Chemical Engineering Journal 370 (2019) 684–694

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Role of extracellular polymeric substance in adsorption of quinolone antibiotics by microbial cells in excess sludge

Da-Qi Cao*, Wen-Yu Yang, Zhen Wang, Xiao-Di Hao*

Sino-Dutch R&D Centre for Future Wastewater Treatment Technologies/Key Laboratory of Urban Stormwater System and Water Environment, Beijing University of Civil Engineering and Architecture, Beijing 100044, China

HIGHLIGHTS

- Occurrence of 7 quinolone antibiotics in excess sludge was evaluated by UPLC-MS/MS.
- EPS facilitated adsorption independent of pH and quinolone antibiotic type.
- Metal ions bound in EPS were predominantly responsible for adsorption.
- pH affected antibiotic patterns, floc zeta potential, and metal ion content.
- The Freundlich model described adsorption behavior due to surface heterogeneity.

ARTICLE INFO

Keywords:
Excess sludge
Quinolone antibiotic
Adsorption
Extracellular polymeric substance
Metal ion

ABSTRACT

Traditional wastewater treatment plants cannot completely remove trace pharmaceutical and personal care products. In particular, quinolone antibiotics are mainly adsorbed on microbial cell surfaces in excess sludge and are released into the water environment during agricultural supplementation, mainly due to the exfoliation of extracellular polymeric substances (EPS) caused by changes in environmental conditions. Here, the occurrence of seven typical quinolone antibiotics from three generations in excess sludge was investigated at trace concentrations using ultra-high performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). EPS facilitated adsorption independent of pH and quinolone antibiotic type, and the solid-liquid distribution coefficient decreased markedly as pH increased (pH 5–9, range of municipal wastewater). Metal ions bound in EPS were predominantly responsible for the adsorption of antibiotics in sludge, rather than the macroscopic size of the sludge floc. pH affected patterns of quinolone antibiotics, the zeta potential of sludge floc, and the contents of metal ions contained in sludge. The adsorption capacity of antibiotics first increased and then decreased with increasing pH in the range of pH 3–11, reaching a maximum (20,506, 14,458, 10,689, 22,854, 20,302, 8494, and 29,547 L/kg for CIP, ENR, LOM, MOX, NOR, OFL, and SAR, respectively) near pH 5, at which the cationic bridging of Ca^{2+} and Mg^{2+} bound in EPS played a major role owing to their larger ion radius and higher contents in excess sludge. Due to high surface heterogeneity of sludge, the Freundlich model was more suitable than the Langmuir model for describing the adsorption behavior of quinolone antibiotics. These results provide further insight into the release of quinolone antibiotics adsorbed in excess sludge, with potential implications for the agricultural use of sludge.

Abbreviations: A^2O, anaerobic/anoxic/oxic process; Biosolid, freeze-dried powder of sediment obtained by centrifuging excess sludge; $Biosolid_{EPS\ free}$, freeze-dried powder of sediment obtained by centrifuging excess sludge in which EPS has been extracted using CER method; CAST, cyclic activated sludge technology; CER, cation exchange resin; CIP, ciprofloxacin; ENR, enrofloxacin; EPS, extracellular polymeric substance; ESI, electrospray ionization; FTIR, Fourier transform infrared; ICP, inductively coupled plasma; LOM, lomefloxacin; MOX, moxifloxacin; MWCO, molecular weight cut-off; NOR, norfloxacin; OFL, ofloxacin; PPCPs, pharmaceutical and personal care products; SAR, sarafloxacin; SM, Supplementary Material; SRM, selective reaction monitoring; TS, total solids; UPLC-MS/MS, ultra-high performance liquid chromatography-tandem mass spectrometry; VS, volatile solids; WWTP, wastewater treatment plant; XPS, X-ray photoelectron spectroscopy

* Corresponding authors.
E-mail addresses: caodaqi18@163.com (D.-Q. Cao), xdhao@hotmail.com (X.-D. Hao).

https://doi.org/10.1016/j.cej.2019.03.230
Received 11 January 2019; Received in revised form 21 March 2019; Accepted 25 March 2019
Available online 26 March 2019
1385-8947/

Nomenclature

C_e	Concentration of quinolone antibiotics in the water at adsorption equilibrium [μg·L^{-1}]
C_0	Initial concentration of quinolone antibiotics in the water [μg·L^{-1}]
K	Langmuir adsorption equilibrium constant defined by Eq. (3) [L·μg^{-1}]
K_d	Solid-liquid distribution coefficient [L·kg^{-1}]
K_f	Freundlich adsorption coefficient defined by Eq. (4) [10^{-6}·L$^{1/n}$·μg$^{-(1/n)}$]
M	Mass of Biosolid or Biosolid$_{EPS\ free}$ [kg]
n	Freundlich adsorption coefficient defined by Eq. (4) [−]
q_e	Concentration of quinolone antibiotics adsorbed on Biosolid or Biosolid$_{EPS\ free}$ at adsorption equilibrium [μg·kg^{-1}]
Q_{max}	Amount of quinolone antibiotics adsorbed to form monolayer coverage defined by Eq. (3) [μg·kg^{-1}]
V	Water solution volume [L]

1. Introduction

Trace pharmaceutical and personal care products (PPCPs) have been detected in environmental media such as surface water, groundwater, and soil. Although the concentration of PPCPs related to human activities is usually on the order of nanograms to micrograms per liter in the water environment [1–5], many PPCPs are discharged continuously into the environment, causing potential risks for human health and the environment due to their ongoing utilization [6–9].

Wastewater treatment plants (WWTPs) are one of the main point sources of PPCP discharge into the environment [10], as it is difficult to biochemically degrade these substances during the conventional wastewater treatment process [11]. As a result, except for a small amount of PPCPs that are released into the atmosphere by escape, some portion of PPCPs remains in the effluent of the wastewater treatment plant, with the remainder present in excess sludge due to adsorption or dissolution [12]. The Water Pollution Prevention Action Plan promulgated in April 2015 in China stipulates that treated sludge cannot contain potential environmental pollutants [13]. When excess sludge containing PPCPs is used for land use and agricultural production activities such as fertilization, PPCPs in the sludge may be released into the environment as the external environment changes [10,14–19], thereby contaminating surface water and groundwater [4,12,18–20].

In recent years, quinolone antibiotics have been one of the most widely used antibiotics in veterinary and medical applications [21]. In China, they are widely used in human clinical settings and livestock breeding for disease prevention, with livestock and poultry farming accounting for about 50% of their use [22]. Moreover, the consumption of quinolone antibiotics has increased significantly; for example, the annual consumption of quinolone antibiotics in humans and animals in 1998 was 1,350 and 470 tons respectively [23], while the annual consumption of ciprofloxacin, norfloxacin, ofloxacin, lomefloxacin, and enrofloxacin in China in 2013 for both humans and animals reached 5340, 5440, 5110, 1250, and 5180 tons, respectively [22].

Four generations of quinolone antibiotics have been developed [24]. At present, the most commonly consumed types in the market are second-generation quinolone antibiotics, including ciprofloxacin, norfloxacin, lomefloxacin, enrofloxacin, and ofloxacin [25]. Among them, ciprofloxacin can cause central nervous system toxicity, hematological toxicity, liver and kidney toxicity, and phototoxicity in the human body. Moreover, bacteria or viruses in the environment can become resistant to antibiotics such as ciprofloxacin [26]. Ciprofloxacin, norfloxacin, lomefloxacin, enrofloxacin, and ofloxacin have a variety of toxicological and toxic effects on algae, cyanobacteria, plants, fish, and

