Article

Adsorption of EDCs on Reclaimed Water-Irrigated Soils: A Comparative Analysis of a Branched Nonylphenol, Nonylphenol and Bisphenol A

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Abstract: Nonylphenol (NP) and bisphenol A (BPA) are two typical endocrine disrupter chemicals (EDCs) in reclaimed water. In this study, the adsorptions of NP, a branched NP (NP₇) and BPA on reclaimed water-irrigated soils were studied by isothermal experiments, and the different environmental factors on their adsorptions were investigated. The results showed that the adsorptions of NP and NP₇ on soils conformed to the Linear model, and the adsorption of BPA conformed to the Freundlich model. The adsorptions of NP, NP₇ and BPA on soils decreased with increasing temperatures and pHs. Adsorption equilibrium constant (K_d or K_f) were maximum at pH = 3, temperature 25 °C and As(III)-soil, respectively. The adsorption capacity of NP, NP₇ and BPA to soils under different cation valence were as follows: neutrally > divalent cations > mono-cations. K_d of NP₇ on soil was less than that of NP under different pH and temperatures, while under different cation concentrations it was the inverse. Fourier Transform Infrared Spectrometer (FTIR) analysis showed alkyl chains of NP and BPA seemed to form van der Waals interactions with the cavity of soil. Results of this study will provide further comprehensive fundamental data for human health risk assessment of NP and BPA in soil.

Keywords: nonylphenol; isomer; bisphenol A; adsorption; mechanism; reclaimed water soil

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1. Introduction

Irrigation with reclaimed water is a key method of alleviating agricultural water shortages (FAO, 2012) [1]. Recycled water can save water resources and promote the circulation of nutrients, but pollutants in reclaimed water and soil have potential to cause health risks to humans, especially the endocrine disrupter chemicals (EDCs), which have attracted wide attention recently. EDCs can lead to endocrine disorders in aquatic organisms, affecting reproductive development and the immune system [2,3].

Reclaimed water from wastewater treatment plants (WWTPs) is regarded as one of the main sources of EDCs in the agricultural environment. In addition to reclaimed water or effluent, treated sewage sludge is also used all over the world in agriculture soil [4–7]. Municipal landfills also contain leachate with significant amounts of EDCs that could migrate into groundwater [8–11]. In recent years, the fate of EDCs in groundwater and reclaimed water has received much attention [12–15].

Nonylphenol (NP) and bisphenol A (BPA) are two typical EDCs with high detection frequencies and concentrations in soils irrigated with reclaimed water [16,17]. The concentrations of NP in reclaimed water and agricultural soils were 0.05–63 µg·L^{−1} and

14.2–60.3 mg·kg^{−1}, respectively [13,18–21]. The concentrations of BPA in reclaimed water and agricultural soil were ND–101.6 µg·L^{−1} and ND–147 µg·kg^{−1}, respectively [16,22–25]. The Danish Institute of Safety and Toxicology (DIST) derived a preliminary tolerable daily intake (TDI) value for NP of 5 µg·(day kg)^{−1} body weight [26]. USEPA estimated a reference dose for BPA of 50 µg·(day kg)^{−1} body weight [27].

NP is composed of varieties of isomers. The estrogenic activity and the environmental fate were heavily dependent on the isomer structures, such as the side-chain length, degree of branching, α-substituent type and steric index [28–30]. The most toxic isomer among these isomers is 4-(3-ethyl-2-methylhexan-2-yl) phenol, which is noted as NP₇ [19,31] (Supplementary Material S1) in this study. Adsorption, migration, and degradation are the main processes for organic substances in soil. Degradation is the main fate of NP and BPA in soil during the reclaimed water irrigation. NP in sewage irrigation soil completed the rapid degradation stage within 20 days, and the removal rates reached above 80% [32], while adsorption is the first step for NP and BPA during the degradation process, which determines the rate of migration and transformation of NP and BPA into groundwater [33]. Adsorption of NP and BPA on soils is affected by a variety of factors, including dissolved organic matter (DOM), temperature, pH and ionic content [34–38], among which dissolved DOM plays a significant role [38–40].

