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RESEARCH ARTICLE

Effect of gastric fluid on adsorption and desorption of endocrine disrupting chemicals on microplastics

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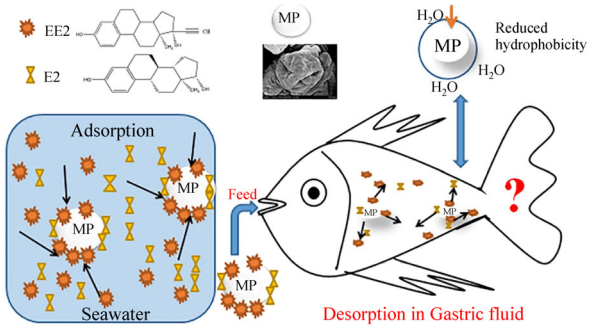
HIGHLIGHTS

- Effect of gastric fluid on EDCs adsorption-desorption to microplastics was evaluated.
- The gastric fluid enhanced desorption of EDCs on the surface of microplastics.
- Adsorption and desorption isotherms fitted the Freundlich model well.
- Desorption ratios of EE2 (55%–59%) on PVC were larger than that of E2 (49%–55%).
- Decrease in pH and increase in ionic strength in gastric fluid strengthen desorption.

GRAPHIC ABSTRACT



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ABSTRACT

Microplastics and endocrine disrupting chemicals are emerging pollutants in the marine environment because of their potential hazards. The effect of gastric fluid on the adsorption and desorption of 17β-estradiol (E2) and 17α-ethynylestradiol (EE2) to microplastics was investigated. The adsorption and desorption isotherms of E2/EE2 on microplastics could be well fitted by the Freundlich model while the Gibbs free energy of these processes were negative, proving that the reaction occurred spontaneously on the heterogeneous surface of the microplastics. Desorption ratios of EE2 (55%–59%) on PVC were larger than that of E2 (49%–55%) to indicate that EE2 was less stable in gastric fluid, which could be explained by the fact that the hydrophobicity of EE2 was greater than E2. E2/EE2 were more easily desorbed from PVC in the gastric fluid and the desorption amount (5.25–12.91/7.19–17.86 μg/g) increased by 2.51 times in comparison with that in saline solution (2.22–7.81/2.87–10.80 μg/g). The decrease of pH and the increase of ionic strength in gastric fluid could further strengthen desorption of E2/EE2 from PVC. The promotion of gastric juice on desorption of PVC was achieved by reducing the hydrophobicity of the PVC surface. The desorption rate of E2/EE2 at 18°C and 38°C was respectively 44%–47%/46%–50% and 49%–55%/56%–59%, indicating that PVC loaded with E2/EE2 had a relatively greater risk of releasing pollutants in the gastric fluid of constant temperature marine organisms while higher temperatures exposed higher hazards for variable temperature animals. The interaction between microplastics and pollutants might be mainly hydrophobic interaction.

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1 Introduction

The pollution of emerging contaminants such as microplastics in the ocean has attracted worldwide attention (Coffin et al., 2019; Cai et al., 2022; Lu et al., 2020a; 2022a). The global use of plastics is more than 400 million tons each year according to statistics, of which 8 million tons are discharged as garbage into the marine environment (Jambeck et al., 2015). Plastic waste on land could enter the marine environment through rivers and wastewater treatment systems or it can be blown into the offshore by the wind (Khalid et al., 2021). Plastic fragments are gradually cracked into smaller and smaller

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fragments under the action of physical, chemical and photodegradation factors, some of which with a particle size of less than 5 mm are called microplastics to be ingested by organisms easily (Liu and Wang, 2020). Microplastics have been detected in the global marine environment including estuaries, coastlines, seawater, sediments, deep seas and the polar region (Stollberg et al., 2021; Khalid et al., 2021). Microplastics can absorb and accumulate pollutants from the water environment to serve as ideal carriers for pollutants due to the characteristics of small particle size, large specific surface area, strong hydrophobicity and high mobility (Liu and Wang, 2020).

Endocrine disrupting chemicals, also known as environmental estrogen, refer to exogenous substances that disturb the balance of secretion in the body (Lu et al., 2021a; 2021b; 2022b). Typical steroid estrogens including 17β-estradiol (E2) and 17α-ethynylestradiol (EE2) can produce endocrine disrupting effects at trace amounts (ng/L) to cause potential influence on individual hormonal control, gender differentiation and reproduction (Lu et al., 2020a). Emerging contaminants including EDCs and microplastics can enter the seawater from wastewater discharge due to the incomplete removal of emerging contaminants by traditional wastewater treatment technology (Torres et al., 2021; Cai et al., 2022; Lu et al., 2020a; 2020b; 2021b). It had been proved that the exposure of endocrine disrupting chemicals in aquatic environment to aquatic organisms could induce a stress response (Lu et al., 2021a). Intake of microplastics increased the bioavailability of persistent organic pollutants in fish (Lee et al., 2019). Particulate materials such as microplastics in the ocean can easily adsorb and accumulate endocrine disrupting chemicals with high octanol/water partition coefficient (Kow) to become one of the reservoirs of pollutants (Stollberg et al., 2021). It was generally believed that the adsorption effect would reduce the harm of pollutants entering the environment to organisms while the ecological toxicity and bioavailability of pollutants would greatly increase once the adsorbed pollutants were desorbed (Stollberg et al., 2021). Microplastics as the carrier of pollutants may release harmful substances into the body if ingested by marine organisms, which is an important way to introduce pollutants into the food chain (Coffin et al., 2019). In particular, the gastric fluid environment of organisms can enhance desorption of persistent organic pollutants from the surface of microplastics in comparison with aqueous solutions (Lee et al., 2019). More importantly, the pollutants desorbed in the gastric fluid were transported to the tissues and organs of organism to cause additional toxic effects (Coffin et al., 2019). The release of chemical pollutants in the digestive juice may be an important process for pollutants to become bioavailable in the ecosystem, which is harmful to the environment and human health (Bakir et al., 2014a). Therefore, the impact of microplastics on the marine ecological environment needs to be investigated thoroughly.

The adsorption and desorption of pollutants on microplastics have been widely studied (Coffin et al., 2019; Lee et al., 2019; Lu et al., 2020a). However, little attention focuses on desorption and release of endocrine disrupting chemicals from microplastics in gastric fluid. This study used laboratory-experiments to explore the adsorption and desorption of E2 and EE2 on microplastics with existence of simulated gastric fluid. Owing to the complexity of factors affecting microplastics adsorption (Coffin et al., 2019), the conditions of microplastics adsorption including different pollutant concentrations and seawater salinity were set to better understand the potential harm of microplastics to the environment. Desorption degree of E2/EE2 from microplastics in simulated gastric fluid was evaluated, which was compared with that under saline conditions. At the same time, simulated gastric fluid environments with different pH and ionic strength conditions were used to investigate the effect of desorption. The conditions represented by cold-blooded and warm-blooded marine organisms were respectively used to explore the desorption rate of pollutants in their gastric fluid. The purpose of this study was to clarify the adsorption and desorption ability of microplastics to target pollutants (E2 and EE2). These findings were of great significance for assessing environmental risks of microplastics and endocrine disrupting chemicals.

