxides and carbon materials are fully integrated, which is also consistent with the analysis in SEM. From the element content results, FeMAC has less metal element content (3.56 %) than FeMSC (8.37 %) and CoMSC (7.71 %).

X-ray Photoelectron Spectroscopy (XPS) analysis further obtained the existing forms of several elements. The element total spectrum, N1s, and O1s spectra of XPS are shown in Fig. S4. It can be found that N-doping only exists in FeMSC and CoMSC, which is due to the amino group contained in GAH. The existing forms of oxygen element in the three materials are basically the same, with three forms of metal oxide, C—O and



Fig. 1. SEM images of (a) FeMAC, (b) FeMSC, (c) CoMSC, (d) FeMAC after PS adsorption (FeMAC-PS), (e) FeMSC after PS adsorption (FeMSC-PS) and (f) CoMSC after PS adsorption (CoMSC-PS). EDX spectrum and element distribution mapping of (g) FeMAC, (h) FeMSC and (i) CoMSC.

C=O. In addition, the metal elements have been fitted in detail in the three materials, as shown in Fig. 2 and Table S1. The Fe2p_{3/2} and Fe2p_{1/2} peaks of Fe₃O₄ in Fe2p are at 710.6 and 724.1 eV, respectively, and the Fe2p_{3/2} and Fe2p_{1/2} peaks of Fe₂O₃ are at 711.0 and 724.8 eV, respectively (Yamashita and Hayes, 2008). The Co2p_{3/2} and Co2p_{1/2} peaks of Co₃O₄ in Co2p are at 780.3 and 794.3 eV, respectively, and the Co2p_{3/2} and Co2p_{1/2} peaks of CoO are at 779.2 and 793.0 eV, respectively (Zhang et al., 2015). The iron elements in FeMAC and FeMSC are dominated by magnetic Fe₃O₄, followed by Fe₂O₃. A small amount of metal iron was also detected in FeMAC. The cobalt element in CoMSC is dominated by magnetic Co₃O₄, followed by CoO. It can be seen that the content of magnetic components in the three materials is the highest, which means that all three materials will have strong magnetism.

The magnetism of the three magnetic materials is tested with a vibrating sample magnetometer (VSM). The hysteresis loops are shown in Fig. S5. The hysteresis loops of the three materials are all S-shaped curves, indicating that the three materials are soft magnetic. The specific saturation magnetization (Ms) of FeMSC is the highest at 42 emu/g, followed by CoMSC at 32 emu/g, and FeMAC at the lowest at 12 emu/g. It is shown that all three materials can be separated entirely from water in the presence of a strong external magnetic field. The specific remanent magnetization (Mr) of FeMAC, FeMSC, and CoMSC was 2.89, 4.39, and 9.22 emu/g, respectively. It means that when the external magnetic field is removed, the magnetism of CoMSC is the strongest.

The FTIR spectroscopy characterization results of the magnetic carbon materials before and after MPs adsorption are shown in Fig. 3. All spectra have a prominent peak at 3400 cm⁻¹, mainly caused by the O—H bond stretching of the water absorbed by the material from the air. The peaks of C—H bond stretching (2850 cm⁻¹), C=O bond stretching (1600–1800 cm⁻¹), and C—O bond stretching (1100 cm⁻¹), which are

common in carbon materials, appear for the three magnetic adsorbents (Tucureanu et al., 2016). The peak formed by Fe—O bond stretching at 592 cm^{-1} can be clearly seen in FeMAC and FeMSC (Baykal et al., 2013). Because the chemical properties of the Co and Fe elements are similar, it is reasonable to speculate that the peak formed at 592 cm^{-1} in CoMSC is formed by the Co-O bond stretching. FeMSC and CoMSC have peaks formed by C—N bond stretching at 1250 cm⁻¹ (Misra et al., 2006), and the peak in CoMSC is significantly larger than that in FeMSC. This indicates that both materials contain nitrogen elements, and the N content in CoMSC is significantly larger than that in FeMSC, which is consistent with the results of XPS analysis. There was no significant difference in the FTIR spectra before and after adsorption. On the one hand, the characteristic peaks in PS overlap with some characteristic peaks in carbon materials. On the other hand, the specific gravity of adsorbed PS is smaller than that of carbon materials. Therefore, the FTIR spectrum of PS is obtained by subtracting the spectra before and after adsorption, as shown in Fig. 3d. There are several peaks caused by methylene stretching (2922 cm⁻¹), C=C bond stretching on the benzene ring (1452–1601 cm^{-1}) and C—H bond bending (720 cm^{-1}) in the difference spectra before and after adsorption of FeMAC, CoMSC and FeMSC, which almost wholly coincide with the characteristic peaks of PS (Zhang et al., 2018). The characteristic peaks of PS reflected in the infrared differential spectra obtained before and after FeMAC adsorption are significantly weaker than those calculated by FeMSC and CoMSC, indicating that the PS adsorbed on FeMAC is less than that on FeMSC and CoMSC, which is consistent with the results obtained from adsorption experiments.

