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Cigarette filters as adsorbents of solid-phase extraction for determination of fluoroquinolone antibiotics in environmental water samples coupled with high-performance liquid chromatography

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ABSTRACT

The potential use of cigarette filters (CFs) as solid-phase extraction (SPE) adsorbents for the preconcentration of six fluoroquinolones (FQs) antibacterial agents prior to liquid chromatography was examined in this paper. In order to find a suitable procedure for extraction of the target FQs in one single step, various parameters probably affecting the extraction efficiency including the eluent kind and volume, sample flow rate, pH, ion strength and sample volume were systematically optimized. Under the optimized conditions, the target FQs could be easily extracted by the proposed SPE cartridge. Combination of SPE with HPLC/UV provided detection limits for different FQs of 2–5 ng L^{-1} when 500 mL of water sample was processed. The precision of the method, expressed as relative standard deviation, ranged from 4.1 to 6.3% for 2.5 μg L^{-1} FQs. The recoveries of FQs spiked in environmental water samples ranged from 76 to 112%. The results obtained from the proposed method demonstrated that CFs-based solid-phase extraction combined with HPLC/UV was suitable for analyzing fluoroquinolones in water samples at ng L^{-1} concentration level.

1. Introduction

In the past decades, large quantities of antibiotics have been widely used against different diseases in human and veterinary medicine. Fluoroquinolones (FQs), piperazinyl derivates of the quinolone nadixilic acid, were a large class of antibiotics, and were initially employed in the treatment of a wide variety of diseases since they are not only more effective against Gram-negative bacterial, but also active against Gram-positive bacterial [1]. Their activity is based on the inhibition of the enzyme DNA gyrase or topoisomerase II, which are responsible for the preservation of the DNA biological activity of bacteria [2,3]. As a consequence of their extensive use, FQs are frequently identified in environmental matrix, especially in aquatic environment. For example, ciprofloxacin, ofloxacin, lomefloxacin and gatifloxacin have been detected at the ng L^{-1} to low μg L^{-1} levels in the aquatic environment [4–7]. Although FQs with ng L^{-1} to low μg L^{-1} concentration levels are probably not active to humans, they are suspected of being responsible for the appearance of antibiotic-resistant bacterial strains [8] and bacterial resistant genes [9]. With respect to the assessment of risk of environmental safety and human health, there is an emerging interest among the scientific community on increasing the knowledge of the consequence that the presence of fluoroquinolone antibiotics in the environment may have effect on human health.

Current research demonstrated that the fluoroquinolone antibacterial agents reaching the sewage treatment plants are not completely removed [2,10], and finally arrive in the natural water columns. It has been reported that FQs are largely excreted unchanged [11] after having been used against various diseases. Also, the FQs are relatively stable in water samples at room temperature. For example, ciprofloxacin was stable for at least 2 weeks in spiked river water when stored at ambient temperature [12]. In order to determine the concentration of FQs, simple and effective methodology that enables the analysis of these compounds in water at trace level is required. In recent years, various analytical techniques such as spectrofluorometry [13], enzyme linked immunosorbent assay (ELISA) [14], chemiluminescence [15,16], capillary electrophoresis [17–20], bioassays [21,22], high-performance liquid chromatography (HPLC) with UV or fluorescence detection [1,23–28] have been developed and evaluated for FQs in environmental samples. Among above-mentioned methods, HPLC is a common as well as excellent analytical method widely used for the determination of FQs in various environmental

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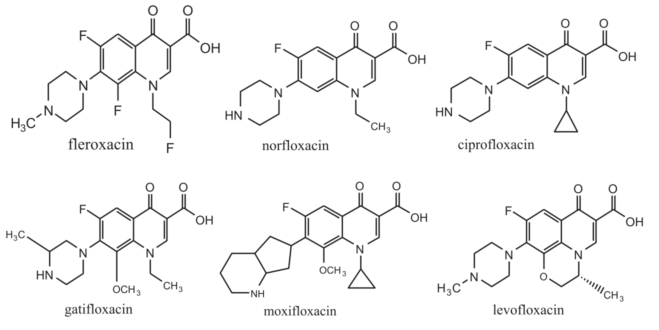

Fig. 1. Chemical structures of the six fluoroquinolone antibiotics.

samples. Due to their low concentrations in environment, it is a great challenge to directly determine trace FQs in natural waters. Hence, sample enrichment is a critical step in the analytical procedure prior to analysis of FQs in environmental samples. Among various sample pretreatment methods, solid-phase extraction (SPE) has been widely used for aqueous sample pretreatment due to its short extraction time, high preconcentration efficiency, low consumption of eluent, and easy automation. For solid-phase extraction (SPE), the selection of packing materials is extremely critical for the recovery of the target compounds since the type of adsorbent materials is one of the most important factors affecting extraction efficiency of target compounds. Adsorbents with excellent performance such as large specific surface area and high adsorptive capacity can be chosen. Various commercial adsorbents including C8, C18 [29] or HLB [30–32] have been used as solid-phase extraction adsorbents for extraction of FQs. Also, several new kinds of materials including ion exchange resins [26,33], carbon nanotubes [20] and molecularly imprinting polymers (MIPs) [34,35] have been adopted as efficient SPE adsorbents for preconcentration of antibiotics from water samples.