2 Materials and methods

2.1 Reagents and chemicals

Target pollutants including 17β-estradiol (E2) and 17α-ethynylestradiol (EE2) with purity greater than 97% were purchased from Tixiai (Shanghai) Chemical Industry Development Co., Ltd. The source of PVC (polyvinyl chloride) with an average size of 0.11 mm was Guangzhou Bofeng Chemical Technology Co., Ltd (China). Pepsin was provided by Beijing Solarbio Science & Technology Co., Ltd. HPLC grade methanol and acetonitrile were supplied by Merk (Germany). The NaCl and HCl purchased from Sinopharm Reagent Beijing Co., Ltd were both analytically pure. The seawater (pH: 7.84–8.09, salinity: 35 ‰) obtained from ocean area of Yantai was filtered by 0.22 μm glass fiber filters (HNTY Company, Haining, China) and sterilized for the adsorption test. The stock solution of E2/EE2 was prepared with methanol at the concentration of 1 g/L and stored in a 4°C refrigerator for one month (Lu et al., 2020a). The reaction solution was obtained by diluting the stock solution according to the experimental needs.

2.2 Absorption experiment

The initial concentrations of E2/EE2 were set to 200, 500 and 1000 μg/L while the salinity of the reaction solution (15 ‰, 25 ‰, and 35 ‰) was obtained by diluting seawater with ultrapure water. Microplastics (0.64 g) were put to each conical flask containing 80 mL reaction solution, which was placed in a light shielded shaking incubator at 170 rpm and 25°C. Samples with volume of 0.5 mL collected at specific time intervals were mixed with 0.5 mL acetonitrile and the mixtures were centrifuged at a high speed (12000 rpm) for 6 min to determine the concentration of E2/EE2 in the sample by UPLC. The control groups without microplastics and E2/EE2 were set respectively to eliminate the interference of external factors affecting the experimental results. Replicate experiments were performed for each test and the relative standard deviation (RSD) of experimental data was less than 5%. Origin 8.0 was used for data processing as well as one-way analysis of variance (ANOVA) was used to compare the difference between adsorption amount under different treatments ($p < 0.05$).

2.3 Desorption experiment

All microplastics with adsorbed pollutants obtained by adsorption experiments were respectively desorbed in simulated gastric fluid, which was acquired through mixing 3.2 g/L of pepsin and 100 mM of sodium chloride solution (United States Pharmacopeial Convention, 1995). The adsorption amount of E2/EE2 on PVC was calculated after the adsorption equilibrium, which was the initial amount of E2/EE2 combined with microplastics in the desorption experiment. The microplastics with adsorbed pollutants were air-dried for 48 h and then placed in conical flasks containing 80 mL simulated gastric fluid without pollutants at the pH of 2. Conical flasks were placed in a dark shaker at 38°C and 170 r/min.

Pollutant-laden microplastics in the adsorption solution with a salinity of 35 ‰ were selected as a representative to carry out experiments of the factors affecting the desorption ability in gastric fluid due to the global average seawater salinity of 35 ‰. The microplastics loaded with EDCs were placed in background solution I (pH = 2, 100 mM NaCl) and background solution II (pH = 7, 100 mM NaCl) to compare the desorption behavior in gastric fluid conditions. Furthermore, the effects of different pH values (2, 4, and 7) and ionic strength (10.0, 100, and 200 mM) in gastric fluid on the desorption behavior of microplastics were investigated. Temperatures 18°C and 37°C were set to investigate the impact of microplastics desorption on variable temperature and constant temperature marine organisms. Changes in the surface of microplastics treated with different solutions were characterized by Fourier transform infrared spectroscopy (Nicolet iS 10, Thermo Fisher, US) and a contact angle analyzer (OCA 50, Dataphysics, Germany). Other experimental steps were same with the adsorption experiment.

2.4 Analytical method

The concentrations of endocrine disrupting chemicals (E2 and EE2) in liquid phase were accurately detected by ultra-high performance liquid chromatography equipped with a fluorescence detector (excitation wavelength: 280 nm, emission wavelength: 310 nm). The C18 reversed phase column (2.1 mm × 50 mm, 1.7 μm) was used for the separation of compounds. The mobile phase consisted of 50% water and 50% acetonitrile at the flow rate of 0.2 mL/min.

2.5 Data treatment

The adsorption amount was calculated based on previous study (Su et al., 2021). The kinetic processes were fitted by pseudo-first-order model, pseudo-second-order model and first-order two-compartment kinetics model (Lu et al., 2020a; Deng, 2020; Vakili et al., 2021), while the Freundlich model was used for adsorption and desorption isotherms (Salimova et al., 2020). Gibbs free energy (ΔG^0) and desorption hysteresis coefficient (HI) were calculated according to formulas (Liu et al., 2012).

3 Results and discussion

3.1 Adsorption of E2/EE2 by microplastics to obtain microplastics loaded with pollutants

The effects of the salinity of reaction solution and the concentration of pollutants on the adsorption of E2/EE2 by microplastics were explored (Fig. 1). The binding ability of microplastics to endocrine disrupting chemicals was related to the concentration of corresponding pollutants and the salinity of water environment (Bakir et al., 2014b; Velzeboer et al., 2014). The adsorption process of E2 and EE2 on microplastics was roughly similar, which could be attributed to three stages including the rapid adsorption process at the initial stage, the slow adsorption process at the intermediate stage and the equilibrium process. A large number of adsorption sites on the microplastics were available for the adsorption of pollutants at the initial stage. The adsorption sites were gradually saturated with the passage of adsorption time to cause a slow increase of adsorption amount and finally adsorption equilibrium was reached (Li et al., 2020; Du et al., 2020; Bao et al., 2021). In all experiments, the adsorption equilibrium of E2/EE2 could be completed within 48 h. Moreover, the adsorption amount of EE2 was always higher than E2, which might be related to the different hydrophobicity of pollutants, indicating that hydrophobicity might play a major role in the adsorption process (Lu et al., 2020a). Specifically, the

enhanced salinity of the reaction solution would promote the adsorption of E2/EE2 by PVC while the higher initial concentration of E2/EE2, the greater the adsorption amount of PVC. The adsorption amount of E2/EE2 by PVC corresponding to pollutants with an initial concentration of 200, 500 and 1000 μg/L was respectively 6.14/8.13, 9.84/12.22 and 13.84/15.73 μg/g at salinity of 16 g/L while that respectively reached 10.48/12.70, 17.32/20.12 and 25.87/30.19 μg/g when the salinity increased to 32 g/L. High salt conditions could improve the adsorption of microplastics to persistent organic pollutants based on the previous study (Velzeboer et al., 2014). The influence of salinity on the adsorption of microplastics could be ascribed to mechanisms with one that high salinity would decrease the electrostatic repulsion between microplastics and pollutants and the other that the enhanced salinity of reaction solution would reduce the solubility of pollutants (Lu et al., 2020a). The promoting effect of initial concentration on the adsorption of microplastics could be explained by these facts that higher initial concentration could provide an important driving force for E2/EE2 to overcome the resistance between aqueous phase and solid phase as well as increased the collision frequency between E2/EE2 and microplastics (Khalid et al., 2021).