The Daxing irrigation district, in the southeastern part of Beijing, China, was one of the typical sewage irrigation districts for more than 40 years. Previous studies of this district focused on inorganic pollution or total NP isomers [41,42]. The study of individual isomers is quite few because of the difficulty in the separation of NP isomers, while the risks of the different isomers to the local ecological environment were different. In particular, the most toxic isomer, NP₇, has much estrogenic activity to the environment, so the study on adsorption and desorption of the NP isomer on field soil is imperative. The aim of this work is to investigate: (1) Comparison of the adsorption of NP, NP₇ and BPA on field soil irrigated with reclaimed water; (2) The effect of different environmental factors of pH, temperature and different polyvalent metal ions (Na⁺, Ca²⁺, As(III)) on the adsorption of NP, NP₇ and BPA; (3) The mechanism of sorption of NP and BPA on soil by Fourier Transform Infrared Spectrometer (FTIR) analysis.

2. Materials and Methods

2.1. Reagents and Materials

Soils (0–20 cm) were collected from Daxing reclaimed water irrigation district, China (39°36′ N, 116°21′ E). After the plants' debris and residues were removed, the soils were freeze-dried at −20 °C and then 0.9 mm-sieved. The physicochemical properties of the soil are shown in Table 1. The background concentrations of NP, NP₇ and BPA in collected soils were 37 µg·kg^{−1}, 2 µg·kg^{−1} and below the method detection limit (MDL), respectively, and are reported in the former study [17].

Table 1. The physicochemical properties of the soil.

Parameters	Values
pH	8.1
OM (g/kg)	4.41
OC (%)	0.47
SSA (m ² /g)	4.79
Clay (%)	15
CEC (cmol/kg)	3.09
NO ₃ [−] (mg/kg)	103.86
PO ₄ ^{3−} (mg/kg)	8.57
Ca (g/kg)	24
Mg (g/kg)	6.16
Na (g/kg)	0.143

Note: CEC: cation exchange capacity; OM: organic matter (Supplementary Material S2); OC: organic carbon; SSA: specific surface area.

NP (0.25 g, 100%) and BPA (0.25 g, 99.8%) were purchased from Dr. Ehrenstorfer GmbH and dissolved in methanol with a concentration of $1000 \text{ mg} \cdot \text{L}^{-1}$ NaN_3 (200 g, 99%). Methanol (HPLC grade) and dichloromethane (HPLC grade) were purchased from Honeywell (Morris Plains, NJ, USA). As(III) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Anhydrous calcium chloride (CaCl_2) (500 g, >96%), sodium chloride (NaCl) (500 g, >99.5%) and anhydrous sodium sulfate (Na_2SO_4) (500 g, >98%) were obtained from the Tianjin Fuchen chemical reagents factory.

2.2. Isothermal Adsorption Experiment

The isothermal adsorption experiments were carried out under experimental conditions of pH7 at 25°C . We added 0.2 g soil into a 40 mL brown vial, with 30 mL 0.01 M CaCl_2 solution as the background electrolyte (except for the polyvalent metal ions experiment). NaN_3 was added at a concentration of $200 \text{ mg} \cdot \text{L}^{-1}$ to sterilize the soil. NP (or BPA) solution was added at an initial concentration of 200, 500, 1000, 1500, 2000, 3000 and $4000 \text{ } \mu\text{g} \cdot \text{L}^{-1}$. The brown bottles were placed in a thermostatic shaker at 25°C . NP and BPA were allowed to adsorb on the soil for 24 h to reach equilibrium. After the samples were centrifuged for 5 min (3000 rpm), NP (or BPA) in the supernatant was extracted (Supplementary Material S3) according to USEPA 3550C [43], and determined by Gas Chromatograph Mass Spectrometer (GC-MS). The effects of different environmental factors on the adsorption were studied, including pH of the solution (pH 3.7, and 11), temperatures (5°C , 25°C and 35°C) and polyvalent metal ions (Na^+ , Ca^{2+} and As(III)) with a concentration of 0.002 M. For the polyvalent metal ions experiment, the background electrolytes were Na^+ , Ca^{2+} and As(III) solution, respectively. The experiment was conducted in triplicate.

