

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 the reclaimed water. 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 Linear model, and the adsorption of BPA conformed to Freundlich model. The adsorptions of NP, NP7 and BPA on soils decreased with the increasing temperatures and pHs, while increased with the cation valence. Adsorption equilibrium constant (K_d or K_f) were maximum at pH=3, temperature 25°C and As (Ⅷ)-soil, respectively; The adsorption capacity of NP, NP7, and BPA to soils increased in accordance with cation valence: trivalent cations > divalent cations > mono- cations. K_d of NP7 on soil was less than that of NP under the different pH and temperatures; while under different cations concentrations, it was 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 nonylphenol in the soil.

1 Introduction

Irrigation with reclaimed water is a key method of alleviating agricultural water shortages (FAO, 2012). Recycled water can save water resources and promote the circulation of nutrients, but pollutants in reclaimed water and soil have potential to cause harm to humans, especially the endocrine disrupter chemicals (EDCs), which has attracted wide attention recently. EDCs can lead to endocrine disorders in aquatic organisms, affecting reproductive development and immune system (Lee et al., 2016; Tabassum et al., 2017).

Reclaimed water from the wastewater treatment plants (WWTPs) is regarded as the main source of EDCs of the agricultural environment. In addition to reclaimed water or effluent, treated sewage sludge is also normally used all over the world in agriculture soil (Hamid et al., 2012; Ömeroğlua et al., 2015; Belhaj et al., 2016; Biel-Maeso et al., 2019). Municipal landfills may also contain leachate with significant amounts of EDCs which could migrate into groundwater or uptaken by plants (Kalmykova et al., 2013; Zhang et al., 2015; Lu et al., 2015; Wang et al., 2019). In recent years, the fate of EDCs in soil-plant ecological system has given much attention (Card et al., 2013; Goeppert et al., 2015; Sidhu et al., 2015; Adeel M. et al., 2017, 2018).

Nonylphenol (NP) and bisphenol A (BPA) are two typical EDCs with high detection frequencies and concentrations in soils irrigated with reclaimed water (Careghini et al., 2015; Wang et al., 2018). The concentrations of NP in reclaimed water and agricultural soils were 0.05-63 $\mu\text{g. L}^{-1}$ and 14.2-60.3 mg. kg^{-1} (Liao et al., 2014; Sidhu et al., 2015; Wang et al., 2015, 2018; Kwak et al., 2017; Bruin et al., 2019). The concentrations of BPA in reclaimed water and agricultural soil were ND-101.6 $\mu\text{g. L}^{-1}$ and ND-147 $\mu\text{g. kg}^{-1}$, respectively (Gibson et al., 2010; USEPA 2010a; Luo, et al., 2014; Careghini et al., 2015; Yacoumas et al., 2020). The Danish Institute of Safety and Toxicology (DIST) derived a preliminary tolerable daily intake

(TDI) value for NP of $5 \mu\text{g} \cdot (\text{day} \cdot \text{kg})^{-1}$ body weight (Danish EPA 2000). USEPA estimated a reference dose for BPA of $50 \mu\text{g} \cdot (\text{day} \cdot \text{kg})^{-1}$ body weight (USEPA-IRIS 2014). NP is composed of varieties of isomers. The estrogenic activity and the environmental fate were heavily dependent on the isomers structures, such as the side-chain length, the degree of branching, α -substituent type, steric index (Gabriel et al., 2008; Lu and Gan 2014; Schick and Oellig, 2019). The most toxic isomer among these isomers is 4-(3-ethyl-2-methylhexan-2-yl) phenol, which is noted as NP7 (Kim et al., 2005; Wang et al., 2015) (Supplementary Material 1). Adsorption, migration, and degradation are the main processes that NP and BPA in soil. Adsorption is vital and determines the rate of migration and transformation (Pollard and Morra, 2017). Adsorption of NP and BPA on soils are affected by a variety of factors, including dissolved organic matter (DOM), temperature, pH and ionic content (Bautista-Toledo et al., 2005; Stumpe et al., 2010; Yang et al., 2011; Soni and Padmaja, 2014; Ding et al., 2019), among which dissolved DOM plays a significant role (Sharma et al., 2009; Wang et al., 2019; Ding et al., 2019).

Daxing irrigation district, in the southeastern part of China, was one of typical sewage irrigation districts for more than 40 years. Previous studies of this district focused on the inorganic pollution or the total NP isomers (Wu et al., 2009; Bao 2014). The study of individual isomer 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 various. Especially the most toxic isomer 4-NP7, have much estrogenic activity to the environment, so the study on adsorption and desorption of 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^+ , Ca^{2+} , As (☒)) 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 (< 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.