To study the adsorption kinetic characteristics of E2/EE2 on PVC under different reaction solution salinity and initial pollutant concentration, pseudo-first-order kinetic model and pseudo-second-order kinetic model were used to fit the experimental results. Both the pseudo-first-order kinetic model and pseudo-second-order kinetic model could describe the adsorption process of microplastics for E2/EE2 since the correlation coefficient (R^2) of the two models was greater than 0.96. However, the equilibrium adsorption amount obtained by fitting the pseudo-first-order kinetic model ($q_{ex,\ cal}$ = 6.06–30.31 μg/g) was closer to the experimental value ($q_{ex,\ exp}$ = 6.14–30.19 μg/g) in comparison with that obtained by fitting the pseudo-second-order kinetic model ($q_{ex,\ cal}$ = 7.08–34.71 μg/g) to indicate that the pseudo-first-order kinetic model was more suitable for describing the adsorption behavior of E2/EE2, revealing that physical process might be the rate limiting step of E2/EE2 adsorption by PVC. It was also confirmed in previous studies that the pseudo-first-order kinetic model had a good fitting effect for PVC adsorption of organic pollutants (Lu et al., 2020a). Pollutants with larger molecular weight had greater molecular power to obtain the more active sites on the surface of PVC, which could also explain the fact that the adsorption amount of EE2 on PVC was greater than that of E2 (Chen et al., 2015).

3.2 Desorption of E2/EE2 adsorbed on PVC in simulated gastric fluid

The PVC loaded with organic pollutants obtained in the adsorption process was desorbed in simulated gastric fluid in order to understand the potential release amount of organic pollutants in the organism. The amount of desorption for E2/EE2 on the microplastics increased with time until desorption equilibrium was reached, and the final desorption amount respectively accounted for about 50% of the adsorption amount (Fig. 2). The overall desorption trend presented that the more pollutants loaded on the microplastics, the higher the corresponding desorption amount. Desorption process reached equilibrium within 24 h and hardly exhibited desorption hysteresis, which was similar to the result of adsorption and desorption for anthracene by PVC (Bao et al., 2021). The adsorption of E2/EE2 on PVC first occupied high-energy sites and then low-energy sites so that E2/EE2 adsorbed on low-energy sites might be first released from PVC during the desorption process (Saini et al., 2021). The desorption amount improved with the increase of the equilibrium adsorption amount of E2/EE2, which could be attributed to the explanation that more low-energy sites on PVC with higher adsorption amount were occupied. Desorption amount of EE2 on PVC was larger than that of E2 to indicate that EE2 was less stable in gastric fluid and easier to be desorbed, which could be explained by the positive correlation between desorption ability of target hormones by microplastics and their hydrophobicity (Lu et al., 2020a). Desorption processes of PVC in simulated gastric fluid environment were fitted with pseudo-first-order and pseudo-second-order kinetic models. The desorption kinetic data were more consistent with the pseudo-first-order kinetic model by comparing the equilibrium adsorption amount and the correlation coefficient of the two models, which was similar to the adsorption process. E2/EE2 adsorbed on PVC could be easily released into the gastric fluid, which would result in higher accumulation and health risk (Bakir et al., 2014a).

3.3 Comparison of E2/EE2 desorption from PVC in three desorption solutions

Three desorption solution conditions (gastric fluid, background solution I and background solution II) were set to explore the effect of pepsin on desorption of endocrine disrupting chemicals by microplastics. The desorption amounts of E2/EE2 in gastric fluid, background solution I and background solution II were respectively 5.25–12.91/7.19–17.86 μg/g, 3.22–7.81/4.28–10.80 μg/g and 2.22–6.78/2.87–8.84 μg/g, showing that the desorption amount was gastric fluid>background solution I>background solution II. The lower pH would promote the desorption of E2/EE2 from microplastics based on two different pH background solutions without pepsin (pH = 2 and 7) while the desorption solutions containing pepsin could desorb more E2/EEE2 based on the two desorption solutions with a pH of 2, which could be speculated that pepsin was the main factor for promoting the increase in desorption.

The desorption process of endocrine disrupting chemicals adsorbed on microplastics in three desorption