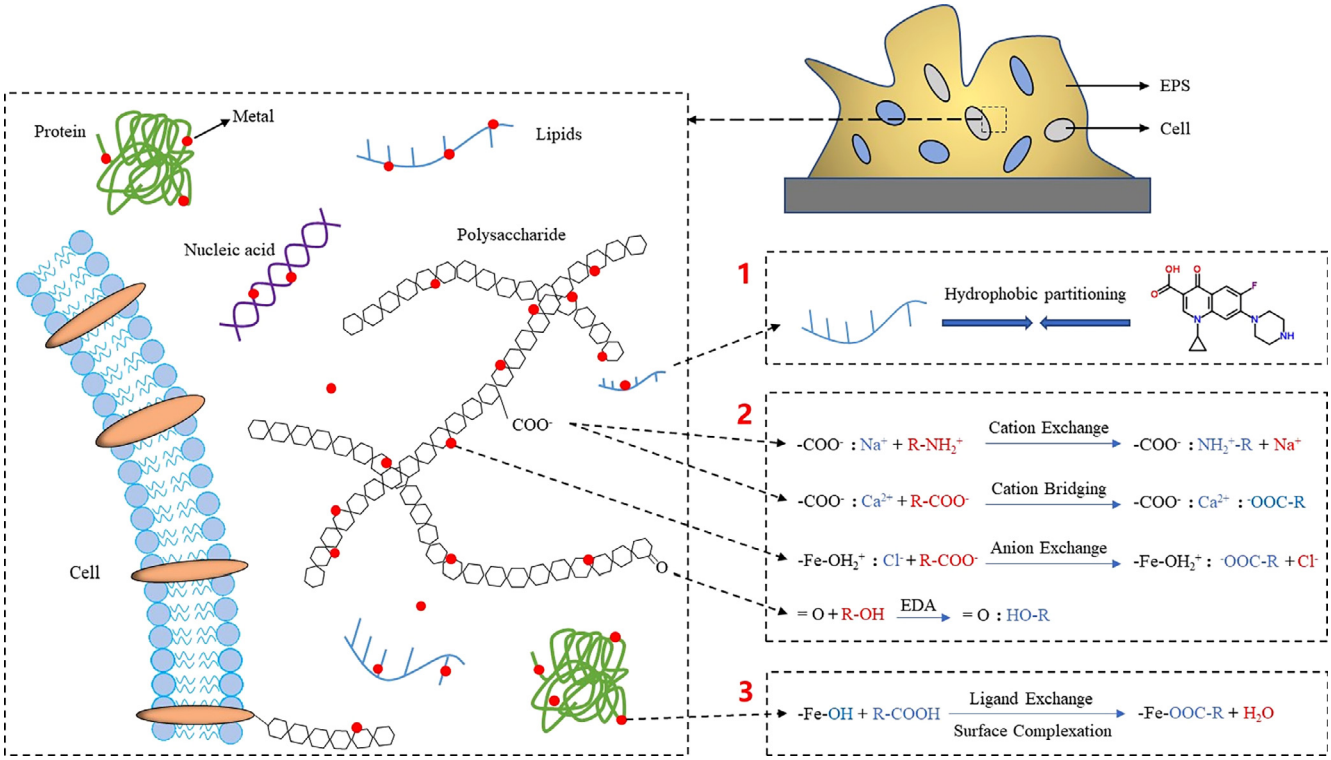


Fig. 1. Schematic diagram of cell body in excess sludge adsorbing quinolone antibiotics. 1) Hydrophobic partitioning; 2) Electrostatic interactions: cation exchange, cation bridging, anion exchange, and electron donor acceptor (EDA); 3) Surface complexation.

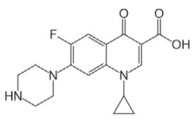
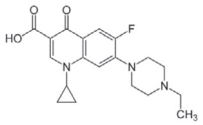
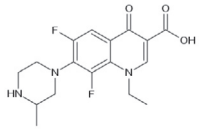
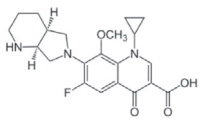
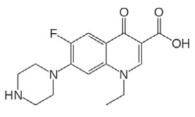
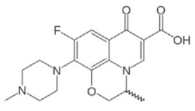
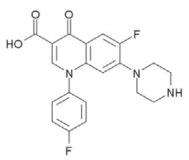
invertebrates [27]. The use of third- and fourth-generation quinolone antibiotics is limited due to serious side effects [28–30]. It has been reported that the genotoxic potential of quinolone antibiotics increases with newly developed generations; for example, fourth-generation quinolones are two orders of magnitude more genotoxic than third-generation quinolones [31–33]. As a typical representative of third-generation quinolone antibiotics and veterinary antibiotics, sarafloxacin has been widely used to treat bacterial diseases of fish and shrimp, such as furunculosis, vibriosis, and enteric red mouth disease [34]. Moxifloxacin, a fourth-generation quinolone antibiotic, was developed by the Bayer Company in Germany and offers many advantages, such as a broader antibacterial spectrum, stronger activity, reduced drug resistance, and fewer adverse reactions.

Because of the high affinity of quinolone antibiotics to sludge [35], most of these compounds are adsorbed on excess sludge [36,37], which is their most common fate in WWTPs [14,38,39]. When excess sludge is used as a fertilizer, quinolone antibiotics can be transferred to plants and enter the human food chain [35]. The presence of quinolone antibiotics in the environment has potential links to the presence of tolerant bacteria in surrounding environments, such as WWTPs, poultry farms, hospitals, and rivers [40–43], which may interfere with aquatic ecosystems and make humans and animals more vulnerable to antibiotic-resistant microbes. Therefore, it is of great theoretical and practical value to comprehensively assess the occurrence and influencing factors of various quinolone antibiotics in excess sludge [36,44].

Extracellular polymeric substances (EPS) play an important role in the adsorption of antibiotic drugs, as microbial cells in excess sludge are encapsulated by EPS [4,45–47]. Fig. 1 presents a schematic diagram showing a microbial cell adsorbing quinolone antibiotics in excess sludge. EPS is mainly composed of proteins, polysaccharides, lipids, nucleic acids, and metal ions [4,46,47]. Since EPS consists of various organic compounds and quinolone antibiotics contain a variety of functional groups, quinolone antibiotics are adsorbed on microbial cell surfaces in excess sludge mainly via one of three mechanisms (Fig. 1) [4,48]: (1) hydrophobic partitioning; (2) electrostatic interactions (cation exchange, cation bridging, anion exchange, electron donor acceptor); and (3) surface complexation. Hence, environmental conditions such as pH and metal cation levels markedly affect the adsorption of quinolone antibiotics on the surfaces of microbial cell bodies as they alter the characteristics of the EPS [4,49–51]. In particular, the bridging action [50–53] and complexation [50,54,55] of metal cations promote the adsorption of quinolone antibiotics on the surfaces of microbial cells in excess sludge. However, when metal ion concentrations exceed a certain value, they may compete with antibiotic ions for adsorption sites [56] or form hydrated outer layers of metal cations that shield adsorption sites [57] on the surfaces of microbial cells in excess sludge, thereby decreasing antibiotic adsorption [4,56,57].

In this study, seven typical quinolone antibiotics from three generations were investigated to reveal for the first time the role of EPS, which is encapsulated on the surfaces of microbial cells in excess sludge, and environmental conditions, such as pH and metal cation concentrations, on the adsorption of quinolone antibiotics on microbial

Table 1
Molecular structures and physicochemical properties of seven typical quinolone antibiotics from three generations.

Compound	MW [g/mol]	Structure	pK_a [58]		$Log K_{ow}$ [59]	Generations [33,60]
			pK_{a1}	pK_{a2}		
Ciprofloxacin (CIP)	331.3		5.9–6.1	8.7–8.9	0.28	2nd
Enrofloxacin (ENR)	359.4		5.9–6.3	7.7–8.0	0.70	2nd
Lomefloxacin (LOM)	351.3		5.8	9.3	−0.30	2nd
Moxifloxacin (MOX)	401.4		6.4	9.5	0.95	4th
Norfloxacin (NOR)	319.3		6.3	8.4	−1.03	2nd
Ofloxacin (OFL)	361.4		6.0	8.2	−0.39	2nd
Sarafloxacin (SAR)	385.4		5.6	8.2	1.07	3rd

cells in excess sludge.

2. Materials and methods

2.1. Materials

Ciprofloxacin (CIP, ≥ 98%) and ofloxacin (OFL, ≥ 98%) were purchased from Sigma-Aldrich Corp., St. Louis, MO, USA. Norfloxacin (NOR, ≥ 98%), enrofloxacin (ENR, ≥ 99%), lomefloxacin (LOM, ≥ 98%), sarafloxacin (SAR, ≥ 97%), and moxifloxacin (MOX, ≥ 99%) were purchased from Aladdin Corp., Shanghai, China. The molecular structures and physicochemical properties of the seven typical quinolone antibiotics from three generations are shown in Table 1.

Methanol, formic acid, and ammonium formate (chromatographically pure) were purchased from Merck Corp., Kenilworth, NJ, USA. Ultrapure water (resistivity ≥ 18.2 MΩ) was obtained by purifying tap water using an Arium Comfort II ultrapure water system for laboratory use (Sartorius Corp., Göttingen, Germany). The dialysis bag [molecular weight cut-off (MWCO) = 3500 Da] was purchased from Viskase Corp., Willowbrook, IL, USA. The 0.22-μm microfiltration membrane was purchased from Millipore Corp., Billerica, MA, USA. HCl, H_3PO_4, $NaH_2PO_4{\cdot}2H_2O$, Na_2HPO_4, NaOH, $MgSO_4{\cdot}7H_2O$, $ZnSO_4{\cdot}7H_2O$, $CaCl_2{\cdot}2H_2O$, $CuCl_2{\cdot}2H_2O$, $MnCl_2{\cdot}4H_2O$, $FeSO_4{\cdot}7H_2O$, and $AlCl_3{\cdot}6H_2O$ (analytically pure) were purchased from Sinopharm Chemical Reagent Corp., Ltd, Shanghai, China.

2.2. Preparation of Biosolid and Biosolid$_{EPS\ free}$

The excess sludge originating from the backflow sludge lines of the Gaobeidian WWTP were collected in a brown glass bottle, and NaN_3 (0.5 g·L^{-1}) was added to inhibit the action of microorganisms. The sample was subsequently stored at 4 °C. The stored sludge was centrifuged at 4000 × *g* and 4 °C for 20 min. The supernatant was removed, and the sediment was collected for experimental analysis and freeze-drying. The obtained powder is denoted as Biosolid.

In order to cause minimal damage to microbial cells, the EPS was extracted by the cation exchange resin (CER) method [47]. In the first step, sludge suspensions were prepared by dispersing 1 g of dry sludge sample in 250 mL of ultrapure water. Subsequently, CER (70 g/g volatile solids; VS) was placed in the sludge suspension, and the mixture was stirred at 500 rpm for 4 h. Finally, the sludge suspensions were centrifuged at 4000 × *g* and 4 °C for 20 min. The sediment obtained after extracting the EPS was washed three times using ultrapure water and freeze-dried to obtain sludge powder with microbial cells but free of EPS (although some EPS may theoretically still exist), denoted as Biosolid$_{EPS\ free}$. Notably, the Biosolid and Biosolid$_{EPS\ free}$ powders were produced in quantities sufficient for the experiments performed, allowing the prepared batches to be used in all experiments and thus ensuring consistency in the characteristics of Biosolid or Biosolid$_{EPS\ free}$. The volume-weighted mean sizes of Biosolid and Biosolid$_{EPS\ free}$ were 40.12 and 25.96 μm, respectively.