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
<i>Note: CEC: cation exchange capacity; OM: organic matter (Supplementary Material 2); OC: organic carbon; SSA: specific surface area.</i>	

NP (0.25 g, 100%) and BPA (0.25 g, 99.8%) were purchased from Dr. Ehrenstorfer GmbH. Methanol (HPLC grade) and Dichloromethane (HPLC grade) were purchased from Honeywell Burdick & Jackson (USA). NP and BPA were dissolved in methanol with a concentration of 1000 mg. L⁻¹ NaN₃ (200 g, 99%) and As(III) were obtained from Sigma-Aldrich. Anhydrous Calcium Chloride (CaCl₂) (500 g, > 96%), Sodium Chloride (NaCl) (500 g, > 99.5%), Anhydrous Sodium Sulfate (Na₂SO₄) (500 g, > 98%) were obtained from 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. 0.2 g soil was added into a 40 mL brown vial, with 30 mL 0.01M CaCl₂ solution as the background electrolyte (except for the polyvalent metal ions experiment). NaN₃ was added at a concentration of 200 mg. 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 µg. 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 hours to reach equilibrium. Then the samples were centrifuged for 5 min (3000 rpm) and NP (or BPA) in the supernatant were extracted (Supplementary Material 2) and determined by Gas Chromatograph Mass Spectrometer (GC-MS). The effects of different environmental factors on the adsorption were studied, including the pH of the solution

(pH 3,7, and 11), temperatures (5°C,25°C, and 35°C) and polyvalent metal ions (Na⁺, Ca²⁺, and As (III)) with a concentration of 0.002M. For the polyvalent metal ions experiment, the background electrolyte was Na⁺, Ca²⁺ 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. The supernatant was measured with TOC.

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

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

K_d: Adsorption equilibrium constant (L. kg⁻¹).

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 (mg. L⁻¹).

2.4.2 Langmuir adsorption model

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

Q_{max}: Maximum sorption amount of pollutants on solids (mg. kg⁻¹).

C_e: Concentration of pollutants in the liquid phase at equilibrium (mg. L⁻¹).

K_L: Adsorption equilibrium constant (L. mg⁻¹).

2.4.3 Freundlich adsorption model

$$C_s = K_f \times C_e^{1/n} \dots\dots\dots(3)$$

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

C_e: Concentration of pollutants in the liquid phase at equilibrium (mg. L⁻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}). Since the main adsorbent is organic carbon in the soil, and K_{oc} is a characterization of the sorption capacity of organic carbon. The formula is:

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

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, 6890N/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, 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 $1 \text{ mL} \cdot \text{min}^{-1}$. 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 $8^\circ \text{C} \cdot \text{min}^{-1}$ and maintained for 1 min, and then heated to 230°C at a rate of $5^\circ \text{C} \cdot \text{min}^{-1}$ 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 was acquired with both Scan and Sim mode, and the scan range was from 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 70–110%, which met the standard of US EPA (Wang et al., 2018).

2.5 FTIR analysis

Soil before and after adsorbed 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.

3 Results And Discussion

3.1 Isothermal adsorption

The adsorption of (a) NP, (b) NP7, and (c) BPA on soil is shown in Fig. 1. The adsorption of NP on soil conforms to 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 Linear model, which were similar with the previous studies. Düring et al. (2002),

Murillo-Torres et al. (2012a) and Martz et al. (2019) concluded that NP followed a linear adsorption model on agricultural soils, while Francis et al. (2005) and Jiang et al. (2012) concluded that Freundlich model and Dubinin–Ashtakhov (DA) model were appropriate for the adsorption of NP on soil. The adsorption of BPA was in accordance with Freundlich model in this study ($R^2 = 0.95$). Tang et al. (2011) found that the adsorption of BPA on herbal peat was in accordance with Langmuir and Freundlich models, while the adsorptions of BPA on soils and sediments were in accordance with Freundlich model (Sun et al., 2012). Some research indicated that EDCs can be attached to several components in soil including clays, iron oxides, and organic matter (Tong et al., 2019). According to previous studies, hydrogen bonding and π - π interactions play a more important role than hydrophobic interaction to the adsorption of EDCs (Karickho et al., 1981; Zhu et al., 2004; Ma et al., 2018). Laboratory experiments demonstrated that EDCs were easily adsorbed by humic acid (HA) via hydrophobic interaction, hydrogen bonding, and p-p electron donor-acceptor interactions (Ren et al., 2017).