2.3. Dissolved Organic Matter (DOM)

In order to verify the effect of temperature on the dissolution of DOM, soil and water were mixed at a ratio of 1:150, shaking for 24 h at 5, 25 and 35°C , respectively. Then the solution was centrifuged at 3000 rpm. DOM in the supernatant solution was measured with TOC instrument.

2.4. Data Analysis

The commonly used isothermal adsorption models are Linear adsorption model, Langmuir model and Freundlich model. The formulas are as follows:

2.4.1. Linear Adsorption Model

$$C_s = K_d \times C_e \quad (1)$$

K_d : Adsorption equilibrium constant ($\text{L} \cdot \text{kg}^{-1}$).

C_e : Concentration of pollutants in the liquid phase at equilibrium ($\text{mg} \cdot \text{L}^{-1}$).

C_s : Concentration of pollutants in the solid phase at equilibrium ($\text{mg} \cdot \text{kg}^{-1}$).

2.4.2. Langmuir Adsorption Model

$$\frac{1}{C_s} = \frac{1}{(Q_{\max} \times K_L \times C_e)} + \frac{1}{Q_{\max}} \quad (2)$$

$Q_{\max}$: Maximum sorption amount of pollutants on solids ($\text{mg} \cdot \text{kg}^{-1}$).

C_e : Concentration of pollutants in the liquid phase at equilibrium ($\text{mg} \cdot \text{L}^{-1}$).

C_s : Concentration of pollutants in the solid phase at equilibrium ($\text{mg} \cdot \text{kg}^{-1}$).

K_L : Adsorption equilibrium constant ($\text{L} \cdot \text{mg}^{-1}$).

2.4.3. Freundlich Adsorption Model

$$C_s = K_f \times C_e^{\frac{1}{n}} \quad (3)$$

K_f : Adsorption equilibrium constant ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{kg}$).

C_e : Concentration of pollutants in the liquid phase at equilibrium (mg L^{-1}).

C_s : Concentration of pollutants in the solid phase at equilibrium ($\text{mg}\cdot\text{kg}^{-1}$).

$1/n$: Adsorption force parameter (dimensionless).

2.4.4. Organic Carbon Adsorption Constants

The soil sorption constants were normalized to the organic carbon sorption constants (K_{oc}). Because the main adsorbent is organic carbon in soil, and K_{oc} is a characterization of the sorption capacity of organic carbon. The formula is:

$$K_{oc} = K_d/f \quad (4)$$

K_{oc} : Adsorption coefficient of pollutants on organic carbon ($\text{mg}\cdot\text{kg}^{-1}$).

K_d : Adsorption coefficient of pollutants on soil ($\text{mg}\cdot\text{kg}^{-1}$).

f : Organic carbon content in soil (%).

2.4.5. Determination of NP and BPA

NP and BPA were detected with GC-MS (Agilent, 6890 N/5975), with automatic sampler (7683B Series), capillary-column ($60 \text{ m} \times 0.25 \mu\text{m} \times 0.25 \text{ mm}$, DB-5MS, Agilent Technologies, Palo Alto, CA, USA). The parameters were as follows: the inlet and the detector temperatures were set at 250°C and 280°C , respectively. Helium was used as the carrier gas, and the flow rate was 1 mL min^{-1} . The injection mode was splitless, at a sample volume of $1 \mu\text{L}$. The oven was heated as follows: Initial temperature was set at 40°C and maintained for 1 min, heated to 150°C at a rate of 8°C min^{-1} and maintained for 1 min, and then heated to 230°C at a rate of 5°C min^{-1} and maintained for 2 min. The ion source was electron impact and the temperatures of the ion source and triple-quadrupole were 230°C and 150°C , respectively; the voltage was 70 eV. Data were acquired with both Scan and SIM mode, and the scan range was 50 to 300 amu. The MDLs for NP isomers were $0.86\text{--}2.65 \mu\text{g}\cdot\text{kg}^{-1}$, and the MDL of BPA was $2.0 \mu\text{g}\cdot\text{kg}^{-1}$. The method recovery for NP and BPA ranged from 70% to 110%, which met the standard of the U.S. EPA [17].