2.3. Determination of solid-liquid distribution coefficient

The solid-liquid distribution coefficient, K_d, can be calculated by Eq. (1) [4]:

$$K_d = \frac{q_e}{C_e} \tag{1}$$

where C_e is the concentration of pharmaceutical in the water at adsorption equilibrium and q_e is the concentration of pharmaceutical adsorbed on the Biosolid or Biosolid$_{EPS\ free}$ at adsorption equilibrium. This latter value is calculated by Eq. (2):

$$q_e = \frac{(C_0 - C_e)\bullet V}{M} \tag{2}$$

where C_0 is the initial concentration of pharmaceutical in the water, V is the water solution volume, and M is the mass of Biosolid or Biosolid$_{EPS\ free}$.

2.4. Adsorption experiment

A phosphate buffer solution of pH 3–11 at 10 mmol·L^{-1} was prepared using H_3PO_4, $NaH_2PO_4{\cdot}2H_2O$, Na_2HPO_4, and NaOH. Various antibiotic aqueous solutions of 100 mg·L^{-1} were prepared as stock solutions and stored at 4 °C. Then, antibiotic aqueous solutions of 350–3500 μg·L^{-1} were prepared by mixing the stock solution and phosphate buffer solution with the corresponding pH. Fifty milligrams of Biosolid or Biosolid$_{EPS\ free}$ was added to 50 mL antibiotic aqueous solution, and the pH was adjusted to the corresponding value using 1 mol·L^{-1} HCl or NaOH solution. The suspension was stirred at 500 rpm and 25 °C for 6 h (until the adsorption equilibrium had been reached) and then filtered through a 0.22-μm membrane. Concentrations of trace antibiotics in water were determined by ultra-high performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). Thus, the adsorption isotherm curves and the K_d values of the antibiotics on Biosolid or Biosolid$_{EPS\ free}$ were obtained.

2.5. Analytical methods

The concentration of pharmaceutical in the water was analyzed according to the EPA method [61] by UPLC-MS/MS (TSQ Quantum Access MAX System, Thermo-Fisher Scientific, Waltham, MA, USA) with an electrospray ionization (ESI) ion source and a chromatography column (Hypersil GOLD 100 × 2.1 mm, 1.9 μm particle size, Thermo-Fisher Scientific). The analysis conditions are provided in the Supplementary Material (SM) (see SM Table S1). Mobile phase A was 0.3% formic acid + 0.1% ammonium formate, and mobile phase B was pure methanol. The gradient elution conditions are shown in SM Table S2. The optimal conditions for the selective reaction monitoring (SRM) of the mass spectrometer, which can realize the qualitative and quantitative analysis of the target pharmaceutical in water, are shown in SM Table S3. Pharmaceutical standard solutions of 1–4000 μg·L^{-1} were prepared with the phosphate buffer solution of pH 7, and then the concentration of pharmaceutical in water was quantified by an external standard method, based on the peak area of the quantified ions.

The powders, including Biosolid, Biosolid$_{EPS\ free}$, and Biosolid with CIP adsorbed, were prepared by vacuum freeze-drying (FD-1A-50, Beijing Boyikang Laboratory Instruments Co., Ltd, Beijing, China). Biosolid and Biosolid$_{EPS\ free}$ suspensions were prepared by adding the corresponding powder into phosphate buffer solution, and the pH was adjusted to the corresponding value using 1 mol·L^{-1} HCl or NaOH solution. Then, the zeta potential value was measured using a zeta potential analyzer (Zetasizer Nano ZS90, Malvern, UK). The 50-mL suspension was stirred at 500 rpm and 25 °C for 3 h and poured into a 3500-Da dialysis bag, and then the bag was added to a 250-mL beaker with 100 mL buffer solution of the corresponding pH before dialysis was carried out for 12 h. Concentrations of metal ions, including those dominant in excess sludge such as Ca, Mg, Fe, Al, Zn, Cu, and Mn [62], were measured in the dialysates using inductively coupled plasma (ICP) spectrometry (ICAP 7000 Series, Thermo-Fisher Scientific). Sixty milligrams Biosolid or Biosolid$_{EPS\ free}$ powder was added to a beaker with 20 mL ultrapure water and stirred at 500 rpm and 25 °C for 30 min; then, the biological phase in the suspension obtained was observed at 400× under a bright-field microscope (Axioskop 40, Zeiss, Germany). The powders were analyzed using a Fourier transform infrared (FTIR) spectrometer (Nicolet iS5, Thermo-Fisher Scientific). The suspension was centrifuged (Sigma 3K15), the trace drug was weighed using an analytical balance (MS105DU, Mettler-Toledo, Greifensee, Switzerland), and the pH of the solution was adjusted using an automatic potentiometric titrator (916 Ti-Touch, Metrohm, Herisau, Switzerland). A laser particle size analyzer (Mastersizer 2000, Malvern, UK) was used to

determine the size distributions of particles such as Biosolid and Biosolid$_{EPS\ free}$ suspended in ultrapure water. The X-ray photoelectron spectroscopy (XPS) spectra of Biosolid and Biosolid$_{EPS\ free}$ were obtained using the Thermo ESCALAB 250 system with non-monochromatized Al Mg radiation as an excitation source (Waltham, MA, USA).

3. Results and discussion

3.1. Role of EPS

The concentrations of the seven typical quinolone antibiotics in the excess sludge from the Gaobeidian WWTP in Beijing were analyzed and are shown in Fig. 2. The Gaobeidian WWTP uses an anaerobic/anoxic/oxic (A^2/O) process with a water treatment amount of 1,000,000 m^3/day. As shown in this figure, all antibiotics except LOM were detected at high concentrations in the excess sludges of the WWTP.

Considering that the pH of municipal wastewater is usually between 6 and 8, pH values of 5, 7, and 9 were investigated in this study. Fig. 3 shows the K_d values of three typical quinolone antibiotics (CIP, SAR, and MOX) from three generations in Biosolid and Biosolid$_{EPS\ free}$ at pH values of 5, 7, and 9. Similar to the characteristics of trace drugs previously detected in sludge [4,45], the K_d values of antibiotics in Biosolid were higher than those in Biosolid$_{EPS\ free}$, independent of pH and quinolone antibiotic type. Moreover, the K_d value decreased markedly as pH increased in the range of pH 5–9 (range of municipal wastewater), as shown in Figs. 3 and 9 (for detailed description, see Section 3.2). The results imply that if the excess sludge is used as an agricultural supplement, the antibiotics adsorbed on the surfaces of microbial cells may be released due to exfoliation of the EPS caused by changes in environmental conditions. This could lead to contamination of the aquatic environment, causing a secondary environmental hazard [4]. WWTPs are the most important emission point sources of trace pharmaceuticals, and the main fate of quinolone antibiotics is excess sludge; therefore, it is especially necessary to further study the characteristics and controlling factors of quinolone antibiotics adsorbed on microbial cells.

Photomicrographs of Biosolid and Biosolid$_{EPS\ free}$ are shown in Fig. 4, verifying that EPS indeed acts as a flocculant in the formation of activated sludge flocs [63]. Furthermore, Fig. 5 shows the typical size distributions of Biosolid and Biosolid$_{EPS\ free}$, which exhibited specific surface areas of 1.04 and 1.37 $m^2 \cdot g^{-1}$, respectively, indicating that the specific surface area of Biosolid$_{EPS\ free}$ was larger than that of Biosolid. Cells in the Biosolid suspension are encased in the surrounding EPS and aggregate into microbial flocs. Biosolid$_{EPS\ free}$ flocs are smaller and looser due to the absence of EPS. Therefore, although the specific surface area of Biosolid$_{EPS\ free}$ is larger than that of Biosolid, Biosolid$_{EPS\ free}$ exhibited a lower antibiotic adsorption capacity (Fig. 3), indicating that the macroscopic size of floc or morphology of microbial cell polymerization is not the main determinant of the adsorption of pharmaceuticals on the surfaces of microbial cells in excess sludge.

The FTIR spectra of Biosolid, Biosolid$_{EPS\ free}$, and Biosolid with CIP adsorbed are shown in Fig. 6. The Biosolid and Biosolid$_{EPS\ free}$ powders showed similar peak positions, indicating that they have similar characteristic functional groups, such as the alcoholic hydroxyl of O – H (3400–3330 cm^{-1}), the carbohydrate of CH_3, CH_2, CH (3000–2900 cm^{-1}), the amino acid amide I of C = O (1654 cm^{-1}), the alkane of CH_3 (1455 cm^{-1}), and the polysaccharide of C – O – C or C – OH (1000–1150 cm^{-1}). In other words, the cell membrane and EPS contain similar organic components, such as polysaccharides, proteins, lipids, and nucleic acids [46,64]. A previous study also demonstrated that the characteristics of ionized pharmaceuticals adsorbed on excess sludge are not dependent on the content or type of organics [4]. However, the antisymmetric (ν_{as}) and symmetric (ν_s) stretching vibration peaks of COO^- for Biosolid$_{EPS\ free}$ are shifted to the right compared to that for Biosolid, with the two variations being 1546 → 1542 cm^{-1} and 1402 → 1396 cm^{-1}, respectively. Hence, it is confirmed that the loss of metal ions in Biosolid$_{EPS\ free}$ after the extraction of EPS caused a shift in the stretching vibration peaks of COO^-, as metal ions can induce shifts in COO^- peak positions [47,65]. This may be the main reason that Biosolid$_{EPS\ free}$ has a lower adsorption capacity for quinolone antibiotics, as shown in Fig. 3. Furthermore, the antisymmetric (ν_{as}) and symmetric (ν_s) stretching vibration peaks of COO^- and the stretching vibration peak of aromatic C – F for Biosolid with CIP adsorbed were more obvious than those for Biosolid, confirming that the quinolone antibiotic was adsorbed on the surfaces of the cells in Biosolid.