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

Adsorption isotherm	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	$K_L(\text{L}\cdot\text{mg}^{-1})$	$Q_{\text{max}}(\text{mg}\cdot\text{kg}^{-1})$	R^2
NP	360.42	0.97	342.41	0.77	0.99	-	-	-
NP7	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 Koc 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 of other agricultural soils, the Koc of NP in which was with a similar magnitude of $10^3 \sim 10^4$ (Wang et al., 2011; Milinovic et al., 2015). Likewise, the Koc of NP adsorbed in the sediments and suspended particles have an equal magnitude to that in this study, which was $10^5 \sim 10^4 \text{ L}\cdot\text{kg}^{-1}$ (Isobe et al., 2001; Hou et al., 2006; Navarro et al., 2009; Ding et al., 2019). The adsorption of NP on soil is not only related to the organic matter (Dodgen 2014), but also depends on the structures of the isomers. NP7, the most toxic isomer, the Koc of which was $6.67 \times 10^4 \text{ L}\cdot\text{kg}^{-1}$, which was 11.77% lower than that of NP. The adsorption of NP isomers has also been studied previously. Düring et al. (2002) found that the Koc 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 Koc of 4-n-NP in sediments from Ebro River was $4.0 \times 10^3 \sim 4.9 \times 10^4 \text{ L}\cdot\text{kg}^{-1}$ (Navarro et al., 2009). Li et al. (2012) reported that the Koc of NP111(4-(1-ethyl-1,3-dimethylpentyl)phenol) on seven sediments was $6.1 \times 10^3 \sim 1.1 \times 10^4 \text{ L}\cdot\text{kg}^{-1}$, which was a little smaller than the Koc of NP7 on the soil in this study. This was because the seven sediments contained over 40% illite and it was not prone for the adsorption of NP. Ding et al. (2019) found the log Koc values was 4.98 in Chaozhou Lake sediments, suggesting a strong adsorption effect of DOM.

Table 3
K_{oc} of NP and NP7

	NP	NP7
K _{oc} (L.kg ⁻¹)	7.56 × 10 ⁴	6.67 × 10 ⁴

3.2 Environmental factors of adsorption

3.2.1 pH

As shown in Fig. 2, the partition coefficients K_ds of NP and NP7 at pH3 were the highest values of 374.36 L.kg⁻¹ and 328.42 L.kg⁻¹, respectively. K_f was 157.76 mg^{1-1/n}.L^{1/n}/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 pH 3, of which the decrease was great. Likewise, the adsorption of BPA varied with pH as well. At pH7 and pH11, the K_f of BPA on soil were 34.5% and 36.9% lower than that at pH3 (Table 4). This trend was consistent with previous results (Bautista-Toledo et al., 2005; Soni and Padmaja, 2014). 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 a decrease in adsorption capacity (Tong et al., 2019). 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 changes the soil pH, therefore may alter the ionic fraction. Empirical relationship has existed between a chemical's lipophilicity and its affinity to adsorption to soil organic matter (Collins et al., 2011; Dodgen, 2014).

Table 4
Freundlich model for BPA on soil at different pH

pH	K _f (mg ^{1-1/n} .L ^{1/n} /kg)	1/n	R ²
3	157.76	0.49	0.96
7	103.28	0.613	0.95
11	98.85	0.653	0.99

3.2.2 Temperature

As shown in Fig. 3, K_d for NP on the soil was 488.5 L.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 L.kg⁻¹. When the temperature 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. 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 (Yang et al., 2011; Wang et al., 2014).

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
5	120.20	0.57	0.93
25	103.28	0.613	0.95
35	63.53	0.61	0.94

It can be seen from Fig. 4 that the DOM in soil at 35 °C was 35.59% and 20.69% higher than that at 5 °C and 25°C, which is mainly caused by molecular thermal motion. Increasing temperature led to the increase of the organic matter dissolved into the aqueous phase, so the adsorption of NP and BPA on soil reduced. Similarly, Sadmani et al. (2014) found that under certain disturbances, DOM can diffuse from soil pore water into water columns, since DOM displays 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 (Sadmani et al., 2014; Chen et al., 2018). Meanwhile, with increasing temperature, the solubility of NP and BPA in water increased and the hydrophobicity weakened, which was also the reason of the adsorptions of NP and BPA decreased with the increasing temperature.

3.2.3 Effects of different polyvalent metal ions

The K_d of NP were $387.8 \text{ L} \cdot \text{kg}^{-1}$, $575.60 \text{ L} \cdot \text{kg}^{-1}$ and $607.9 \text{ L} \cdot \text{kg}^{-1}$, while the K_d of NP7 were 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 $\text{As}(\text{V})$, respectively (Fig. 5). The adsorption of NP on soil increased with the 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 $\text{As}(\text{V})$ -soil system, respectively; while in soil- Na^+ system, it was inverse. Similarly, K_f of BPA in $\text{As}(\text{V})$ -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).