2.4.6. FTIR Analysis

Soil before and after adsorption by NP and BPA were characterized by FTIR-650 with a deuterated triglycine sulfate (DTGS) detector. The instrument was under continuous dry air purge to eliminate atmospheric water vapor. Interferograms were averaged for 400–4000 scans at 4 cm^{-1} resolutions.

2.4.7. Statistical Analysis

IBM SPSS Statistics 22 software was used for the statistical analysis. The statistical differences were assessed using the one-way ANOVA test. The significance level of 0.05 and 0.001 was selected for all tests. In addition, different adsorption models and thermodynamic equations were used to fit the experimental data. The plotting and fitting of data were conducted using the Origin 9 software (OriginLab Corporation, Northampton, MA, USA).

3. Results and Discussion

3.1. Isothermal Adsorption

The adsorption of (a) NP, (b) NP₇ and (c) BPA on soil is shown in Figure 1. The adsorption of NP on soil conforms to the Linear and Freundlich models with the correlation coefficient of greater than 0.97 (Table 2). The correlation coefficient of NP₇ was 0.98 for the Linear model, so generally the adsorption of NP and NP₇ on soil followed the Linear model and were similar with the previous studies. Düring et al. [44], Murillo-Torres et al. [45] and Martz et al. [46] concluded that NP followed a Linear adsorption model on agricultural soils, while Francis et al. [47] and Jiang et al. [48] concluded that the Freundlich model and Dubinin–Ashtakhov (DA) model were appropriate for the adsorption of NP on soil. The adsorption of BPA was in accordance with the Freundlich model in this

study ($R^2 = 0.95$). Tang et al. [49] found that the adsorption of BPA on herbal peat was in accordance with the Langmuir and Freundlich models, while the adsorptions of BPA on soils and sediments were in accordance with the Freundlich model. Some research indicated that EDCs can be attached to several components in soil, including clays, iron oxides and organic matter [50,51]. According to previous studies, hydrogen bonding and π - π interactions play a more important role than hydrophobic interaction in the adsorption of EDCs [52–54]. Laboratory experiments demonstrated that EDCs were easily adsorbed by humic acid (HA) via hydrophobic interaction, hydrogen bonding and p-p electron donor–acceptor interactions [55].

Figure 1. Adsorption of (a) NP, (b) NP₇ and (c) BPA on soil. Note: C_e indicates the concentrations of pollutants in the liquid ($\text{mg}\cdot\text{L}^{-1}$). C_s indicates the concentrations of pollutants adsorbed on the soil ($\text{mg}\cdot\text{kg}^{-1}$).

Table 2. Adsorption models for NP, NP₇ and BPA on soil.

	Linear		Freundlich			Langmuir		
	K_d ($\text{mg}\cdot\text{kg}^{-1}$)	R^2	K_f ($\text{mg}^{1-1/n}\cdot\text{L}^{1/n}/\text{kg}$)	$1/n$	R^2	K_L ($\text{L}\cdot\text{mg}^{-1}$)	$Q_{\max}$ ($\text{mg}\cdot\text{kg}^{-1}$)	R^2
NP	360.42	0.97	342.41	0.77	0.99	-	-	-
NP ₇	318.30	0.98	137.00	0.77	0.93	-	-	-
BPA	81.65	0.81	103.28	0.61	0.95	4	125	0.90