The Zeta potentials of PS, FeMSC, FeMAC, and CoMSC were tested at different pH values, as shown in Fig. S6. At pH = 3, the Zeta potentials of PS, FeMSC, FeMAC, and CoMSC are 10.83 mV, 10.93 mV, 22.80 mV, and 25.77 mV, respectively, indicating that there are some positive charges on



Fig. 2. Fe2p spectra of (a) FeMAC and (c) FeMSC. Co2p spectra of (b) CoMSC. (d) The proportion of different forms of metal elements.

the surfaces of these four substances, and more positive charges are distributed on the surfaces of FeMAC and CoMSC. As the pH increases, the Zeta potential of all four materials gradually decreases. At pH = 7, the Zeta potential of PS is -16.77 mV, while the Zeta potential of FeMSC and CoMSC reduces to -2.45 mV and 2.84 mV. In this case, due to the relatively small surface charge distribution of FeMSC and CoMSC, there will be no significant electrostatic repulsion effect between the adsorbents of these two materials and PS. At pH = 7, the Zeta potential of FeMAC decreases to -8.81 mV, which results in a relatively strong electrostatic repulsion with PS. Under strong alkaline conditions with pH = 11, the Zeta potentials of all four substances are very negative, indicating that a large number of negative charges are distributed on the surfaces of all four materials. This means that under strong alkaline conditions, the electrostatic repulsion interaction between the three adsorbents and PS will be strong. Therefore, it can be inferred that different pH values will affect the adsorption performance of magnetic sponge carbon on PS.

Finally, the pore structure characteristics of the three materials are also tested. The adsorption isotherms and pore size distribution characteristic curves of the material are shown in Fig. S7, and the specific results are shown in Table S2. The highest specific surface area of FeMSC is 491.46 m²/g, and the three materials are mainly mesoporous. Due to the average particle size of PS being 1 μ m, it can be inferred that the nanopore structure has little effect on its adsorption performance. From the

experiment, it was found that the specific surface areas of FeMSC and CoMSC are very different, but there is little difference in the adsorption capacity of PS between the two materials, while the adsorption properties of PS on FeMAC and CoMSC with the similar specific surface area are very different. It can be seen that there is no correlation between specific surface area and adsorption performance. In addition, the total pore volume, micropore specific surface area and pore volume all show this law, which further proves that the nano-pore structure has almost no effect on the adsorption performance of PS.

3.2. MPs adsorption properties

3.2.1. Adsorbent dosage

To choose a suitable amount of adsorbent for subsequent experiments, 5, 10, and 15 mg were taken for adsorption experiments. The MPs adsorption efficiencies of the three materials under different adsorbent dosages are shown in Fig. 4a. The highest adsorption efficiency was 98.63 % when 15 mg FeMSC was used. Compared with the other two materials, FeMAC has a lower adsorption efficiency. The adsorption efficiency is only 58.70 % at 5 mg, and the highest is only 87.68 % at 15 mg. In general, the adsorption efficiencies of FeMSC and CoMSC were both above 90 % under different adsorbent dosages, while FeMAC did not reach 90 %. Considering that the adsorption efficiency of FeMSC and CoMSC were both as



Fig. 3. FTIR spectrum of (a) FeMAC, (b) FeMSC and (c) CoMSC before and after MPs adsorption. (d) Difference FTIR spectra of PS before and after.

high as 96 % at 10 mg, and the adsorption efficiency did not increase obviously when the dosage increased to 15 mg, 10 mg was selected as the adsorbent dosage for subsequent experiments.