Table 6. Freundlich model for BPA on soil saturated with different polyvalent metal ions

Metal ions	$K_f \cdot \text{mg}^{1-1/n} \cdot \text{L}^{1/n} / \text{kg}$	1/n	R ²
Na ⁺	16.69	1.26	0.93
Ca ²⁺	24.25	1.10	0.91
As ³⁺	32.25	1.16	0.95

The adsorption capacity of NP, NP7, and BPA to soils increased in accordance with cation valence: trivalent cation > divalent cation > mono- cation, which was similar with Shchegolikhina et al (2014). There are other studies about the effects of different polyvalent metal ions to different pollutants. Lu et al. (2002) reported that the divalent cations like Ca²⁺ and Mg²⁺ were about 28 times more effective with respect to polyacrylamide adsorption than monovalent cations like Na⁺ and K⁺, which was the 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 (Yang et al., 2011). Experiments with HA saturated with Ca²⁺ or Al³⁺ 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. Al³⁺, Fe³⁺, Ca²⁺, and Mg²⁺ can be coordinated to multiple functional groups of organic matter in soil (Schnitzer and Scinner, 1965) and form cation bridges or water-cation complexes (Kunhi Mouvenchery et al., 2012). This may decrease the flexibility of the soil organic matter (SOM) matrix and hence raise the diffusional resistance of partitioned molecules (Yang et al., 2011; Lu and Pignatello, 2004). Alteration of SOM by formation or breaking of these cross-linking bridges may provide more sorption sites in soil, leading to an increasing sorption ability (Varadachari et al., 1997).

3.3 FTIR spectra analysis

Soils and soils adsorbed with NP and BPA were characterized by FTIR-650 shown in Fig. 6. The infrared spectroscopy (IR) was normalized with respect to the C- O stretching at the band of 1000-1260cm⁻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 (Jackson et al., 1997). 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 (Melin et al., 2001; Severcan et al., 2005b).

There were no big differences of spectrums for soil and soil after NP adsorption. But differences between soil and soil after BPA adsorption was 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; 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.), and/or amide and amine

N–H. There is 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.

4 Conclusion

This study, based on laboratory batch experiments, had been 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, while increased with the cation valence. The adsorption capacity of NP, NP7, and BPA to soils increased in accordance with cation valence: trivalent cations > 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 was quite complex, and the mechanism of the differences between the total NP and individual isomer need further study. This study can provide indispensable foundations for the human health risks of EDCs in the future.

Declarations

Conflict of interest

The authors declare no conflict of interest.

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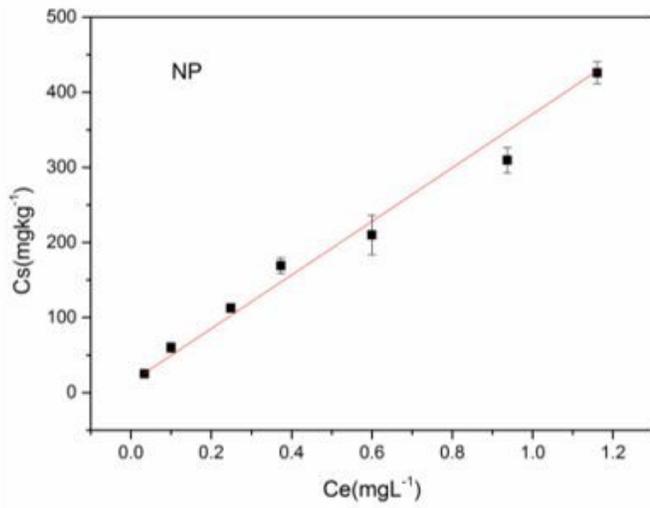
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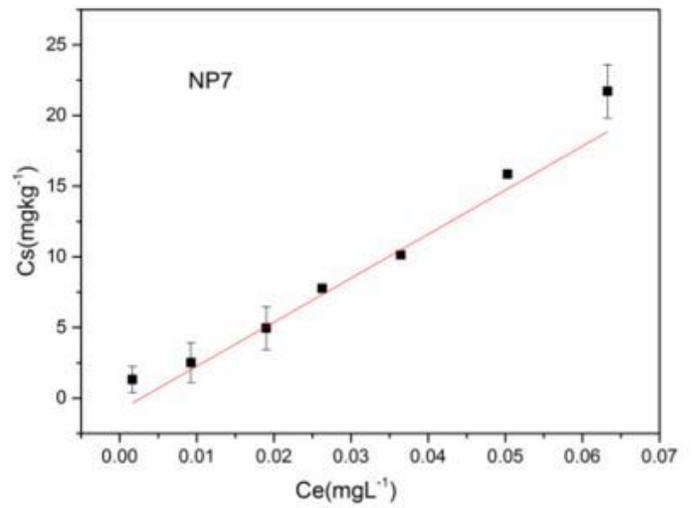
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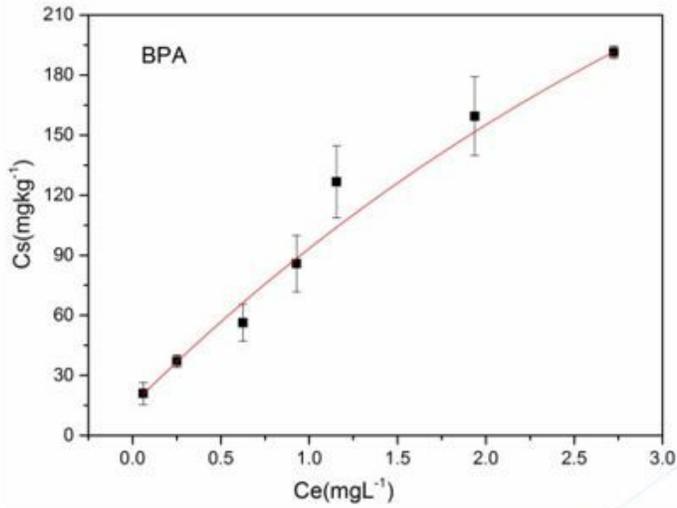
Figures