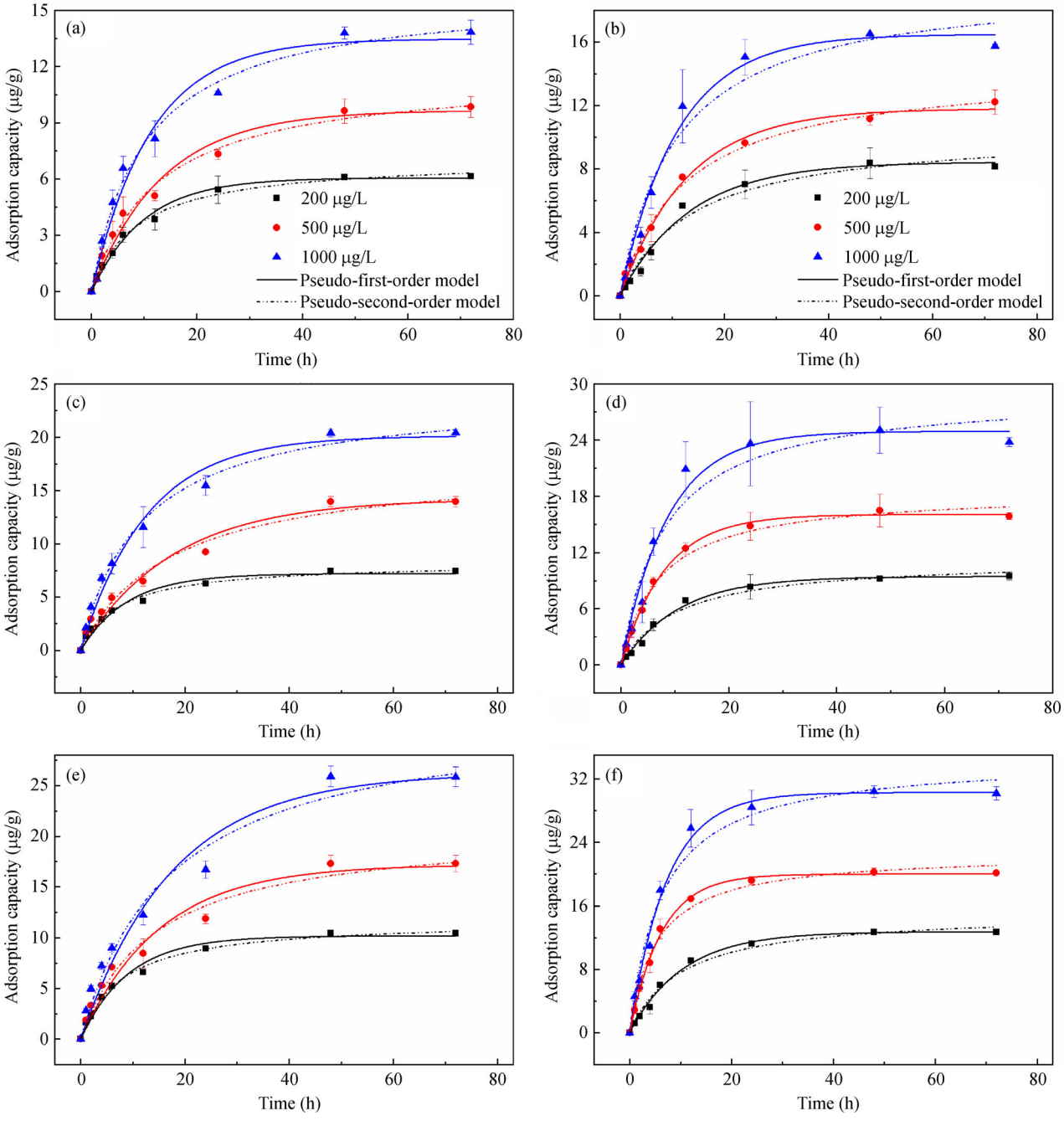

Fig. 1 The adsorption kinetics of E2 (a, c, e) and EE2 (b, d, f) on microplastics in seawater with salinity of 15 ‰ (a, b), 25 ‰ (c, d) and 35 ‰ (e, f), respectively, fitted by pseudo-first-order and pseudo-second-order kinetic model.

solutions accorded with first-order two-compartment kinetics model (R^2>0.96) to illustrate that the desorption process consisted of fast desorption stage and slow desorption stage (Fig. 3). Moreover, the fast desorption phase could be completed within 2 h while the slow desorption phase was as long as several months. The study mainly evaluated the rapid desorption stage to explore the desorption mechanism of E2/EE2 from PVC due to the limitation on actual digestion time of marine organisms (Lee et al., 2019). The desorption of E2 and EE2 on microplastics showed the same trend that fast stage desorption value (F_{fast}) of simulated gastric fluid containing pepsin was greater than that of the background solution without pepsin, indicating that microplastics loaded with EDCs increased the risk of EDCs being transferred to gastric fluid once entered the organism. E2 and EE2 in the gastric fluid were easier to be released from PVC than the background solution without pepsin according to the

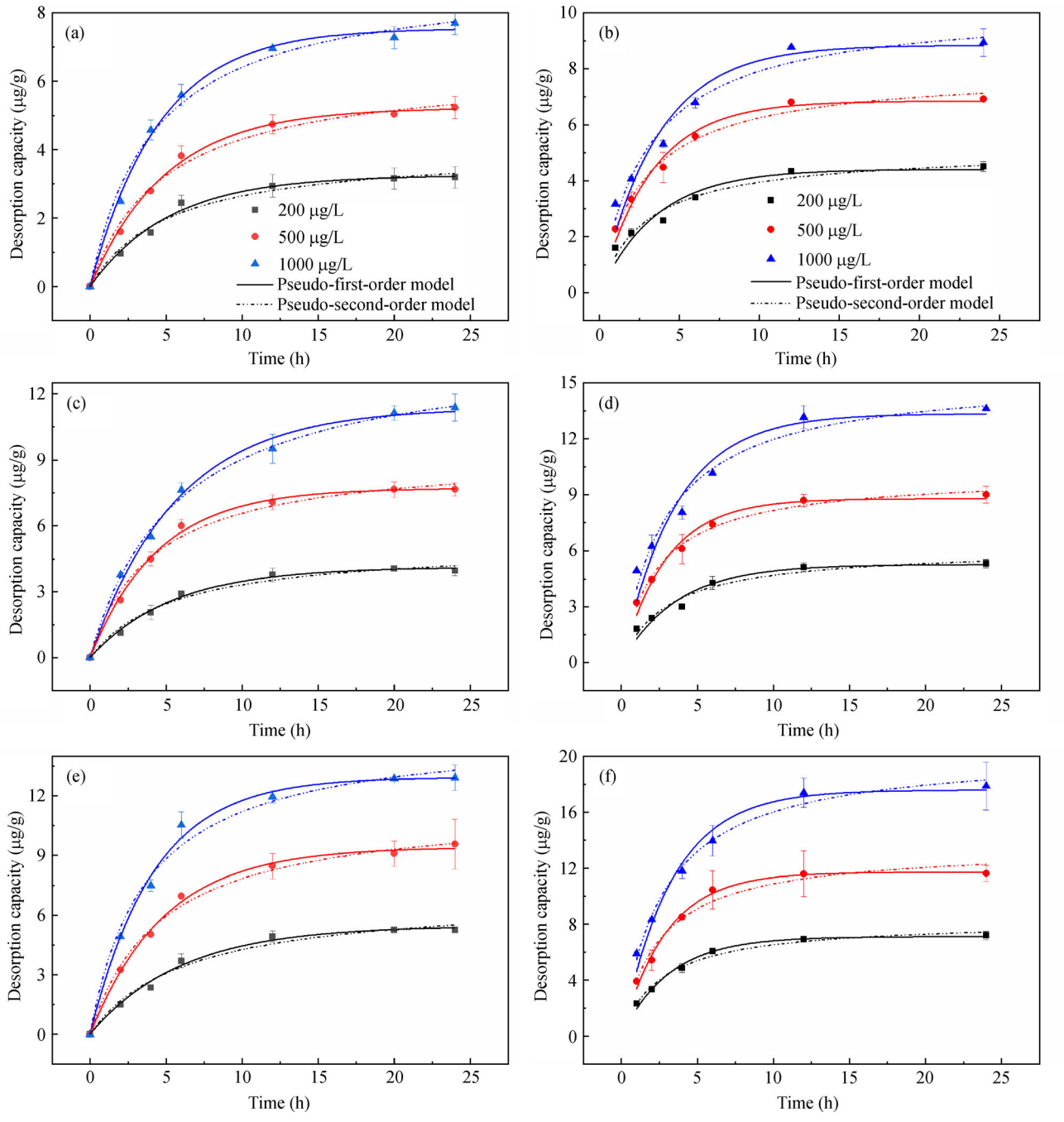

Fig. 2 The desorption kinetics of E2 and EE2 on microplastics in simulated gastric fluid, respectively, fitted by pseudo-first-order and pseudo-second-order kinetic model. (a–f) in the desorption process respectively corresponded to (a–f) in the adsorption process in Fig. 1.

calculated value of the rapid desorption rate constant. Similarly, the desorption amount of compounds immersed in gastric fluid was 20 times higher than that in distilled water and seawater if immersing plastic fragments with decabromodiphenyl ether in different solutions (Tanaka et al., 2015).