3.2.2. Adsorption capacity

The adsorption capacities of several adsorbents in 200 mg/L microplastic solutions are shown in Fig. 4b. The adsorption capacity of commercial activated carbon (AC) was also briefly tested. The average

adsorption amount of AC was about 40.33 mg/g, much lower than FeMAC's (170.89 mg/g). The adsorption capacities of FeMSC and CoMSC were both about 9 times that of AC, and the highest FeMSC reached 369.07 mg/g. Under the same experimental conditions (the type of microplastic as PS, the adsorption concentration of microplastic as 200 mg/L, the dosage of adsorbent around 10 mg, and the adsorption reached stable adsorption), the adsorption capacities of FeMSC and CoMSC were much higher than the highest adsorption capacities in the published studies (Peng et al., 2022;



Fig. 4. (a) Adsorption efficiency of microplastics with different adsorbent dosages. (MPs concentration = 50 mg/L, Adsorption time = 10 min, pH = 7). (b) Adsorption capacities of microplastics with different adsorbents (MPs concentration = 200 mg/L, Adsorbent dosage = 10 mg, Adsorption time = 10 min, pH = 7).

Tiwari et al., 2020; Wang et al., 2021; Zhuang et al., 2022). The specific adsorption capacity comparison of several materials is shown in Table S3.

3.2.3. Adsorption kinetics

In addition to high adsorption capacity, an excellent adsorbent should also have competitive kinetic properties. The adsorption kinetics curves of the three adsorbents for PS are shown in Fig. 5a–c. The kinetic process of FeMAC was relatively long, and the saturated adsorption could not be reached within 20 min. Both FeMSC and CoMSC can reach >50 % of the saturated adsorption capacity within 30 s and 90 % in 5 min. Both materials can reach the saturated adsorption capacity within 10 min, which shows that the adsorption process is speedy. This adsorption rate is the fastest compared to previous studies (Chen et al., 2020; Peng et al., 2022; Sun et al., 2020, 2021; Tang et al., 2021; Zhuang et al., 2022), and the comparison with other studies can be seen in Table S3.

Then, the pseudo-first-order kinetic model, pseudo-second-order kinetic model, and Avrami model (Avrami, 1939) were used to fit the adsorption kinetic curves of the three materials, respectively. The equations of the three kinetic models and the specific meaning of each parameter can be found in the adsorption kinetics section of supplementary materials. The fitting results are shown in Fig. 5a-c and Table S4. The pseudo-secondorder kinetics and Avrami kinetic models can fit the adsorption kinetics of MPs well ($R^2 > 0.98$), which shows that the adsorption is dominated by chemical adsorption. The specific adsorption mechanism will be discussed in detail in the subsequent theoretical calculation. From the fitted equilibrium adsorption capacity (qe), the results obtained by the pseudofirst-order kinetics and pseudo-second-order kinetic models are more in line with the experimental values. And the $q_{\rm e}$ of FeMSC obtained by the Avrami model is 106.88 mg/g, which is impossible. The Avrami model will seriously overestimate qe because the maximum value of qe under the current experimental conditions is 100 mg/g. In addition, the laws obtained by the three kinetic models are consistent: both the equilibrium adsorption capacity and the kinetic rate constant are FeMAC < CoMSC < FeMSC.

Therefore, FeMSC is the best adsorbent among the three adsorbents in terms of adsorption kinetics.

3.2.4. Adsorption isotherm

The adsorption isotherms of the three adsorbents in different concentrations of MPs are shown in Fig. 5d-f. When the concentration of MPs reaches 200 mg/L, the increased rate of FeMAC adsorption capacity has been significantly slowed down. However, the adsorption capacity of FeMSC and CoMSC has maintained a significant increase, and the adsorption capacity is almost linearly related to the concentration of microplastics. It reflects that the two magnetic sponge materials show excellent adsorption performance at higher concentrations. Furthermore, the Langmuir model and the Freundlich model are used to fit the three isotherms, and the results are shown in Fig. 5d-f and Table S5, respectively. The equations for the two models can be found in the adsorption isotherms section in the supplementary materials. It can be seen that both models can describe the adsorption behavior well, especially for FeMSC and CoMSC ($R^2 > 0.999$). The saturated adsorption capacities of FeMAC, FeMSC and CoMSC predicted by the Langmuir model were 385.71, 4805.57, and 4994.32 mg/g, respectively. It can be seen that the saturated adsorption capacity of the two magnetic sponge carbons is much higher than that of FeMAC. For FeMSC and CoMSC with the same isotherm type, the K_F and n of FeMSC obtained during the Freundich model were both slightly larger than that of CoMSC, indicating that the adsorption performance of FeMSC was slightly better than that of CoMSC, which is also consistent with the conclusions directly obtained in the above experiments.