The K_{oc} of NP in irrigated soil was $7.56 \times 10^4 \text{ L}\cdot\text{kg}^{-1}$ in this study (Table 3), which was similar to the study on other agricultural soils with a similar magnitude of 10^3 – 10^4 [56,57]. Likewise, the K_{oc} of NP adsorbed in the sediments and suspended particles has an equal magnitude to that in this study, which was 10^4 – $10^5 \text{ L}\cdot\text{kg}^{-1}$ [39,58–60]. The adsorption of NP on soil is not only related to the organic matter [39], but also depends on the structures of the isomers. NP₇, the most toxic isomer, the K_{oc} of which was $6.67 \times 10^4 \text{ L}\cdot\text{kg}^{-1}$, was 11.77% lower than that of NP. The adsorption of NP isomers has also been studied previously. Düring et al. [44] found that the K_{oc} of 4-n-NP was $7.9 \times 10^4 \text{ L}\cdot\text{kg}^{-1}$ on soils, which was eight times higher than that of other branched NP. The K_{oc} of 4-n-NP in sediments from the Ebro River was 4.0×10^3 – $4.9 \times 10^4 \text{ L}\cdot\text{kg}^{-1}$ [60]. Li et al. [61] reported that the K_{oc} of NP111 (4-(1-ethyl-1,3-dimethylpentyl) phenol) on seven sediments was 6.1×10^3 – $1.1 \times 10^4 \text{ L}\cdot\text{kg}^{-1}$, which was a little smaller than the K_{oc} of NP₇ on the soil in this study. This was because the seven sediments contained more than 40% illite and were not prone for adsorption of NP. Ding et al. [39] found the log K_{oc} value was 4.98 in Chaozhou Lake sediments, suggesting a strong adsorption effect of DOM.

Table 3. K_{oc} of NP and NP₇ on soil.

Organic Carbon Sorption Constant	NP	NP ₇
$K_{oc} (\text{L}\cdot\text{kg}^{-1})$	7.56×10^4	6.67×10^4

3.2. Environmental Factors of Adsorption

3.2.1. pH

As shown in Figure 2, the partition coefficients K_d of NP and NP₇ at pH3 have the highest values of $374.36 \text{ L}\cdot\text{kg}^{-1}$ and $328.42 \text{ L}\cdot\text{kg}^{-1}$, respectively. K_f was $157.76 \text{ mg}^{1-1/n}\cdot\text{L}^{1/n}/\text{kg}$ for BPA (Table 4). The adsorption of NP and BPA on soils decreased with increasing pH. At pH7, the K_d of NP and NP₇ decreased by 3.7% and 3.0% when compared with pH3. The K_d of NP and NP₇ decreased by 58.1% and 31.9%, respectively, at pH11 compared with pH3, of which the decrease was greater. Likewise, the adsorption of BPA decreased with pH as well. At pH7 and pH11, the K_f of BPA on soil was 34.5% and 36.9% lower than that at pH3 (Table 4). This trend was consistent with previous results [34,37]. The reason for this change was that NP and BPA were deprotonated when the solution pH reached their dissociation constants (pka), which enhanced the electrostatic interactions between the pollutants and soils by converting molecules into ions when the solution pH reached their pka. As the soil surface was negatively charged, the electrostatic repulsion between EDCs and soil increased with the alkaline conditions of solution, resulting in a decrease in adsorption capacity [49]. Many other factors are likely to be important as well as the electrostatic repulsion, including hydrogen bonding, surface complexation and cation exchange. In addition, the partitioning behavior of the ionizable EDCs is highly susceptible to change the soil pH and therefore may alter the ionic fraction. An empirical relationship exists between a chemical's lipophilicity and its affinity to adsorption on soil organic matter [62].

Table 4. Freundlich model for BPA on soil at different pHs.

pH	$K_f (\text{mg}^{1-1/n}\cdot\text{L}^{1/n}/\text{kg})$	1/n	R^2	p Value
3	157.76	0.49	0.96	<0.001
7	103.28	0.613	0.95	<0.001

Figure 2. Adsorption of (a) NP, (b) NP₇ and (c) BPA on soil at different pHs.