On the one hand, the π - π interaction, which was considered to be the important mechanism of E2/EE2 adsorption, would be blunted under the action of proteins such as pepsin. On the other hand, the aromatic hydrocarbon of protein would compete with the pollutants for the adsorption sites on the microplastics, which impelled desorption of pollutants from the microplastics (Coffin et al., 2019). Furthermore, pepsin formed micelles in the solution to increase the solubility of the hydrophobic compounds adsorbed on the microplastics, which could reduce the apparent adsorption distribution coefficient of pollutants (Bakir et al., 2014a).

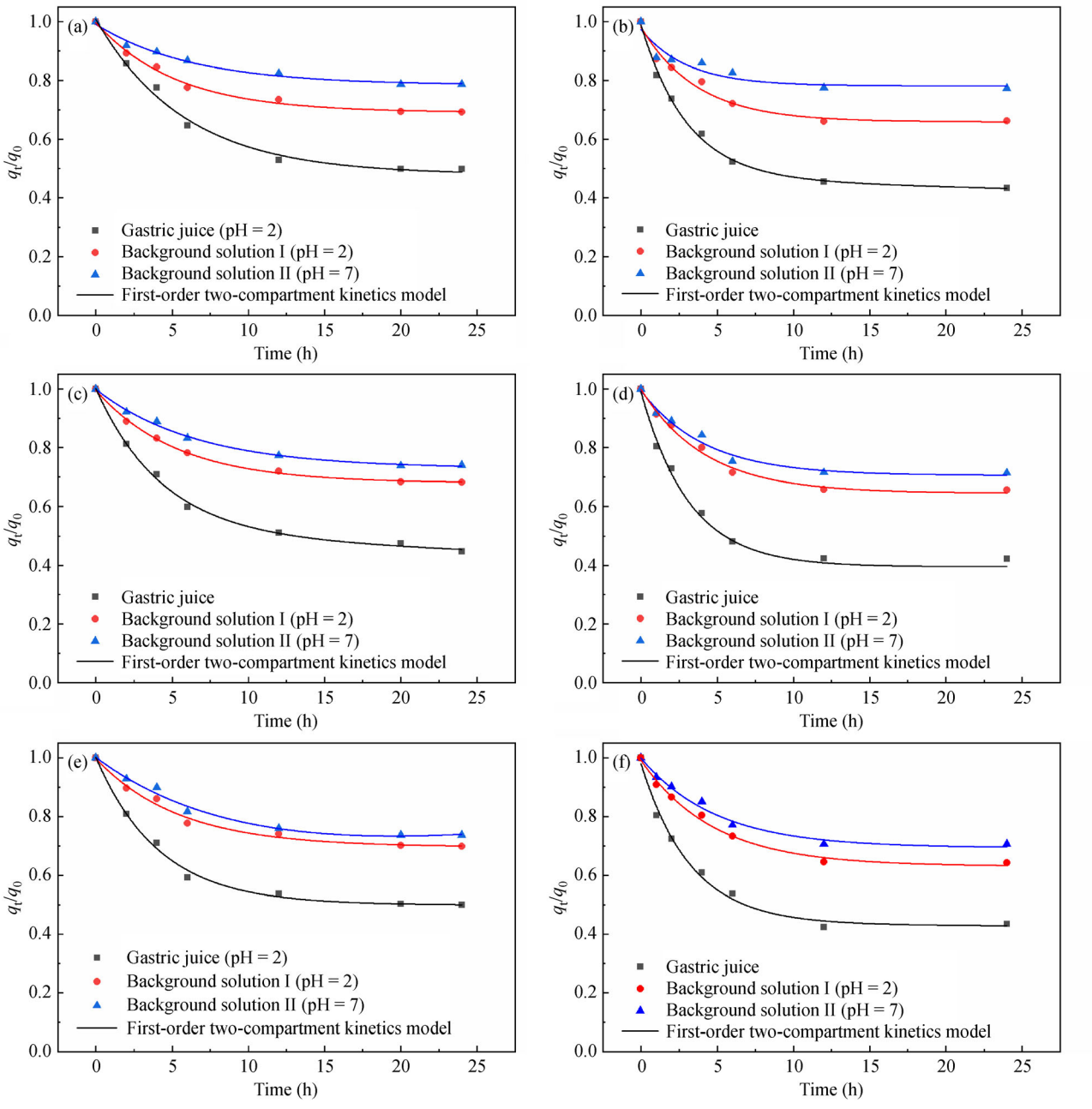

Fig. 3 Comparison of E2 (a, c, e) and EE2 (b, d, f) desorption from PVC in three desorption solutions. (a) and (b), (c) and (d), (e) and (f) respectively represented the initial concentration of pollutants with 200, 500, 1000 μg/L in the adsorption solution. The desorption kinetics was fitted by first-order two-compartment kinetics.

3.4 Desorption behavior in different gastric fluid environments

Desorption was one of the basic processes to control the distribution, persistence and ecological impact of hydrophobic pollutants in aquatic systems (Tanaka et al., 2015). The gastric fluid environment of different species was different and that of the same species might also be different due to the fasting or eating state so that the desorption behavior of contaminants in gastric fluid might be affected by various factors (Bucking and Wood, 2009). The ability of PVC for desorption of E2/EE2 was further explored in different gastric fluid environments including pH and salinity (Fig. 4).

The desorption amount of PVC to E2/EE2 increased with the decrease of pH in the gastric fluid ($p < 0.05$), which meant that more acidic environment would promote desorption (Fig. 4a). Desorption amount of E2 and EE2 decreased by 1.36–1.55 times and 1.49–1.61 times at the pH of gastric fluid increasing from 2.0 to 7.0, respectively.