3.2.5. Anti-interference performance

All the above experiments were carried out in ultrapure water. To understand the anti-interference ability of the three adsorbents and their performance in practical applications, the adsorption capacities of these adsorbents were first tested in different pH solutions (Fig. 6a) and then under different water quality (Fig. 6b).



Fig. 5. Experimental and fitted adsorption kinetic curves of (a) FeMAC, (b) CoMSC, and (c) FeMSC. (MPs concentration = 50 mg/L, Adsorbent dosage = 10 mg, pH = 7). Experimental and fitted adsorption isotherm curves of (d) FeMAC, (e) CoMSC, and (f) FeMSC (Adsorption time = 10 min, Adsorption temperature = $25 \degree$ C, Adsorbent dosage = 10 mg, pH = 7).

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The adsorption capacities of the three adsorbents at each pH were always FeMAC < CoMSC < FeMSC from low to high. Overall, the variation law of adsorption capacity with pH of all adsorbents is basically the same: the adsorption amount in acidic solution and weak alkaline solution is almost the same as that in neutral solution, but it decreases significantly in strong alkaline solution. The main reason for its decrease is that both the adsorbent surface and the MPs surface have a large number of negative charges (the Zeta potential is very negative) in the strong alkaline solution, resulting in a large electrostatic repulsion interaction, which hinders the adsorption. Specifically, there are slight differences in the impact of pH on adsorption capacity. All three adsorbents exhibited the highest adsorption capacity in a neutral solution with pH = 7. FeMSC and CoMSC showed significantly higher adsorption capacity than FeMAC due to their low surface charge distribution (low absolute Zeta potential value). The adsorption capacity of all three adsorbents will decrease with the increase or decrease of pH. The adsorption capacity of FeMSC in a strongly acidic solution with pH = 3 is still as high as 94.79 mg/g, which is only 2.92 % lower than under neutral conditions. In contrast, the adsorption capacity of FeMAC in a strongly acidic solution is relatively reduced by 5.87 %. This is mainly because at pH = 3, the surfaces of PS, FeMSC, and FeMAC all contain a large number of positive charges, resulting in a significant electrostatic repulsion between PS and the adsorbent, leading to a decrease in adsorption performance. The surface distribution of FeMAC has more positive charges (Zeta potential = 22.8 mV), so the reduction in FeMAC is more significant. Under strong alkaline conditions (pH = 11), the adsorption capacity of FeMSC decreased by 19.81 % compared to neutral conditions, while under the same conditions, the relative decrease in FeMAC was as high as 58.38 %. From the Zeta potential, at pH = 11, the PS surface contains a large number of negative charges (Zeta potential = -34.9 mV), and the FeMSC and FeMAC surfaces also contain more negative charges, and the FeMAC surface has more negative charges (Zeta potential = -37.9 mV). Therefore, the higher electrostatic repulsive interaction between FeMAC and PS leads to a more significant decrease in adsorption capacity. Based on the above analysis, it can be seen that FeMSC can consistently exhibit good adsorption performance over a wide pH range, even in strongly alkaline solutions, exhibiting a high adsorption capacity of 78.35 mg/g.

It can be seen from Fig. 6b that the adsorption capacities of the three adsorbents under different actual water qualities are decreased compared with deionized water. According to the investigation, Chemical oxygen demand (COD), natural organic matter (NOM) and ion concentration in different types of water are the main factors affecting the adsorption of MPs (Peng et al., 2022; Wang et al., 2021). The COD levels of tap, river, and lake water used in this study were 0.9 mg/L, 10.8 mg/L, and 6.0 mg/L, respectively. The high COD content in the river water reduces the adsorption capacity of the adsorbent on MPs. In addition, there is competitive adsorption between NOM and MPs in river water, leading to a further decrease in adsorption capacity (Kilduff et al., 1998). We focused on studying the effects of anions and cations on seawater with high levels of ions. The seawater used in this study mainly contains several ions, such as Na⁺, Mg²⁺, Cl⁻ and SO_4^{2-} , with concentrations of 10.2 g/L, 1.2 g/L, 18.5 g/L, and 2.6 g/L, respectively. Although the ion concentration in seawater is high, the adsorption capacity of magnetic sponge carbon to MPs in seawater is still high. This indicates that ions have little influence on the adsorption performance of MPs, which is consistent with the research results of Wang et al. (2021). From the perspective of the impact of different water qualities on the adsorption capacity, the adsorption capacity of FeMAC in all three types of water, except seawater, has significantly decreased. The adsorption capacity of FeMAC in river water is the lowest, only 23.55 mg/g. In contrast, the adsorption capacity of CoMSC and FeMSC did not significantly decrease under different water quality conditions, and the adsorption capacity of FeMSC in river water remained around 70 mg/g. Overall, CoMSC and FeMSC can still maintain high adsorption levels in practical applications.