(a)



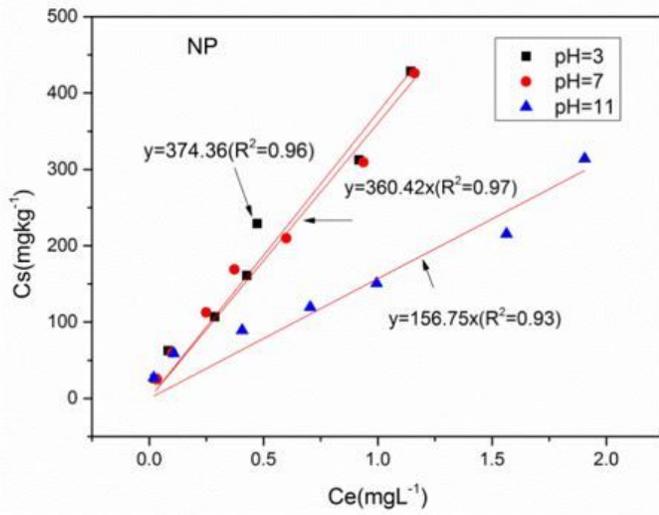
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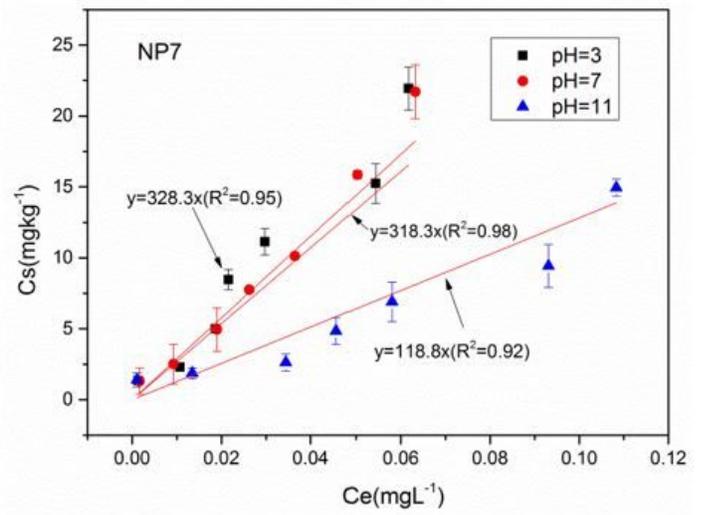
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Figure 1

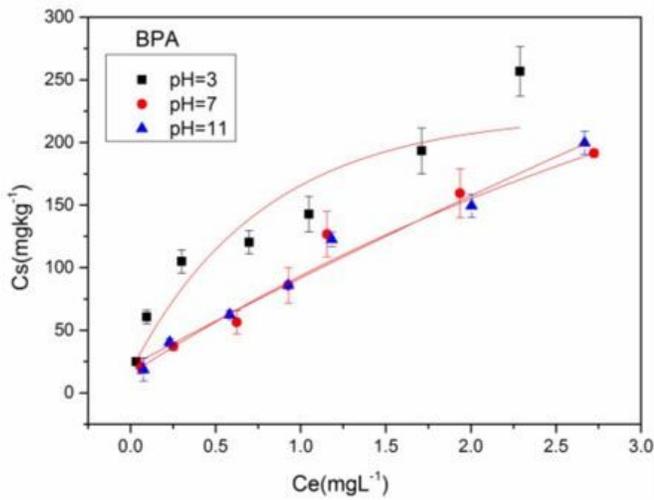
Adsorption of (a) NP, (b) NP7, and (c) BPA on soil



(a)