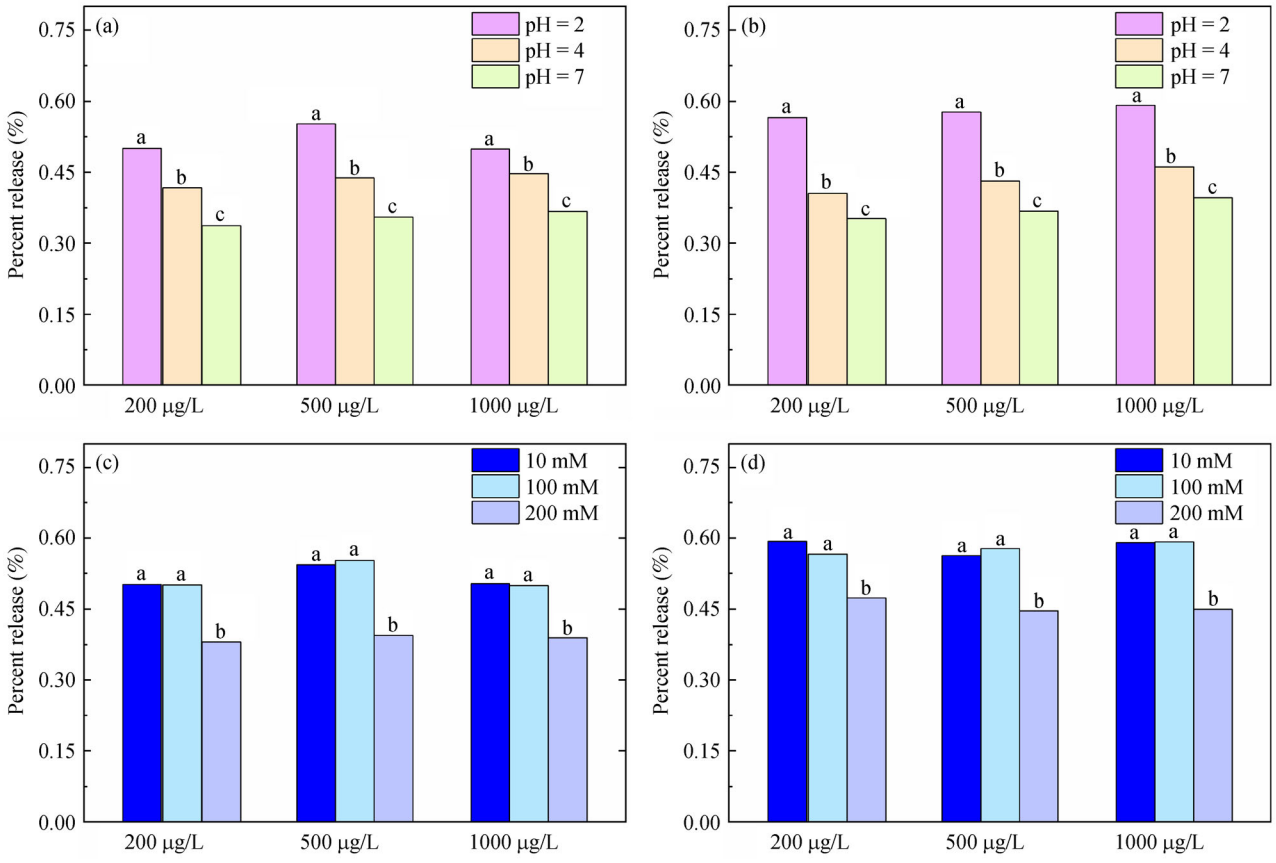

Fig. 4 Desorption behavior of E2 (a, c) and EE2 (b, d) in gastric fluid with different pH (a, b) and ionic strength (c, d).

The effect of pH on desorption might be related to the different solubility of endocrine disrupting chemicals at different pH values. The distribution of pollutants in solid and water phases was affected by their solubility, which would have a potential impact on desorption of pollutants on microplastics (Khalid et al., 2021). Kurnia speculated that the solubility of Gamavuton-0 in solution was related to the molecular morphology of Gamavuton-0 in different pH solutions. The presence of organic matter in protonated form would increase its solubility in solution (Kurnia et al., 2019). E2/EE2 containing hydroxyl groups tended to be protonated under acidic conditions to increase its solubility, promoting desorption of E2/EE2 from microplastics (Bao et al., 2021). In addition, abundant H + in the solution competed with E2/EE2 for adsorption sites on PVC at a lower pH value to cause an increase in the amount of desorption. The concentration of H^+ in the solution decreased to a certain extent as the pH value increased and the competition between H^+ and E2/EE2 weakened to bring about the decrease of desorption amount (Saini et al., 2021). The pH value of gastric fluid under fasting state was approximately 2 so that the intake of E2/EE2 m light be higher than that in eating state to increase ecological health risk in the aquatic system once the PVC loaded with E2/EE2 entered the organism under fasting state.

For E2 and EE2, increasing ionic strength significantly inhibited desorption in gastric fluid ($p < 0.05$) (Fig. 4b). The desorption amount of E2 and EE2 were respectively 5.25–13.02 μg/g and 7.35–17.84 μg/g at the ionic strength of 10 mM, almost 1.3 times that of 200 mM. The structure of pepsin would be changed under high salinity conditions to interfere the interaction of pepsin with EDCs and microplastics, which might be the reason for the decrease in the amount of E2/EE2 desorption (Mahapatra and Roy, 2019). Moreover, high salinity would also accelerate the salting- out effect of organic compounds to reduce the solubility of organic pollutants so as to strengthen the distribution of pollutants to the solid phase. Besides, the surface of PVC was positively charged (PZC = 5.99) in the gastric fluid environment with pH 2.0 as well as E2/EE2 molecules would also be positively charged in the solution under protonation, leading to the effect of electrostatic repulsion between pollutants and microplastics (Saini et al., 2021). The increase in salinity could neutralize the surface charge of the microplastics by compressing the

electric double layer to reduce the electrostatic repulsion between the pollutants and the microplastics, which would weaken desorption of EDCs from the microplastics surface (Lee et al., 2019).

3.5 The influence of external temperature on the release of E2/EE2 on microplastics

The desorption of E2/EE2 in gastric fluid at 18°C and 38°C was explored (Fig. 5), of which the conditions of 18°C and 38°C were used to simulate the gastric fluid ambient temperature of variable temperature and constant temperature marine organisms, respectively (Tanaka et al., 2015). The desorption rate of E2 at 18°C and 38°C was respectively 44%–47% and 49%–55% while that of EE2 was 46%–50% and 56%–59%. The desorption rate of E2/EE2 in constant temperature marine organisms were higher than that in variable temperature marine organisms, inferring that constant temperature marine organisms had higher bioavailability of pollutants, which was similar to