3.2.2. Temperature

As shown in Figure 3, K_d for NP on the soil was $488.5 \text{ L} \cdot \text{kg}^{-1}$ at 5°C . At 25°C and 35°C , it decreased by 26.2% and 28.5%, respectively. For NP₇, at 5°C , K_d in soil was $369.7 \text{ L} \cdot \text{kg}^{-1}$. When the temperatures were 25°C and 35°C , K_d decreased by 13.9% and 19.2%, respectively. The effect of temperature on NP₇ was less than that of NP. The adsorption capacity of NP was 34.6%, 13.2% and 16.9% higher than that of NP₇ at 5°C , 25°C and 35°C , respectively. Thus, the adsorption capacity of NP₇ on soil was lower than other isomers. Statistical analysis of the effect of temperature on the adsorption of NP and NP₇ was conducted (Supplementary Material S4). The difference of the temperature effect on the adsorption of NP₇ and NP at 5°C was not significant ($p > 0.05$), while the difference of the temperature effect at 25°C and 35°C was significant ($p < 0.05$). What's more, the difference was more significant at 35°C than 25°C . It indicated that with the temperature increasing, the difference between the effect of temperature on NP₇ and NP was more significant.

At 5°C , the K_f for BPA was $120.2 \text{ mg}^{1-1/n} \cdot \text{L}^{1/n} / \text{kg}$. The adsorption capacity of BPA decreased by 14.1% and 47.1% at 25°C and 35°C , respectively (Table 5). It can be seen that the adsorption of NP, NP₇, and BPA on the soil all decreased with increasing temperature, which was similar with the results of previous studies [37,38].

Figure 3. Adsorption of (a) NP, (b) NP₇ and (c) BPA on soil at different temperatures.

Table 5. Freundlich model for BPA on soil at different temperatures.

Temperature (°C)	K_f ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n}/\text{kg}$)	$1/n$	R^2	p Value
5	120.20	0.57	0.93	<0.001
25	103.28	0.613	0.95	<0.001
35	63.53	0.61	0.94	<0.001

It can be seen from Figure 4 that the DOM dissolved from soil at 35 °C was 35.59% and 20.69% higher than that at 5 °C and 25 °C, indicating that increasing the temperature led to the increase of the organic matter dissolved into the aqueous phase. Sadmani et al. [63,64] found that under certain disturbances, DOM can diffuse from soil pore water into water columns since DOM displays a high capacity of BPA and NP binding with its natural ligands and adsorption sites. Therefore, the decrease of DOM in soil would lead to the decrease of adsorption of EDCs. On the other hand, DOM can be adsorbed on the soil particles again, causing a redistribution of EDCs in aquatic systems [63,65]. Meanwhile, with increasing temperature, the solubility of NP and BPA in water increased and the hydrophobicity weakened, which was also the reason that the adsorptions of NP and BPA decreased with the increasing temperature.

Figure 4. DOM in soil at different temperatures.

3.2.3. Effects of Different Polyvalent Metal Ions

The K_d of NP was $387.8 \text{ L} \cdot \text{kg}^{-1}$, $575.60 \text{ L} \cdot \text{kg}^{-1}$ and $607.9 \text{ L} \cdot \text{kg}^{-1}$, while the K_d of NP₇ was 341.7 , 629.2 and $741.7 \text{ L} \cdot \text{kg}^{-1}$ with a concentration of 0.002 M for Na^+ , Ca^{2+} and As(III) , respectively (Figure 5). Similarly, K_f of BPA in As(III) -soil system, which was $32.25 \text{ mg}^{1-1/n} \cdot \text{L}^{1/n} / \text{kg}$, was greater compared with Ca^{2+} -soil system and Na^+ -soil system (Table 6). The adsorption of NP on soil varied with the different cation valence. NP₇ followed the same trend. K_d of NP₇ was 8.52% and 18.04% higher than that of NP for Ca^{2+} -soil and As(III) -soil system, respectively, while in the soil- Na^+ system, it was the inverse.

Figure 5. Adsorption of (a) NP, (b) NP₇ and (c) BPA on soil saturated with different polyvalent metal ions.

Table 6. Freundlich model for BPA on soil at different polyvalent metal ions conditions.