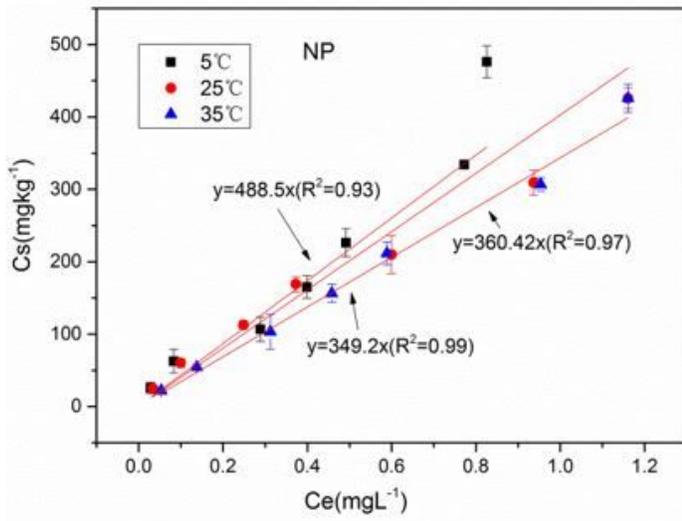
(b)



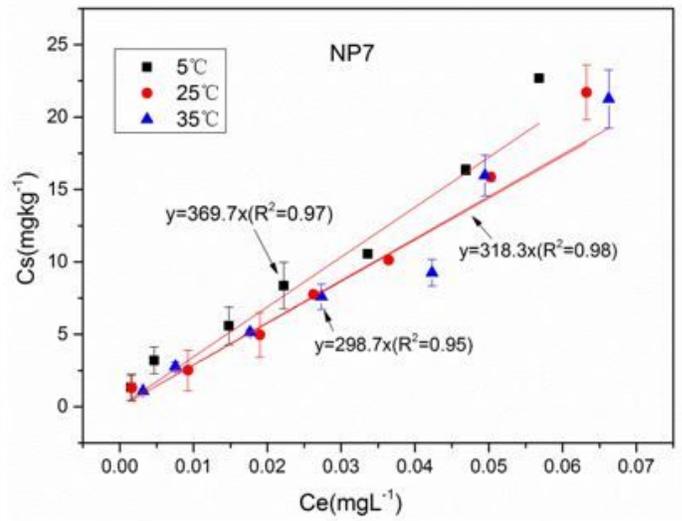
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Figure 2

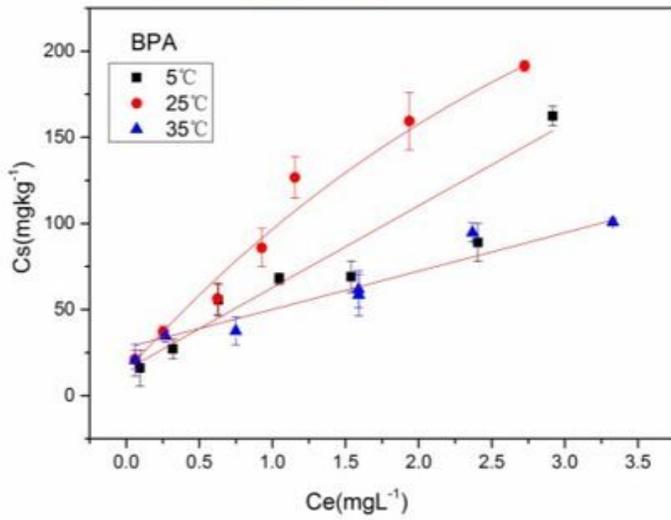
Adsorption of (a) NP, (b) NP7, and (c) BPA on soil at different pHs.



(a)



(b)



(c)