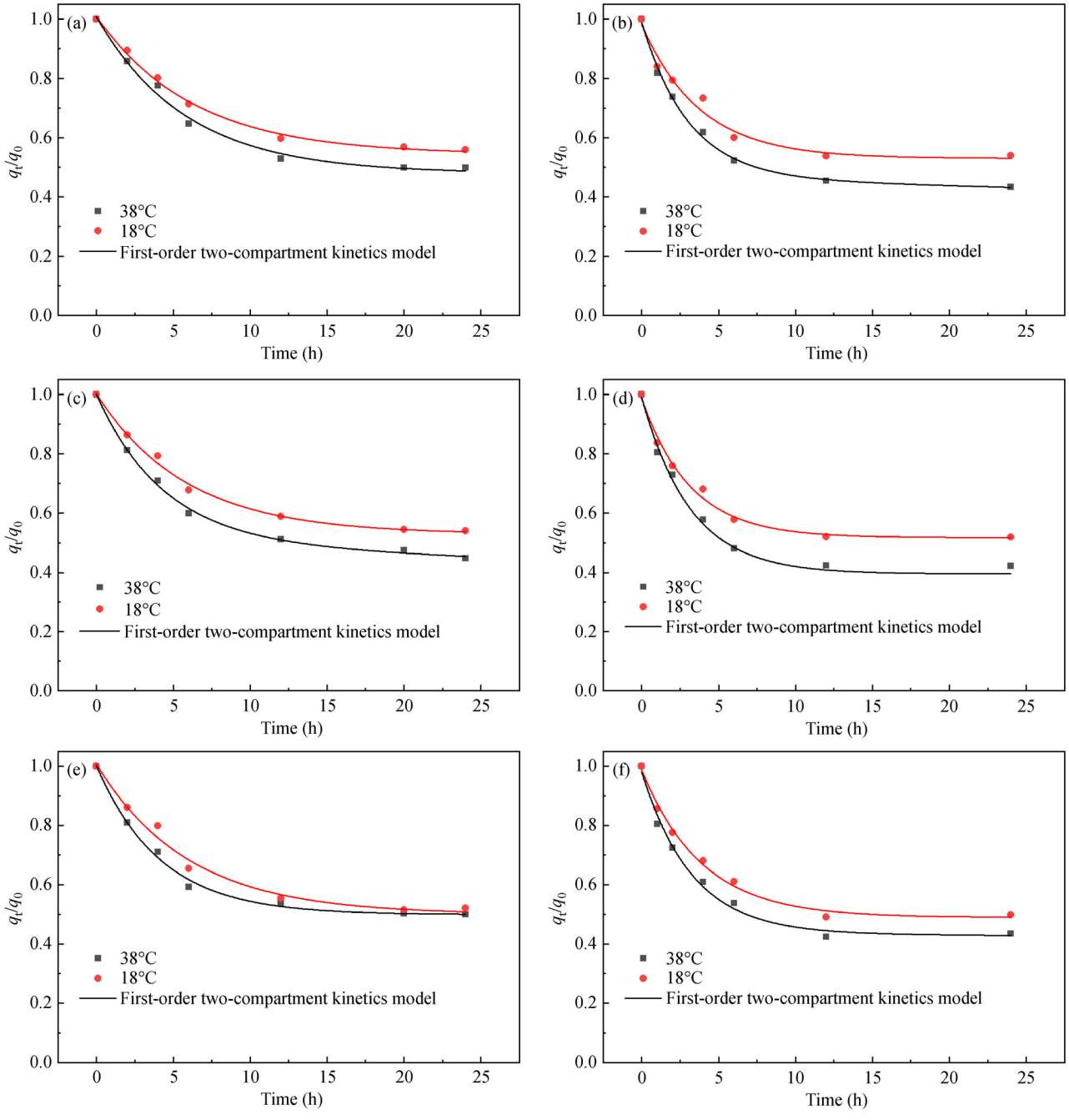

Fig. 5 The influence of external temperature on the release of E2 (a, c, e) and EE2 (b, d, f) on microplastics. (a) and (b), (c) and (d), (e) and (f) respectively represented the initial concentration of pollutants with 200, 500, 1000 μg/L in the adsorption solution. Desorption kinetics was fitted by first-order two-compartment kinetics.

the results of DDT desorption on microplastics (Bakir et al., 2014a). In addition, the F_{fast} value of constant temperature animals was higher than that of variable temperature animals by fitting the first-order two-compartment kinetics, which could also indicate that constant temperature animals had a higher risk of exposure to pollutants (Khalid et al., 2021).

3.6 Adsorption/desorption isotherm

The adsorption process of endocrine disrupting chemicals in seawater and desorption process in three different desorption solutions could be fitted with the Freundlich model (Fig. 6 and Table 1), showing that adsorption and desorption occurred on heterogeneous surfaces of PVC (Zhang et al., 2019). For the adsorption, the degree of linearity (N) fitted by the Freundlich model was less than 1 to indicate that PVC had good adsorption performance for E2/EE2 while the adsorption capacity of PVC to EE2 was greater than E2 ($K_{F\ (EE2)}$ 1.197 (μg/g)/(μg/L) ^{N}>$K_{F\ (E2)}$ 0.705 (μg/g)/(μg/L) ^{N}) to further illustrate the stronger adsorption amount of PVC to EE2. Parameters of desorption process in gastric juice corresponded to the smallest N value and the largest K_F value in comparison with the other two desorption liquids, which could also prove the strengthening effect of gastric fluid on PVC desorption. It could be inferred that both the adsorption and desorption reactions spontaneously occurred due to the negative value of ΔG^0 (Lu et al., 2020a). For the desorption process of PVC in three desorption solutions, the absolute value of ΔG^0 in the gastric fluid was the largest, meaning that desorption of PVC was the easiest (Wu et al., 2019). The desorption reaction had no obvious hysteresis (HI>1) to infer that the adsorption reaction was reversible (Liu et al., 2012).

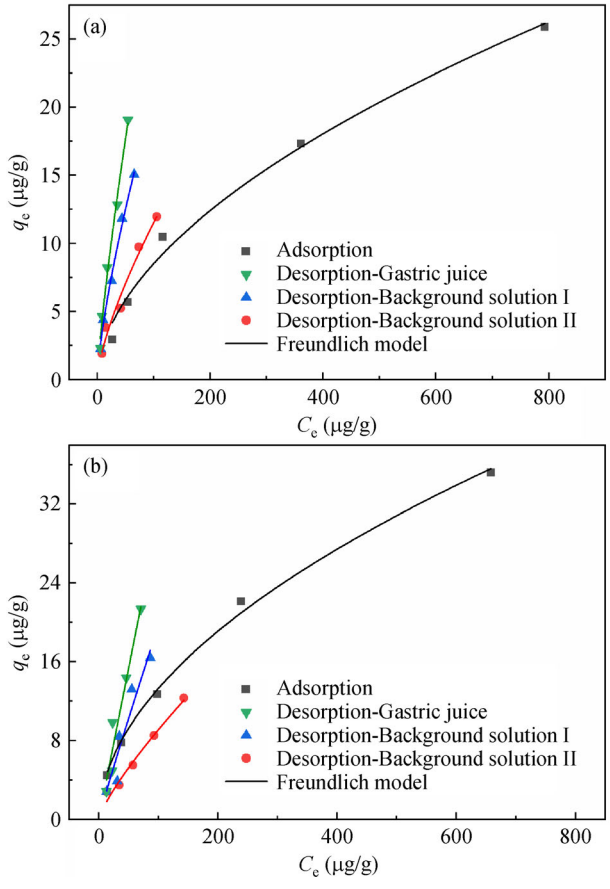

Fig. 6 The adsorption and desorption thermodynamic isotherms of E2 (a) and EE2 (b) fitted by Freundlich model.