In order to elucidate the elementary compositions of the surfaces of microbial cells in excess sludge, XPS spectra were obtained to characterize the difference between Biosolid and Biosolid$_{EPS\ free}$. The XPS spectra of Biosolid and Biosolid$_{EPS\ free}$ are shown in Fig. 7. Both full spectrum diagrams contained obvious peaks, such as O 1 s (510 eV), N 1 s (400 eV), C 1 s (285 eV), P 2 s (191 eV), P 2p (134 eV), Al 2 s (119 eV), and Al 2p (74 eV). The peak of Ca 2p (347 eV) was stronger in Biosolid, whereas the peak of Fe (712.00 eV) was weak in both substances, and that of Mg 2p (50.25 eV) was detected only in Biosolid. Table 3 shows the elementary compositions (atomic %) obtained by XPS spectra of the surfaces of microbial cells for Biosolid and Biosolid$_{EPS\ free}$. Based on these, we concluded that the content of metals such as Ca, Mg, Fe, and Al was higher in Biosolid than in Biosolid$_{EPS\ free}$, indicating that a decrease in the content of metals bound to the EPS could be the major reason for the adsorption capacity difference between the two substances and suggesting that the metals bound to the EPS may play a key role in the adsorption of antibiotics in excess sludge.

3.2. Effect of pH value

Fig. 8 shows the relationship between the zeta potential and pH of Biosolid and Biosolid$_{EPS\ free}$. It is clear from the figure that both powders carry a negative charge at pH > 3, regardless of the presence of EPS, and that the negative potential of the microbial cell floc decreases with increasing pH. Therefore, the adsorption capacities of antibiotics on Biosolid and Biosolid$_{EPS\ free}$ decreased markedly over the range of pH 5–9 (range of municipal wastewater), showing an exponential decline in K_d values (Fig. 3).

Considering that quinolone antibiotics are ionic compounds in water, the K_d values of seven typical quinolone antibiotics (CIP, SAR, MOX, NOR, LOM, ENR, and OFL) adsorbed on Biosolid were investigated at pH 3–11, as shown in Fig. 9. The K_d values of all quinolone antibiotics first increased and then decreased with increasing pH,

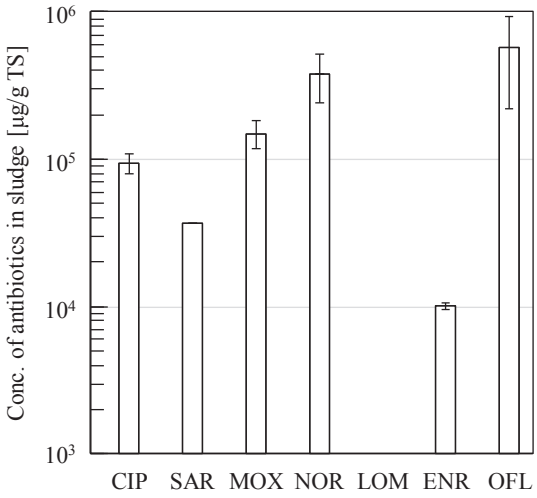


Fig. 2. Concentrations of seven typical quinolone antibiotics in excess sludge from the Gaobeidian WWTP in Beijing.

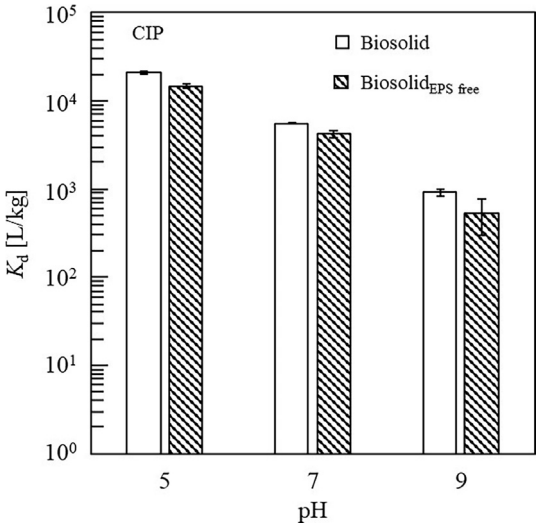


Fig. 3. Solid-liquid partition coefficients (K_d) of typical quinolone antibiotics from three generations in Biosolid and Biosolid$_{EPS\ free}$. (a) CIP; (b) SAR; (c) MOX.

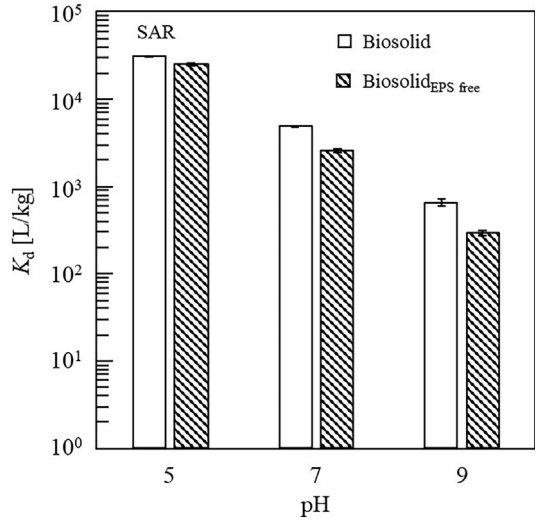


Fig. 3. (*continued*)

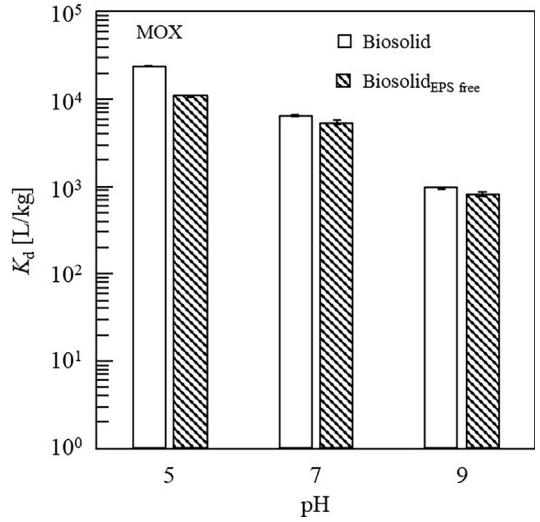


Fig. 3. (*continued*)

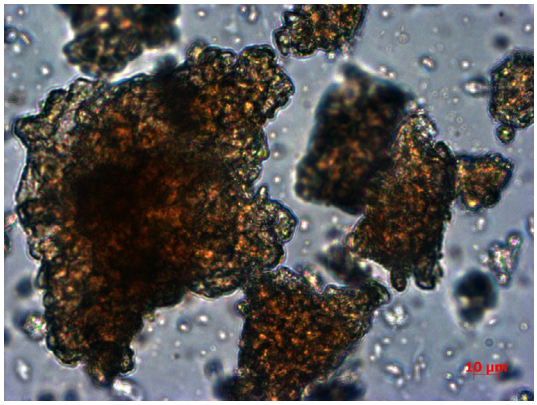


Fig. 4. Typical photomicrographs of suspensions of (a) Biosolid and (b) Biosolid$_{EPS\ free}$.

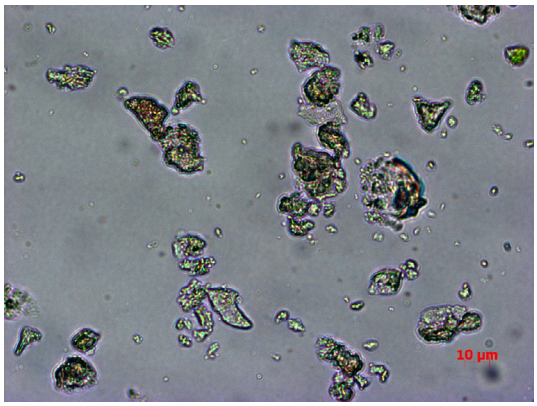


Fig. 4. (*continued*)

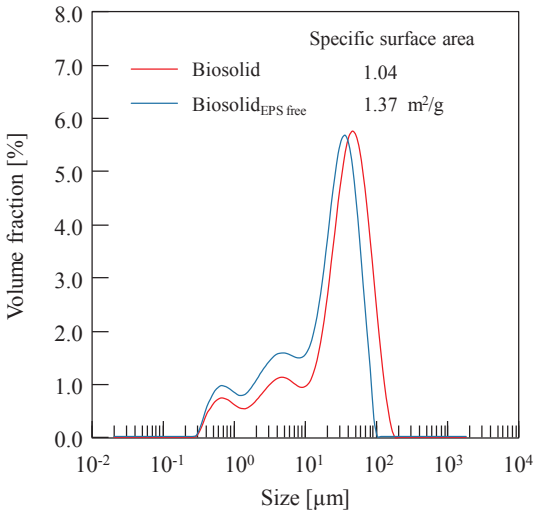


Fig. 5. Size distributions of Biosolid and Biosolid$_{EPS\ free}$.

reaching a maximum at about pH 5. Therefore, the zeta potential of Biosolid is not the main determinant of the adsorption of antibiotics on the surfaces of microbial cells in excess sludge at pH 3–11, because of the monotonic relationship between the zeta potential of Biosolid and pH (Fig. 8). Based on the pK_a values of the seven antibiotics (Table 1), the speciation fractions of cations, zwitterions, and anions were calculated as a function of pH (see SM), and the results are shown in SM Fig. S1. At pH 3, quinolone antibiotics present as predominantly cationic because their −NH or −N binds to H^+ [66] and the microbial cell floc in Biosolid is electropositive (Fig. 8); therefore, the K_d value (or

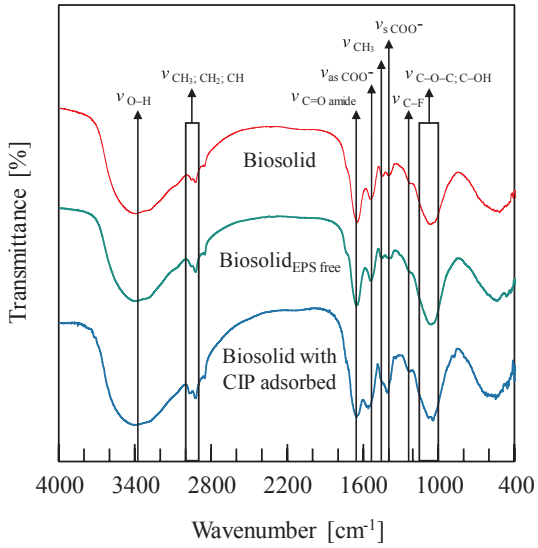


Fig. 6. FTIR spectra of Biosolid, Biosolid$_{EPS\ free}$, and Biosolid with CIP adsorbed.