Figure 3

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

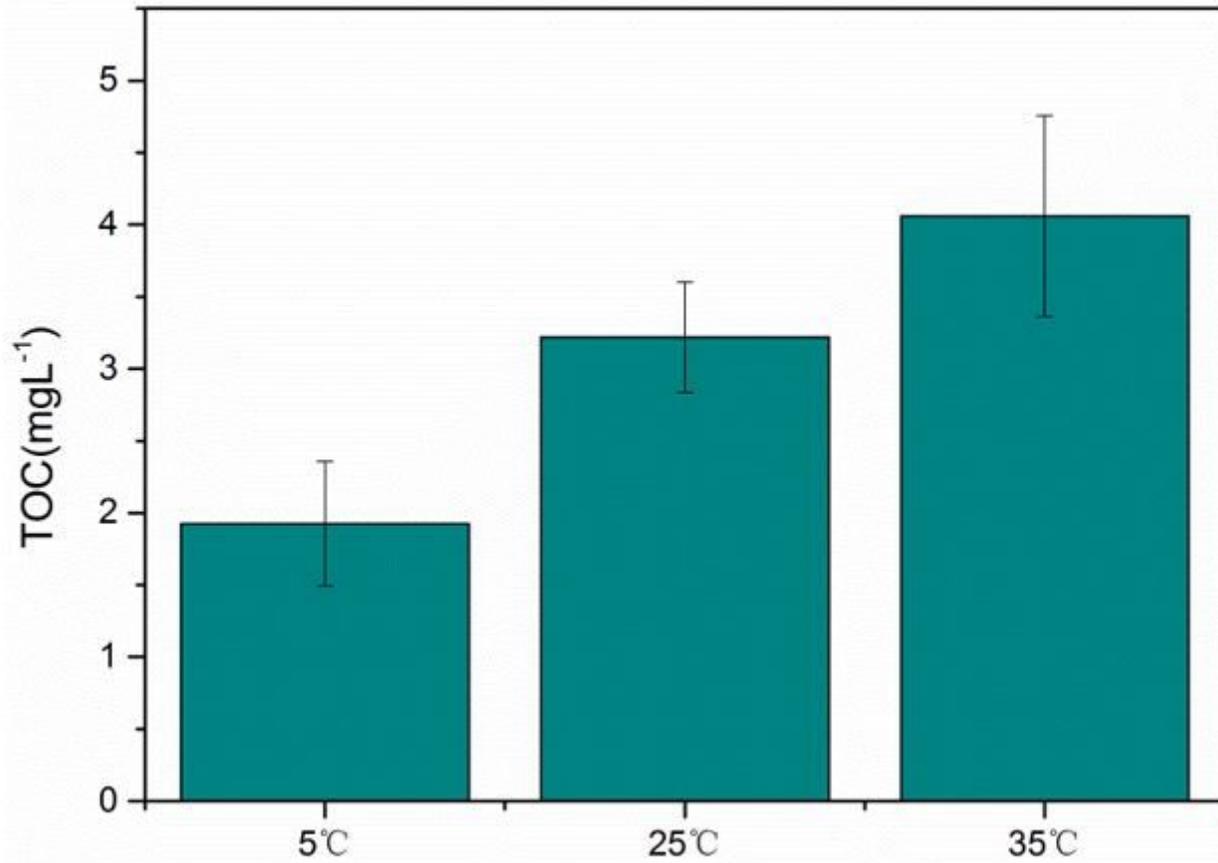


Figure 4

DOM in soil at different temperatures

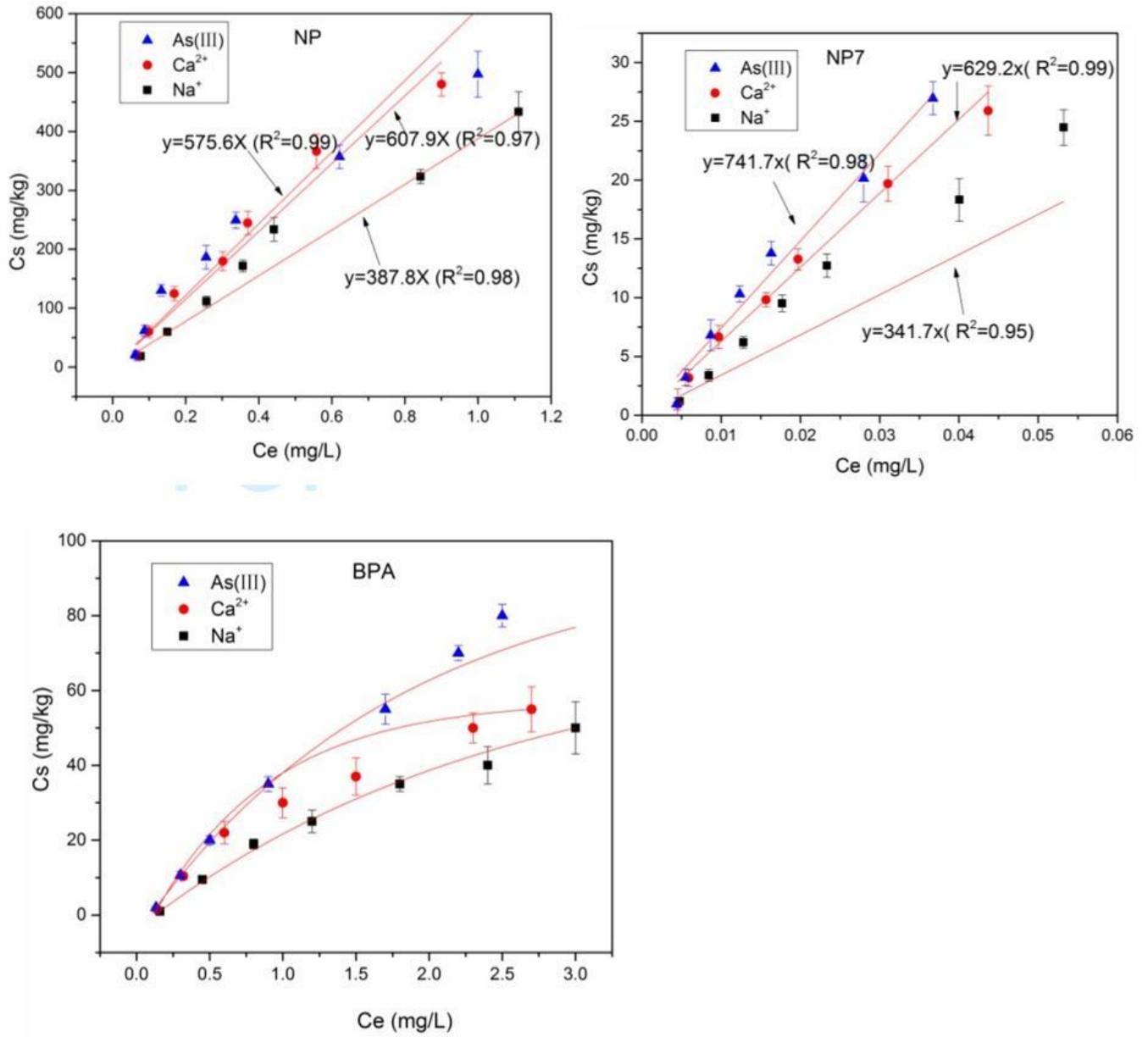


Figure 5