3.2.6. Cyclability

Cyclic adsorption performance is an important property of adsorbent. At present, there are two types of methods for the desorption of microplastics from adsorbents: one is thermal degradation, and the other is multiple washing with a certain solvent. Considering that thermal degradation will generate many polluting gases (Chen et al., 2022), anhydrous ethanol washing was used for desorption in this study. The five-cycle adsorptiondesorption efficiencies of FeMSC are shown in Fig. S8. It can be seen from Fig. S8 that the adsorption efficiency decreases with each cycle. By the fifth adsorption, its adsorption efficiency had reduced to 61 %, which was 38 % lower than that of the first adsorption. Compared with some current studies (Chen et al., 2020; Sun et al., 2020, 2021) (see Table S3 for more comparisons), the cyclic adsorption-desorption efficiency is not high. The main reason for the decreased adsorption efficiency was that the desorption method of ethanol washing could not completely desorb the MPs. Therefore, finding a solvent that can desorb as much MP as possible is also the future direction to explore. In this way, efficient cyclic adsorption and desorption can be achieved in a green and environmentally friendly manner.

3.3. Exploration of MPs adsorption mechanism

3.3.1. Adsorption energy analysis

The adsorption of PS on the surface of carbon material was calculated using the styrene model as PS. The adsorption configurations of PS on different carbon materials are shown in Fig. S9. The adsorption distance between PS and pristine carbon is 3.51 Å, a typical weak interaction adsorption distance. It is speculated that the adsorption of PS on the pristine carbon is physical adsorption. While the adsorption distances of PS on Fe—N carbon and Fe—O carbon are only 2.08 Å and 2.11 Å, respectively,



Fig. 6. Anti-interference performance of three adsorbents under different conditions. Adsorption capacities in (a) different pH, (b) different water quality (MPs concentration = 50 mg/L, Adsorbent dosage = 10 mg, Adsorption time = 10 min).

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Table 1

Adsorption energies of three carbon material models for PS in water.

E_{C+PS} (a.u.)	E _{PS} (a.u.)	E _C (a.u.)	E _{ad} (kJ/mol)
-3174.01	- 309.62	-2864.35	-108.47
-3255.60	-309.62	-2945.95	-91.28
-1920.04	-309.62	-1610.40	-61.22
	$\begin{array}{c} E_{C+PS} \text{ (a.u.)} \\ -3174.01 \\ -3255.60 \\ -1920.04 \end{array}$	$\begin{array}{c} E_{C+PS}\left(a.u.\right) & E_{PS}\left(a.u.\right) \\ \hline -3174.01 & -309.62 \\ -3255.60 & -309.62 \\ -1920.04 & -309.62 \end{array}$	$\begin{array}{c c} E_{C+PS} \left(a.u. \right) & E_{PS} \left(a.u. \right) & E_{C} \left(a.u. \right) \\ \hline & -3174.01 & -309.62 & -2864.35 \\ -3255.60 & -309.62 & -2945.95 \\ -1920.04 & -309.62 & -1610.40 \end{array}$

which is much shorter than the adsorption distance between PS and pristine carbon. It means there will be both physical and chemical adsorption between Fe-doped carbon materials and PS.

To further quantify the adsorption strength of PS on the carbon material surface, the adsorption energy of PS was calculated on the carbon material in an aqueous solution. The adsorption energy calculation formula is shown in Eq. (S6). The adsorption energies of PS on the surface of carbon materials in aqueous solution are shown in Table 1. The adsorption energy of PS on pristine carbon was -61.22 kJ/mol, while that on Fe—O carbon and Fe—N carbon was -91.28 kJ/mol and -108.47 kJ/mol, respectively. It can be seen that the closer the adsorption distance between PS and carbon

material, the stronger the adsorption energy. In short, Fe-doping can significantly improve the adsorption strength of carbon materials to PS. Moreover, Fe—N carbon has a more significant lifting effect than Fe—O carbon. Since the Fe-doping content in FeMSC is much higher than that in FeMAC, and the distribution is more uniform, the adsorption performance of FeMSC is much higher than that of FeMAC.