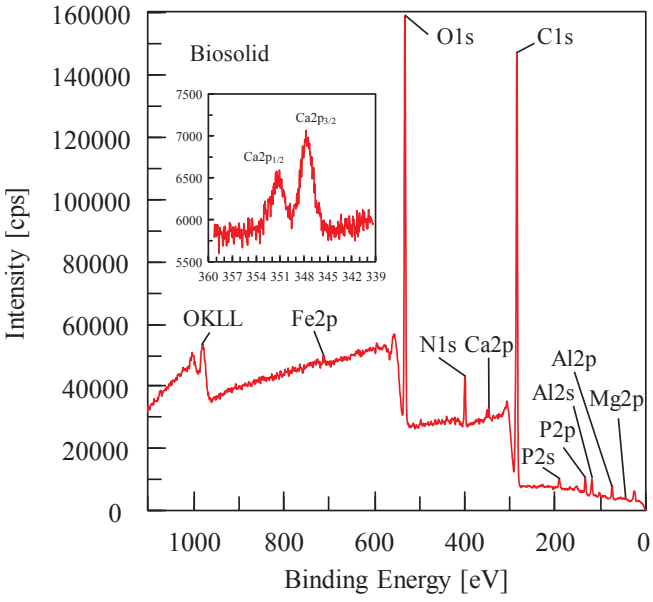


Fig. 7. XPS spectra of (a) Biosolid and (b) Biosolid$_{EPS\ free}$.

adsorption capacity) is low because of electrostatic repulsion. At pH 3–5, a portion of quinolone antibiotics become amphoteric or anionic as the pH increases (see SM Fig. S1); the −COOH of the antibiotics loses H^+, becoming $-COO^-$ [66], and then cationic bridging occurs due to the interaction of the $-COO^-$ in the antibiotic and metal cations in the EPS of sludge cells [50–53]. Thereby, the adsorption content of antibiotics is promoted in Biosolid. At pH ≥ 5, the cation fractions of the seven antibiotics gradually decreased (see SM Fig. S1), as did the corresponding K_d values (Fig. 9), indicating that the electrostatic interaction between the cationic antibiotics and the negatively charged microbial cell floc may dominate [4].

3.3. Role of metal ions

Based on the results presented in the previous two sections and the mechanism of antibiotic adsorption in excess sludge (Fig. 1), we speculated that the metal ions bound to the EPS may play a key role in the adsorption of antibiotics in excess sludge. Therefore, the typical dominant metal ions in excess sludge, such as Ca, Mg, Fe, Al, Zn, Cu,

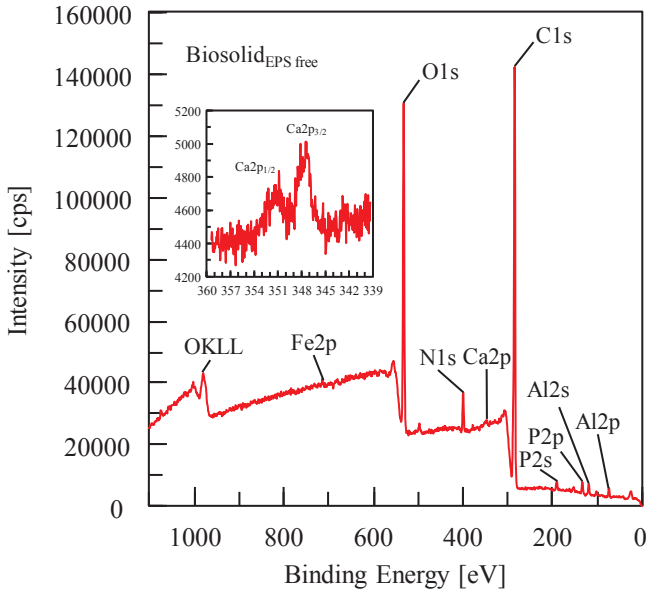


Fig. 7. (*continued*)

Table 2
Ion radii and contents of typical metal ions in Biosolid.

Metal ions	Ion radius [pm]	Content* [mg·(g TS**)$^{-1}$]
Al^{3+}	55	38.18
Ca^{2+}	100	20.68
Cu^{2+}	73	0.57
Fe^{3+}	53.5	11.06
Mg^{2+}	72	4.11
Mn^{2+}	67	0.11
Zn^{2+}	74	1.05

*Contents of corresponding metals including all valence states in dry sludge (Biosolid).
**TS, total solids.

Table 3
Elementary compositions (atomic %) obtained by XPS spectra of the surfaces of microbial cells for Biosolid and Biosolid$_{EPS\ free}$.

Element	Biosolid [%]	Biosolid$_{EPS\ free}$ [%]
C	66.28	71.88
N	3.83	3.34
O	22.87	20.28
P	1.86	1.55
Al	3.30	2.30
Ca	0.94	0.33
Fe	0.39	0.32
Mg	0.53	0.00

and Mn [62], were investigated, and their concentrations were measured (Table 2). Fig. 10 shows the concentrations of seven metal ions adsorbed in the sludge solid phase (Biosolid) at various pH values. The concentrations of Ca and Mg increased with increasing pH, and the concentration of Fe was basically invariable. Since Al is an amphoteric metal, the content of Al (Al^{3+} and AlO^{2-}) first increased and then decreased as pH increased. While the concentrations of Zn, Cu, and Mn were low in the sludge, those of Zn and Mn increased while that of Cu remained constant with increasing pH.

In order to study the role of metal ions in the adsorption of quinolone antibiotics in excess sludge, the adsorption properties of three typical quinolone antibiotics (CIP, SAR, and MOX) from three generations in dry excess sludge (Biosolid) were investigated. Fig. 11 shows the variation in the concentrations of metals in Biosolid with CIP

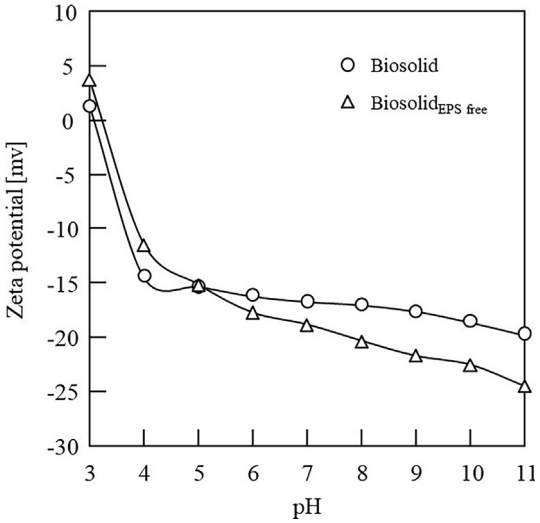


Fig. 8. Zeta potentials of Biosolid and Biosolid$_{EPS\ free}$ as a function of pH.

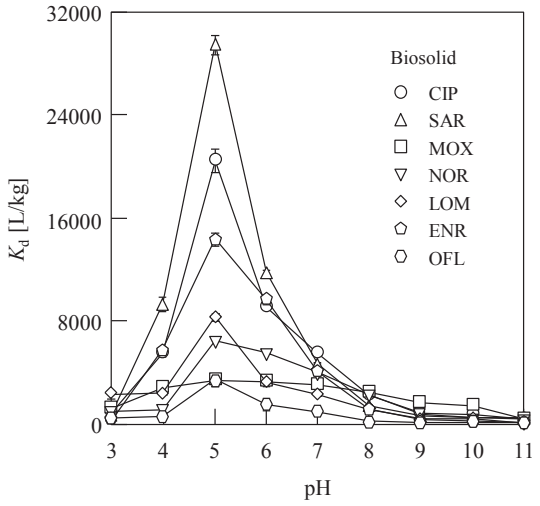


Fig. 9. Solid-liquid distribution coefficient of quinolone antibiotics in Biosolid at various pH values.