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

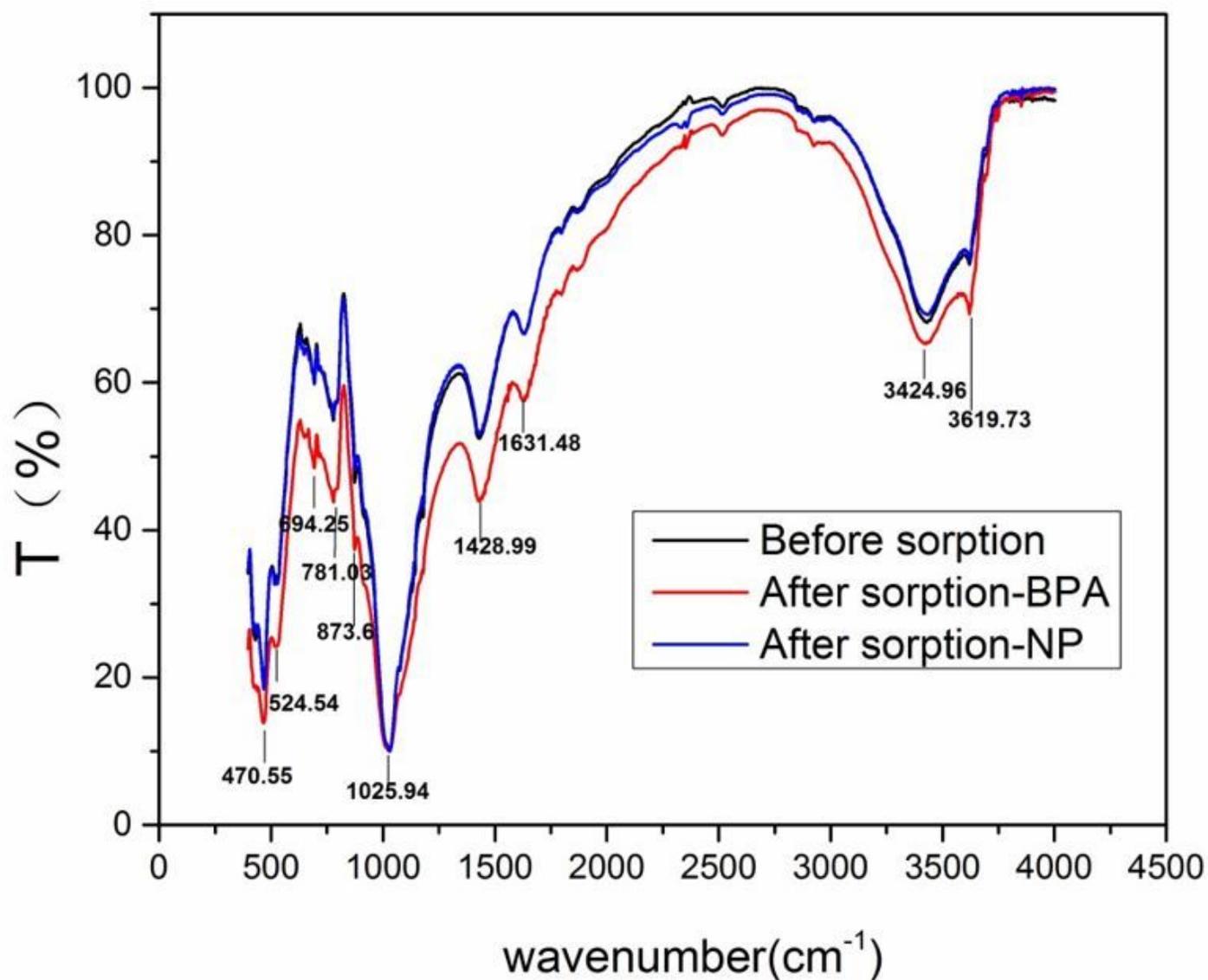


Figure 6

FTIR spectra of adsorption of NP and BPA on soil

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