In addition, the adsorption energies of PS were also calculated on carbon materials in an ethanol solution, as shown in Table S6. The adsorption energies of PS on pristine carbon, Fe—O, and Fe—N in ethanol solution were -53.06 kJ/mol, -83.83 kJ/mol, and -100.16 kJ/mol, respectively. It is found that the adsorption energy in ethanol solution is lower than that in water, which is why ethanol can desorb PS from carbon materials. It is worth mentioning that the adsorption energy in ethanol is still relatively high (although lower than that in water), resulting in an incomplete desorption process.

3.3.2. Visualized interactions analysis

In order to study the various interactions in the adsorption system more intuitively, the IRI isosurface of the adsorption system is shown in Fig. 7.



Fig. 7. Diagrams of all interactions present in the system when PS is stably adsorbed on (a) Fe-N carbon, (b) Fe-O carbon, and (c) pristine carbon.

Covalent interactions (blue), van der Waals (vdW) interactions (green), and steric hindrance (red) are present in the three systems. For the adsorption process, focusing on the interaction region between molecules is necessary. The adsorption between PS and pristine carbon presents a large vdW interaction region, which is mainly the π - π interaction formed by the benzene ring on PS and the benzene ring on the carbon material. In addition to the vdW interaction, the adsorption of PS on Fe-N carbon and Fe-O carbon also has Fe-C bonds (blue) formed by C on PS and Fe on carbon materials. The Mayer bond level was calculated to measure the strength of the Fe--C bond, as shown in Fig. 7. The Fe-C bond Mayer bond order in Fe-N carbon is 0.358 and 0.346, respectively, while in Fe-O carbon is 0.357 and 0.279, respectively. Mayer bond-level analysis showed that Fe-doping enhanced adsorption by forming chemical bonds, and the chemical bond strength was higher in Fe-N carbon. This can also be reflected from the highest adsorption energy of PS on Fe-N carbon. However, the Mayer bond level of the C—C bond between PS and the pristine carbon is only 0.009, obviously, no chemical bond is formed, that is, there is only physical adsorption.

In addition, the electron density difference isosurface map was also plotted during the adsorption system, as shown in Fig. S10. There is a small amount of electron density reduction isosurface between PS and pristine carbon due to the electron density reduction caused by Pauli repulsion. However, since the adsorption at this time is physical adsorption dominated by weak interactions, the electron density difference is very small ($\Delta \rho = -0.0005$ a.u.). Both Fe—N carbon and Fe—O carbon form chemical adsorption with PS, and the electron density increases greatly in the region where chemical bonds are formed. At this moment, the electron density difference is relatively large ($\Delta \rho = 0.008$ a.u.), which reveals the chemisorption mechanism between Fe-doped carbon and PS from the charge transfer.

4. Conclusions

In this study, magnetic sponge carbon for MPs adsorption was prepared using glucosamine hydrochloride as a carbon source and melamine as a foaming agent. Because FeMSC is fluffy and contains up to 8.37 % iron, the adsorption capacity of PS in 200 mg/L MPs solution is up to 369.07 mg/g. Moreover, the study of adsorption kinetics found that the material can reach adsorption saturation within 10 min, thus realizing rapid adsorption and separation. The fitting results of the adsorption isotherm show that the theoretical maximum adsorption capacity of the material is 4994.32 mg/g, which indicates that the material has excellent development prospects. FeMSC also has strong anti-interference capability. Except in strong alkaline solution with pH = 11, it has good adsorption performance in other pH solutions and different water quality. In addition, based on the characterization and experimental results, the adsorption mechanism was further analyzed by theoretical calculation on the atomic scale. The calculation results show that the adsorption between the pristine carbon material and PS is mainly π - π interaction, which is typical physical adsorption. The iron atoms in FeMSC can form chemical adsorption with PS, significantly improving its PS adsorption capacity. In short, this material can quickly and efficiently adsorb MPs from water and quickly separate MPs from water, which is a promising microplastic adsorbent.

CRediT authorship contribution statement

Hongxian Li: Methodology, Investigation, Analysis, Writing; Minghui Tang: Methodology, Investigation, Writing - Review & editing; Jun Wang: Investigation, Methodology; Lulu Dong: Investigation, Methodology; Ling Wang: Methodology, Investigation; Qi Liu: Methodology, Investigation; Qunxing Huang: Writing - Review & editing, Supervision; Shengyong Lu: Writing - Review & editing, Supervision.

Data availability

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.

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Appendix A. Supplementary data

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