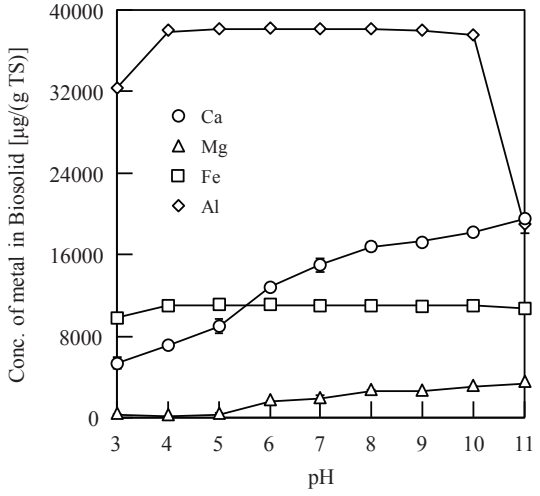


Fig. 10. Concentrations of metals in Biosolid without antibiotic adsorption at various pH values. (a) Ca, Mg, Fe, and Al; (b) Zn, Cu, and Mn.

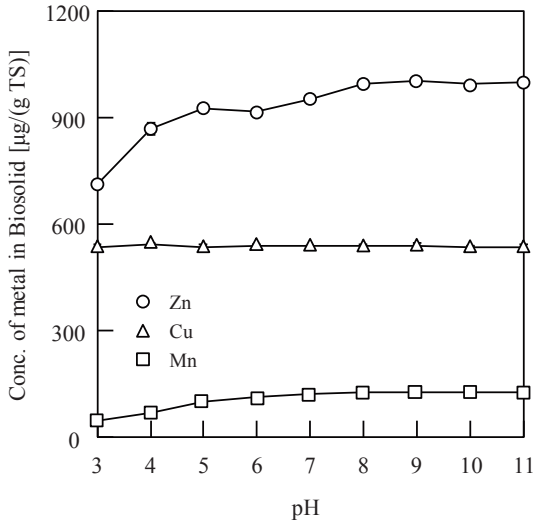


Fig. 10. (*continued*)

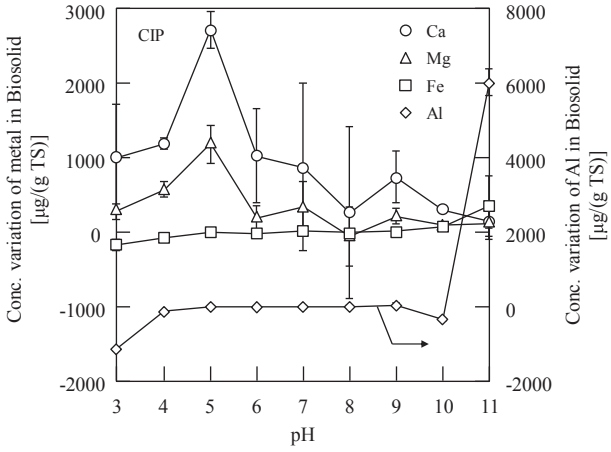


Fig. 11. Variations in concentrations of metals in Biosolid with CIP adsorption at various pH values. (a) Ca, Mg, Fe, and Al; (b) Zn, Cu, and Mn.

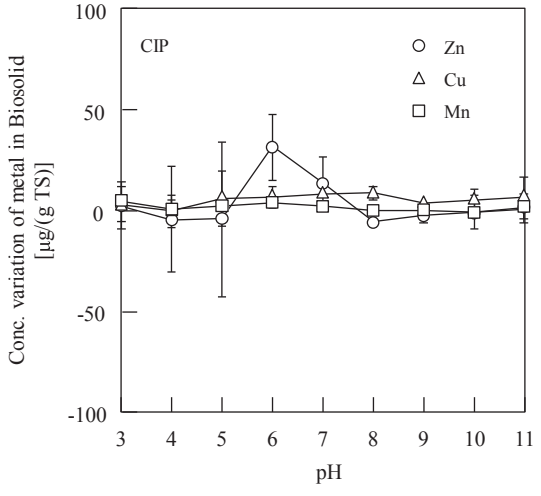


Fig. 11. (*continued*)

adsorption across various pH values. The concentration of Fe remained unchanged as the pH value increased, whereas that of Al increased suddenly at pH 11, probably because of the presence of formed AlO^{2-}, which combines with the cations in EPS (Fig. 1). The concentrations of Zn, Cu, and Mn also remained unchanged, probably because their low

absolute concentrations had less of an effect on the adsorption of antibiotics. Surprisingly, the variation in the concentrations of Ca and Mg in Biosolid peaked at about pH 5, while the variations in the other five metals were minimal, and this was notably the pH at which the K_d values (or adsorption capacities) of the quinolone antibiotics in Biosolid were also at a maximum (see Fig. 9). This may be due to the larger ion radius and higher contents of Ca^{2+} and Mg^{2+} in excess sludge (see Table 2). Therefore, this result indicates that the cationic bridging of Ca^{2+} and Mg^{2+} in the sewage sludge may be predominantly responsible for the quinolone adsorbed on the surface of microbial cell floc in excess sludge [50–53]. Similar results were also obtained for SAR and MOX (SM Figs. S2 and S3).

3.4. Adsorption isotherms of typical pharmaceuticals

Generally, the temperature of the wastewater in WWTPs is constant (for example, 20–24 °C in summer and 10–15 °C in winter), and the adsorption behaviors of quinolone antibiotics are considered to reach an adsorption equilibrium because of the continuous influx and efflux of wastewater or sludge in WWTPs. Therefore, the practical significance of the kinetics and thermodynamic parameters commonly used in the adsorption materials field was not investigated in this study. This manuscript focused instead on the antibiotic adsorption capacities of microbial cells in excess sludge, and all experimental data were obtained after the adsorption equilibrium had been reached. For simplicity, in this study, we investigated the adsorption isotherms of trace amounts of three typical quinolone antibiotics—CIP (second-generation), SAR (third-generation), and MOX (fourth-generation)—on microbial cells in excess sludge. In our experiments, the concentration of Biosolid was 1.0 g/L, and the initial concentrations of quinolone antibiotics were 350–3500 μg/L; therefore, the adsorbent (Biosolid) was present in excess relative to the adsorbates (quinolone antibiotics). SM Figure S4 shows the variation in the concentrations of CIP, SAR, and MOX in solution with adsorption time, and it is clear that the adsorption equilibrium had been reached after 2 h. SM Figure S5 shows ordinary coordinate plots (C_e vs q_e) that indicate that a saturation state had not yet been reached because of the low initial concentrations (350–3500 μg/L) of quinolone antibiotics.

The adsorption isotherms of three typical quinolone antibiotics (CIP, SAR, and MOX) from three generations in Biosolid are shown in Fig. 12, with C_e/q_e vs q_e plotted in Fig. 12(a) on ordinary coordinates and C_e vs q_e plotted in Fig. 12(b) on a double-logarithmic scale. Two classical adsorption isotherm models were used to evaluate the adsorption properties of quinolone antibiotics in excess sludge. The Langmuir model formula is expressed as Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}K} + \frac{C_e}{Q_{max}} \quad (3)$$

where Q_{max} is the amount of quinolone antibiotics adsorbed to form monolayer coverage, and K is the Langmuir adsorption equilibrium constant. The Freundlich model formula is expressed as Eq. (4):

$$q_e = K_f C_e^{1/n} \quad (4)$$

where K_f and n are the Freundlich adsorption coefficients. Here, K_f is related to adsorption capacity and adsorbate-adsorbent affinity; $1/n$ ranges between 0 and 1 and is a measure of the adsorption intensity or surface heterogeneity, becoming more heterogeneous and more favorable for adsorption as its value gets closer to zero [67]. As shown in Fig. 12, the Freundlich model was more suitable than the Langmuir model, similar to results previously reported in the literature [44,55,68]. The Langmuir model assumes that the surface of the adsorbent is uniform and that the adsorbate is a monolayer adsorption; however, multi-layer or even more complex adsorption may occur for the quinolone antibiotics adsorbed on the surface of microbial cells in excess sludge. The Freundlich model is an empirical formula and has been adopted widely. As shown in Eq. (4), the value $1/n$ reflects whether the adsorption of antibiotics on the surface of microbial cells in excess sludge is favorable; the smaller the value, the stronger the heterogeneity of the adsorbed surface, generating more favorable adsorption [67]. Therefore, the surface heterogeneity of microbial cells in excess sludge is high and favorable for adsorption because the value ($1/n$) obtained for each pharmaceutical was < 1 in this study. Table S4 shows the adsorption properties of Biosolid in this study and the adsorbents reported in the literature. The obtained Q_{max} values from the Langmuir isotherm correlations for CIP, SAR, and MOX were 10.66, 22.93, and 14.27×10^6 μg·kg^{-1}, respectively, which are lower than those of other adsorbents reported in the literature, probably due to Biosolid's low surface area (1.04 m^2·g^{-1}) and fewer adsorption sites. It should be noted that our research objectives were not to obtain an adsorption material such as Biosolid from excess sludge but to illuminate the adsorption properties of quinolone antibiotics on microbial cells in excess sludge.