Metal Ions	K_f ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n}/\text{kg}$)	$1/n$	R^2	p Value
Na^+	16.69	1.26	0.93	<0.001
Ca^{2+}	24.25	1.10	0.91	<0.001
As(III)	32.25	1.16	0.95	<0.001

The As(III) is neutrally charged at most soil pH. The adsorption capacity of NP, NP₇ and BPA to soils varied with different cation valence: neutrally > divalent cation > monocation, which was similar with the study of Shchegolikhina et al. [66]. There are other studies about the effects of different polyvalent metal ions to different pollutants. Lu et al. [67] reported that divalent cations such as Ca^{2+} and Mg^{2+} were about 28 times more effective with respect to polyacrylamide adsorption than monovalent cations such as Na^+ and K^+ , which was similar with this study. That was due to the stronger flocculation power and, consequently, to a higher charge screening ability of polyvalent cations, which increased the ability of soil particles to adsorb contaminants [36]. Experiments with HA saturated with Ca^{2+} or Al^{3+} revealed that the type of cation can significantly influence the adsorption of organic pollutants. This trend is in accordance with the increase of cation valence. Al^{3+} , Fe^{3+} , Ca^{2+} and Mg^{2+} can be coordinated to multiple functional groups of organic matter in soil [68] and form cation bridges or water-cation complexes [69]. This may decrease the flexibility of the soil organic matter (SOM) matrix and hence raise the diffusional resistance of partitioned molecules [36,70]. Alteration of SOM by formation or breaking of these cross-linking bridges may provide more sorption sites in soil, leading to an increasing adsorption ability [71].

3.3. FTIR Spectra Analysis

Soils and soils adsorbed with NP and BPA were characterized by FTIR-650 shown in Figure 6. The infrared spectroscopy (IR) was normalized with respect to the C=O stretching at the band of $1000\text{--}1260\text{ cm}^{-1}$. The area of adsorptions arising from a particular species is directly proportional to the concentration of that species. Thus, in principle, it was possible to determine the concentration of multiple analytes from a single spectrum [72]. Shifts in peak positions, changes in bandwidths, intensities and band area values of the infrared bands were used to obtain valuable structural and functional information about interactions between the matters [73,74].

Figure 6. FTIR spectra of adsorption of NP and BPA on soil.

There were no big differences of spectrums for soil and soil after NP adsorption. However, differences between soil and soil after BPA adsorption were significant. It was obvious that T of the peaks after BPA adsorption were much smaller than soil before adsorption. Bands at 693,777 and 873 cm^{-1} regions were by phenyl and phenol groups, such as phenyl C-P or C-H bending vibration. Bands at 1428 cm^{-1} were caused by scissor bending vibration, and bands at about 1620–1640 cm^{-1} were caused by the stretching vibration of C=O incorporated in amide groups of proteins or C=C stretching vibration in aromatic ring alkenes. Bands at about 3400 and 3600 cm^{-1} were O–H in phenol, ethanol (etc.)s and/or amide and amine N–H. There were no shifts in peak positions, but changes occurred in intensities of band. This result meant that alkyl chains of NP and BPA seemed to form van der Waals interactions with the cavity of soil [75].

4. Conclusions

This study, based on laboratory batch experiments, was successful in studying the thermodynamics of adsorption of NP and NP₇ on reclaimed water-irrigated soils. The results indicated that the adsorptions of NP and NP₇ on soil were in accordance with the Linear model, and the adsorption of BPA on soil was in accordance with the Freundlich model. The adsorptions of NP, NP₇ and BPA on soils decreased with the increasing temperatures and pH. The adsorption capacity of NP, NP₇ and BPA to soils was different with different cation valence: neutrally > divalent cations > mono- cations. The adsorption of NP₇ on soil was quite different from the total NP, which was a further study of the previous study focusing on the total NP. Alkyl chains of NP and BPA seemed to form van der Waals interactions with the cavity of soil. But reclaimed water-irrigated soils are quite complex, and the mechanism of the differences between the total NP and individual isomer need further study. This study makes the risk assessment of NP isomers more targeted. In the future, researchers can assess the NP risks, not from the points of total NP but focusing on the isomer, which has higher estrogen activity. This study provided indispensable foundations for the human health risks of EDCs in the future.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13182532/s1>, S1: Separation of NP isomers; S2: Detection of dissolved organic matter (DOM); S3: The extraction of NP and BPA; S4: Statistical analysis of the effect of temperature on the adsorption of NP and NP₇.

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