3.7 Adsorption/desorption mechanism

The changes of microplastics samples treated in different environments could not be observed by Fourier transform infrared spectroscopy (Fig. 7a). The hydrophobicity of microplastics was tested by water contact angle to observe a significant change between the virgin and treated samples (Fig. 7b). Interestingly, the hydrophobicity of microplastics treated by seawater with different salinity was enhanced in comparison with the virgin sample and the salinity was positively correlated with hydrophobicity, which could also be used to explain the conclusion that the increase of seawater salinity promoted adsorption amount of PVC, fortunately. Another reason for the increased adsorption amount in the seawater with higher salinity might be that the salting-out effect was more intense (Lu et al., 2020a; Bakir et al., 2014a; Spiteri et al., 2008). Desorption amount was positively related to adsorption amount to be explained by the fact that low energy sites in microplastics loaded with more pollutants were more likely to be occupied while pollutants adsorbed at low-energy sites were easier to be desorbed. The addition of pepsin in desorption solution reduced the hydrophobicity of the microplastics surface to make desorption of pollutants enhanced compared with the pepsin-free background solution, indicating that the gastric fluid mainly affected desorption process by changing the hydrophobicity of the microplastics (Fig. 8). Pepsin might compete with E2/EE2 for adsorption sites on the PVC surface, which could also explain the fact that gastric fluid increased desorption of PVC. In summary, the differences of adsorption and desorption results in different solution media were caused by the changes of solid and liquid media to speculate that the interaction between the microplastics and the pollutants was mainly hydrophobic interaction.

4 Conclusions

Microplastics could be regarded as the sink and source of endocrine disrupting chemicals in the marine environment, which meant that pollutants could be adsorbed and desorbed by microplastics. The gastric fluid enhanced

Table 1 Parameters of Freundlich adsorption and desorption of E2/EE2 on PVC in three desorption solutions

EDCs	Process	K_F ((μg/g)/(μg/L)^N)	N	R^2	ΔG^0 (KJ/mol)	HI
E2	Adsorption	0.705	0.541	0.987		
	Desorption-Gastric fluid	0.315	0.799	0.948	– 13.996	1.309
	Desorption-Background solution I	0.255	0.944	0.996	– 15.394	1.351
	Desorption-Background solution II	0.229	0.993	0.990	– 16.062	1.482
EE2	Adsorption	1.197	0.523	0.996		
	Desorption-Gastric fluid	0.765	0.708	0.971	– 13.192	1.527
	Desorption-Background solution I	0.714	0.731	0.874	– 13.235	1.805
	Desorption-Background solution II	0.443	0.802	0.923	– 13.426	1.899

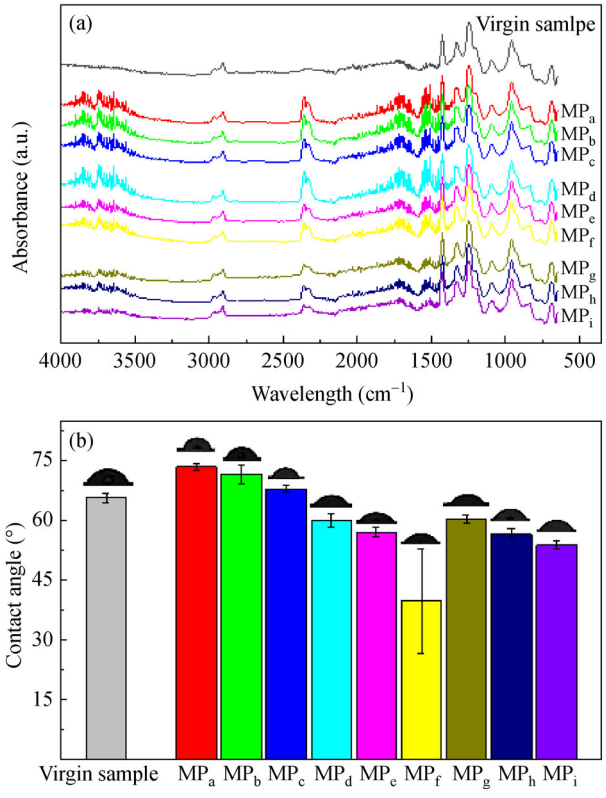

Fig. 7 The changes of microplastics samples treated in different solutions were observed by Fourier transform infrared spectroscopy and a water contact angle (MP_a: seawater with the salinity of 35 ‰, MP_b: seawater with the salinity of 25 ‰, MP_c: seawater with the salinity of 15 ‰, MP_d: simulated gastric fluid with 200 mM NaCl, MP_e: simulated gastric fluid with 100 mM NaCl, MP_f: simulated gastric fluid with 10 mM NaCl, MP_g: simulated gastric fluid at pH of 7, MP_h: simulated gastric fluid at pH of 4, MP_i: simulated gastric fluid at pH of 2).

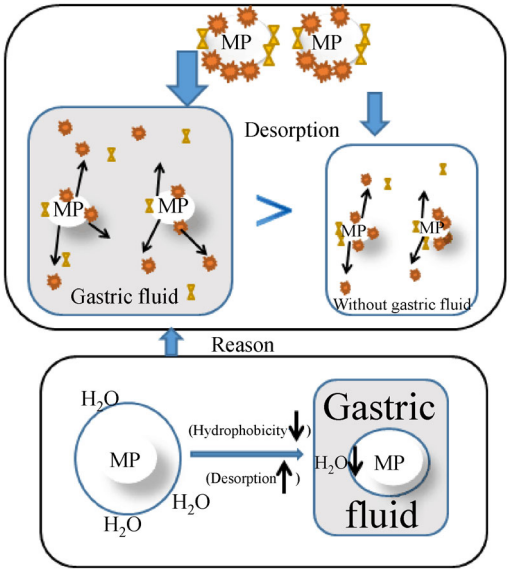

Fig. 8 The influence of gastric fluid on the desorption of endocrine disrupting chemicals on microplastics.

desorption of EDCs on the surface of microplastics due to the reduced hydrophobicity of the microplastics surface. Ionic strength was significantly related to desorption of E2/EE2 and it might become the most important factor for desorption of E2 and EE2 on PVC microplastics influenced by gastric fluid. The adsorption amount of PVC to E2/EE2 increased with the heightened solution salinity and pollutant concentration as well as the adsorption process was reversible based on the calculated desorption hysteresis coefficient (HI>1). Constant temperature marine organisms would undergo the possibility of more pollutants entering the digestive fluid and face higher exposure risk. This study will provide new insight on the adsorption and desorption behavior of pollutants on microplastics and the role of microplastics in the migration of pollutants.

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