4. Conclusions

The occurrence of seven typical quinolone antibiotics from three generations in excess sludge was investigated at trace concentrations. EPS plays an important role in the adsorption of quinolone antibiotics by microbial cells in excess sludge and can facilitate adsorption independent of pH and antibiotic type. The solid-liquid distribution coefficient, K_d, decreases markedly as pH increases (pH 5–9, range of municipal wastewater). Metal ions bound to EPS are predominantly responsible for the adsorption of antibiotics in sludge, rather than the macroscopic size of the sludge floc. The pH value affects the patterns of quinolone antibiotics, the zeta potential of sludge floc, and the contents of metal ions contained in the sludge. The adsorption capacity of antibiotics in the excess sludge first increased and then decreased with increasing pH at pH 3–11 and reached a maximum value (20,506, 14,458, 10,689, 22,854, 20,302, 8494, and 29,547 L/kg for CIP, ENR, LOM, MOX, NOR, OFL, and SAR, respectively) at pH 5. Also, at this pH, the cationic bridging of Ca^{2+} and Mg^{2+} bound in the EPS plays a major role due to their larger ion radius and higher contents in excess sludge. The Freundlich model is more suitable than the Langmuir model for describing the adsorption behavior of quinolone antibiotics in excess sludge because of the high surface heterogeneity of the sludge. Our results imply that quinolone antibiotics adsorbed on the surfaces of microbial cells may be released upon the exfoliation of EPS caused by changes in environmental conditions when excess sludge is used as an

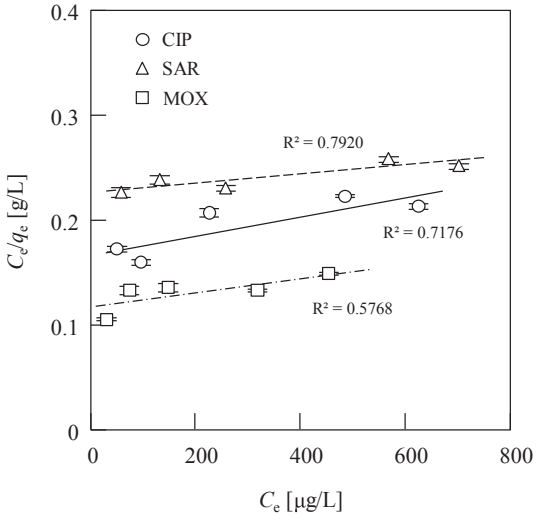


Fig. 12. Langmuir (a) and Freundlich (b) sorption isotherms for typical quinolone antibiotics from three generations.

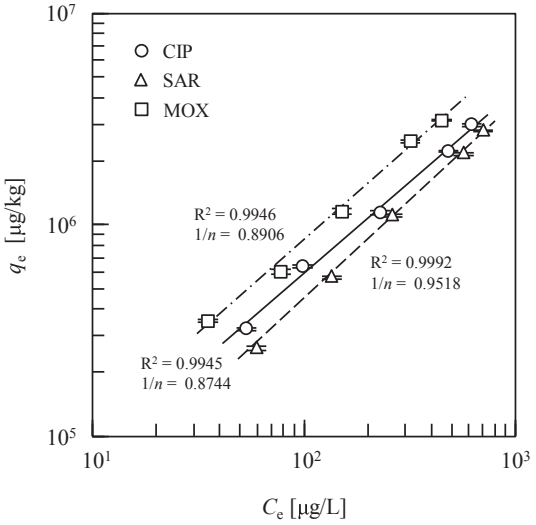


Fig. 12. (*continued*)

agricultural supplement, thereby contaminating the aquatic environment and causing a secondary environmental hazard. Thus, additional measures are necessary to remove antibiotics from excess sludge before agricultural use, and future studies should investigate the development and efficacy of such measures.

Acknowledgments

Funding: This study was partially supported by the China Postdoctoral Science Foundation (Grant No. 2015M580968), the Beijing Postdoctoral Research Foundation, the Beijing Outstanding Talents Training, Science and Technology Programs of the Beijing Municipal Education Commission (Grant No. SQKM201710016001), and the Beijing Advanced Innovation Center for Future Urban Design. The funding agencies did not influence the study design, data collection, analysis, and interpretation, report writing, or the decision to submit this article for publication.

Declarations of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2019.03.230.

References

[1] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: agents of subtle change? Env. Heal. Perspect. 107 (1999) 907–938.
[2] H. Zhou, J. Liu, H. Xia, Q. Zhang, T. Ying, T. Hu, Removal and reduction of selected organic micro-pollutants in effluent sewage by the ozone-based oxidation processes, Chem. Eng. J. 269 (2015) 245–254.
[3] O.M. Rodriguez-Narvaez, J.M. Peralta-Hernandez, A. Goonetilleke, E.R. Bandala, Treatment technologies for emerging contaminants in water: a review, Chem. Eng. J. 323 (2017) 361–380.
[4] D.-Q. Cao, Z. Wang, X.-D. Hao, Q.-H. Wang, Controlling factors of excess sludge on adsorbing trace typical pharmaceuticals, CIESC. J. 68 (2017) 3266–3274.
[5] N.H. Tran, M. Reinhard, K.Y. Gin, Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review, Water Res. 133 (2018) 182–207.
[6] D.A. Palacio, B.L. Rivas, B.F. Urbano, Ultrafiltration membranes with three water-soluble polyelectrolyte copolymers to remove ciprofloxacin from aqueous systems, Chem. Eng. J. 351 (2018) 85–93.
[7] Z. Ma, H. Wu, K. Zhang, X. Xu, C. Wang, W. Zhu, W. Wu, Long-term low dissolved oxygen accelerates the removal of antibiotics and antibiotic resistance genes in swine wastewater treatment, Chem. Eng. J. 334 (2018) 630–637.
[8] Z. Wang, X.H. Zhang, Y. Huang, H. Wang, Comprehensive evaluation of pharmaceuticals and personal care products (PPCPs) in typical highly urbanized regions across China, Environ. Pollut. 204 (2015) 223–232.
[9] I. Martínez-Alcalá, J.M. Guillén-Navarro, C. Fernández-López, Pharmaceutical biological degradation, sorption and mass balance determination in a conventional activated-sludge wastewater treatment plant from Murcia, Spain, Chem. Eng. J. 316 (2017) 332–340.
[10] H. Zhou, Z. Zhang, M. Wang, T. Hu, Z. Wang, Enhancement with physicochemical and biological treatments in the removal of pharmaceutically active compounds during sewage sludge anaerobic digestion processes, Chem. Eng. J. 316 (2017) 361–369.
[11] C. Grandclement, I. Seyssiecq, A. Piram, P. Wong-Wah-Chung, G. Vanot, N. Tiliacos, N. Roche, P. Doumenq, From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: a review, Water Res. 111 (2017) 297–317.
[12] J. Wang, S. Wang, Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review, J. Environ. Manage. 182 (2016) 620–640.
[13] Central People's Government of the People's Republic of China, Water Pollution Prevention and Control Action Plan (in Chinese) released on April 2015 and available at: http://www.gov.cn/zhengce/content/2015-04/16/content_9613.htm, 2015 (accessed on 14 June 2018).
[14] E.M. Golet, I. Xifra, H. Siegrist, A.C. Alder, W. Giger, Environmental exposure assessment of fluoroquinolone antibacterial agents from sewage to soil, Environ. Sci. Technol. 37 (2003) 3243–3249.
[15] T.A. Ternes, N. Herrmann, M. Bonerz, T. Knacker, H. Siegrist, A. Joss, A rapid method to measure the solid-water distribution coefficient (K_d) for pharmaceuticals and musk fragrances in sewage sludge, Water Res. 38 (2004) 4075–4084.
[16] S. Suárez, M. Carballa, F. Omil, J.M. Lema, How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? Rev. Environ. Sci. Biotechnol. 7 (2008) 125–138.
[17] J. Radjenović, M. Petrović, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, Water Res. 43 (2009) 831–841.
[18] D.-Q. Cao, Z. Wang, X.-D. Hao, X. Song, Role of extracellular polymeric substance in adsorption of pharmaceutical by microbial cell, in: POPs Forum 2017 & 12th Symposium on POPs, China, Wuhan, 2017.
[19] D.-Q. Cao, W.-Y. Yang, Z. Wang, X.-D. Hao, Effect of environmental conditions on adsorption of trace quinolone antibiotics by excess sludge, POPs Forum 2018 & 13th Symposium on POPs, China, Chengdu, 2018.
[20] M. Stuart, D. Lapworth, Emerging organic contaminants in groundwater, in: S.C. Mukhopadhyay, A. Mason (Eds.), Smart Sensors for Real-Time Water Quality Monitoring, Springer, Berlin, Heidelberg, 2013.
[21] V.T. Andriole, The quinolones: past, present, and future, Clin. Infect. Dis. 41 (Suppl 2) (2005) S113–119.
[22] Q.-Q. Zhang, G.-G. Ying, C.-G. Pan, Y.-S. Liu, J.-L. Zhao, Comprehensive evaluation of antibiotics emission and fate in the river basins of China: source analysis, multimedia modeling, and linkage to bacterial resistance, Environ. Sci. Technol. 49 (2015) 6772–6782.
[23] P. Sukul, M. Spiteller, Fluoroquinolone antibiotics in the environment, in: G.W. Ware, D.M. Whitacre (Eds.), Reviews of Environmental Contamination and Toxicology, Springer, New York, 2007.
[24] C. Schelhorn, V.T. Andriole, Classification of quinolones by V. Andriole, Infection 26 (1998) 64.
[25] C.M. Oliphant, G.M. Green, Quinolones: a comprehensive review, Am. Fam. Physician 65 (2002) 455–464.
[26] B. Halling-Sørensen, S.N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Holten Lutzhoft, S.E. Jorgensen, Occurrence,, fate and effects of pharmaceutical substances in the environment-a review, Chemosphere 36 (1998) 357–393.
[27] L. Meng, B. Yang, N.-D. Xue, A review on environmental behaviors and ecotoxicology of fluoroquinolone antibiotics, Asian J. Ecotoxicolo. 10 (2015) 76–88.
[28] B.A. Lipsky, C.A. Baker, Fluoroquinolone toxicity profiles: A review focusing on newer agents, Clin. Infect. Dis. 28 (1999) 352–364.
[29] G.A. Faich, J. Morganroth, A.B. Whitehouse, J.S. Brar, P. Arcuri, S.F. Kowalsky, D.C. Haverstock, R.A. Celesk, D.A. Church, Clinical experience with moxifloxacin in patients with respiratory tract infections, Ann. Pharmacother. 38 (2004) 749–754.
[30] C. Yip, A.J. Lee, Gatifloxacin-induced hyperglycemia: A case report and summary of the current literature, Clin. Ther. 28 (2006) 1857–1866.
[31] A. Hartmann, E.M. Golet, S. Gartiser, A.C. Alder, T. Koller, R.M. Widmer, Primary DNA damage but not mutagenicity correlates with ciprofloxacin concentrations in german hospital wastewaters, Arch. Environ. Contam. Toxicol. 36 (1999) 115–119.
[32] J. Hu, W. Wang, Z. Zhu, H. Chang, F. Pan, B. Lin, Quantitative structure-activity relationship model for prediction of genotoxic potential for quinolone antibacterials, Environ. Sci. Technol. 41 (2007) 4806–4812.
[33] Y. Xiao, H. Chang, A. Jia, J. Hu, Trace analysis of quinolone and fluoroquinolone antibiotics from wastewaters by liquid chromatography-electrospray tandem mass spectrometry, J. Chromatogr. A 1214 (2008) 100–108.
[34] Z. Cao, R. Liu, B. Yang, Potential toxicity of sarafloxacin to catalase: spectroscopic, ITC and molecular docking descriptions, Spectrochim. Acta. A. 115 (2013) 457–463.
[35] V.M.F. Frade, M. Dias, A.C.S.C. Teixeira, M.S.A. Palma, Environmental contamination by fluoroquinolones, Brazilian J. Pharm. Sci. 50 (2014) 41–54.
[36] Q. Sun, M. Li, C. Ma, X. Chen, X. Xie, C.-P. Yu, Seasonal and spatial variations of PPCP occurrence, removal and mass loading in three wastewater treatment plants located in different urbanization areas in Xiamen, China, Environ. Pollut. 208 (2016) 371–381.
[37] B. Tiwari, B. Sellamuthu, Y. Ouarda, P. Drogui, R.D. Tyagi, G. Buelna, Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using

biological approach, Bioresour. Technol. 224 (2017) 1–12.
[38] J.L. Conkle, C. Lattao, J.R. White, R.L. Cook, Competitive sorption and desorption behavior for three fluoroquinolone antibiotics in a wastewater treatment wetland soil, Chemosphere 80 (2010) 1353–1359.
[39] A. Jia, Y. Wan, Y. Xiao, J. Hu, Occurrence and fate of quinolone and fluoroquinolone antibiotics in a municipal sewage treatment plant, Water Res. 46 (2012) 387–394.
[40] P.N. Gaunt, L.J.V. Piddock, Ciprofloxacin resistant *Campylobacter* spp. in humans: An epidemiological and laboratory study, J. Antimicrob. Chemother. 37 (1996) 747–757.
[41] K.E. Smith, J.M. Besser, C.W. Hedberg, F.T. Leano, J.B. Bender, J.H. Wicklund, B.P. Johnson, K.A. Moore, M.T. Osterholm, Quinolone-resistant *Campylobacter jejuni* infections in Minnesota, 1992–1998, N. Engl. J. Med. 340 (1999) 1525–1532.
[42] F.F. Reinthaler, J. Posch, G. Feierl, G. Wüst, D. Haas, G. Ruckenbauer, F. Mascher, E. Marth, Antibiotic resistance of *E. Coli* in sewage and sludge, Water Res. 37 (2003) 1685–1690.
[43] J. Hu, J. Shi, H. Chang, D. Li, M. Yang, Y. Kamagata, Phenotyping and genotyping of antibiotic-resistant Escherichia coli isolated from a natural river basin, Environ. Sci. Technol. 42 (2008) 3415–3420.
[44] F. Polesel, K. Lehnberg, W. Dott, S. Trapp, K.V. Thomas, B.G. Plósz, Factors influencing sorption of ciprofloxacin onto activated sludge: experimental assessment and modelling implications, Chemosphere 119 (2015) 105–111.
[45] H. Zhang, Y. Jia, S.K. Khanal, L.-U. Hui, H. Fang, Q. Zhao, Understanding the role of extracellular polymeric substances (EPS) on ciprofloxacin (CIP) adsorption in aerobic sludge, anaerobic sludge and sulfate-reducing bacteria (SRB) sludge systems, Environ. Sci. Technol. 52 (2018) 6476–6486.
[46] H.-C. Flemming, J. Wingender, U. Szewzyk, P. Steinberg, S.A. Rice, S. Kjelleberg, Biofilms: an emergent form of bacterial life, Nat. Rev. Microbiol. 14 (2016) 563–575.
[47] D.-Q. Cao, X. Song, X.-M. Fang, W.-Y. Yang, X.-D. Hao, E. Iritani, N. Katagiri, Membrane filtration-based recovery of extracellular polymer substances from excess sludge and analysis of their heavy metal ion adsorption properties, Chem. Eng. J. 354 (2018) 866–874.
[48] A.A. MacKay, D. Vasudevan, Polyfunctional ionogenic compound sorption: challenges and new approaches to advance predictive models, Environ. Sci. Technol. 46 (2012) 9209–9223.
[49] D. Vasudevan, G.L. Bruland, B.S. Torrance, V.G. Upchurch, A.A. MacKay, pH-dependent ciprofloxacin sorption to soils: interaction mechanisms and soil factors influencing sorption, Geoderma 151 (2009) 68–76.
[50] Z. Pei, X.-Q. Shan, J. Kong, B. Wen, G. Owens, Coadsorption of ciprofloxacin and Cu (II) on montmorillonite and kaolinite as affected by solution pH, Environ. Sci. Technol. 44 (2010) 915–920.
[51] Z.-G. Pei, X.-Q. Shan, S.-Z. Zhang, J.-J. Kong, B. Wen, J. Zhang, L.-R. Zheng, Y.-N. Xie, K. Janssens, Insight to ternary complexes of co-adsorption of norfloxacin and Cu(II) onto montmorillonite at different pH using EXAFS, J. Hazard. Mater. 186 (2011) 842–848.
[52] J.R.V. Pils, D.A. Laird, Sorption of tetracycline and chlortetracycline on K- and Ca-saturated soil clays, humic substances, and clay-humic complexes, Environ. Sci. Technol. 41 (2007) 1928–1933.
[53] N. Carmosini, L.S. Lee, Ciprofloxacin sorption by dissolved organic carbon from reference and bio-waste materials, Chemosphere 77 (2009) 813–820.
[54] D. Perez-Guaita, S. Boudesocque, S. Sayen, E. Guillon, Cu(II) and Zn(II) complexes with a fluoroquinolone antibiotic: Spectroscopic and X-ray absorption characterization, Polyhedron 30 (2011) 438–443.
[55] L.M. Peruchi, A.H. Fostier, S. Rath, Sorption of norfloxacin in soils: analytical method, kinetics and Freundlich isotherms, Chemosphere 119 (2015) 310–317.
[56] Y. Wang, Z. Pei, X. Shan, G. Chen, J. Zhang, Y. Xie, L. Zheng, Effects of metal cations on sorption-desorption of *p*-nitrophenol onto wheat ash, J. Environ. Sci. 23 (2011) 112–118.
[57] G.-C. Chen, X.-Q. Shan, Z.-G. Pei, H. Wang, L.-R. Zheng, J. Zhang, Y.-N. Xie, Adsorption of diuron and dichlobenil on multiwalled carbon nanotubes as affected by lead, J. Hazard. Mater. 188 (2011) 156–163.
[58] T.A. Ternes, A. Joss, Human Pharmaceuticals, Hormones and Fragrances, in: The Challenge of Micropollutants in Urban Water Management, IWA Publishing, London, UK, 2006.
[59] Calculated by EPI SuiteTM developed by USEPA.
[60] P.C. Sharma, A. Jain, S. Jain, Fluoroquinolone antibacterials: A review on chemistry, microbiology and therapeutic prospects, Acta. Pol. Pharm. 66 (2009) 587–604.
[61] USEPA, Method 1694: pharmaceuticals and personal care products in water, soil, sediment, and biosolids by HPLC/MS/MS: EPA-821-R-08-002, (2007) Washington, DC.
[62] P. Westerhoff, S. Lee, Y. Yang, G.W. Gordon, K. Hristovski, R.U. Halden, P. Herckes, Characterization, recovery opportunities, and valuation of metals in municipal sludges from US wastewater treatment plants nationwide, Environ. Sci. Technol. 49 (2015) 9479–9488.
[63] J. Xu, H.-Q. Yu, X.-Y. Li, Probing the contribution of extracellular polymeric substance fractions to activated-sludge bioflocculation using particle image velocimetry in combination with extended DLVO analysis, Chem. Eng. J. 303 (2016) 627–635.
[64] H.-C. Flemming, J. Wingender, The biofilm matrix, Nat. Rev. Microbiol. 8 (2010) 623–633.
[65] B. Pan, M. Qiu, M. Wu, D. Zhang, H. Peng, D. Wu, B. Xing, The opposite impacts of Cu and Mg cations on dissolved organic matter-ofloxacin interaction, Environ. Pollut. 161 (2012) 76–82.
[66] K. He, A.D. Soares, H. Adejumo, M. McDiarmid, K. Squibb, L. Blaney, Detection of a wide variety of human and veterinary fluoroquinolone antibiotics in municipal wastewater and wastewater-impacted surface water, J. Pharm. Biomed. Anal. 106 (2015) 136–143.
[67] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, Desalination 225 (2008) 13–28.
[68] J. Tolls, Sorption of veterinary pharmaceuticals in soils: a review, Environ. Sci. Technol. 35 (2001) 3397–3406.