The cigarette filters (CFs) play a very important role in alleviating the poisonous effect on smokers, and have been successfully used as the adsorbent for the preconcentration and separation of the MeHg–DDTC, Hg–APDC chelates [36,37], polycyclic aromatic hydrocarbons [38], As(III) and As(V) in water samples [39]. The results obtained from these works have demonstrated the good performance of CFs as adsorbent of SPE for the determination of target compounds in environmental water samples with simplicity, sensitivity and cost-effect. However, no research on its application to preconcentration of trace FQs pollutants as SPE format in the field of environmental analysis has been reported. Herein, we for the first time demonstrated the potential of CFs as a SPE adsorbent and its application in extraction of six FQs (Fig. 1), namely fleroxacin (FLE), levofloxacin (LEV), norfloxacin (NOR), ciprofloxacin (CIP), gatifloxacin (GAT) and moxifloxacin (MOX), at low ng L^{-1} levels in water samples. The off-line SPE followed by HPLC/UV method were chosen for monitoring FQs in aqueous environmental samples. The developed method was successfully applied to the analysis of FQs in aqueous samples.

2. Experimental

2.1. Chemicals and reagents

The fleroxacin hydrochloride, levofloxacin hydrochloride, ciprofloxacin lactate, gatifloxacin, moxifloxacin hydrochloride and norfloxacin standards were purchased from Sigma–Aldrich. All the stock standard solutions were stored in dark at 4 °C and the working solutions were prepared freshly by appropriate dilution of the stock solutions with water. Acetonitrile and methanol were of the HPLC grade (Scharlau Chemie S.A., Spain). Tetrabutylammonium bromide (TBAB), sodium chloride, acetone, dichloromethane, hydrochloric acid, formic acid and all other chemicals used were of analytical reagent grade and were purchased from Chongqing Chemical Reagents Co. Ltd. The ultra pure water used in this study was prepared in the lab using a water treatment device. All the glassware used in experiments were cleaned with ultra pure water, then soaked with 10% (v/v) nitric acid for at least 24 h, cleaned with water, dried in a clean oven prior to use.

2.2. SPE procedure

The cigarette filter was obtained from the Hongsheng cigarettes (Hongsheng Cigarette Factory, Chongqing, China). CFs was firstly cut into a small piece (about 0.5 mm × 0.5 mm). 0.4 g CFs were packed in an empty 6 mL-polypropylene cartridge, which was purchased from SUPELCO Corporation, USA. The polypropylene upper frit was reset at the upper end of the cartridge to hold the CFs packing in place. Then the outlet tip of the cartridge was connected to a model SHBIII vacuum pump (Yuhua Instrument Co. Ltd., Zhengzhou, Henan), and the inlet of cartridge was connected to PTFE suction tube whose other end was inserted into sample solution. The CFs packed column was washed with the proper amount of methanol and ultra pure water before the first use, respectively. Before extraction, 5 mL of methanol and 5 mL of ultra pure water (pH 3.0) were adopted, respectively, to pass through the CFs packed cartridge for the purpose of precondition. Extraction of the target FQs compounds was carried out by adding 100 mL of the FQs standard (or 500 mL of sample solution) at the desired concentration to pass through the CFs packed cartridge under vacuum at a certain flow rate, followed by a rinsing step using 5 mL of ultra pure water. And then the cartridge was dried under a certain negative pressure (20 mmHg) for 15 min. The concentrated target FQs compounds were eluted with the optimal organic solvent (4 mL of methanol solution containing 20% ammonia), and the eluates were evaporated to dryness by a stream of nitrogen gas at 40 °C, and the residue was dissolved with 1.0 mL of 0.1% formic acid containing 0.01 mol L^{-1} TBAB. Finally, a volume of 20 μL was injected into the HPLC. The recovery was used as criterion to optimize the parameters for CFs-based SPE. The recovery was calculated as the ratio of the amount of FQs with and without preconcentration.

2.3. Instrumental analysis

The HPLC system (JASCO Corporation, Japan) used for the sample analysis was composed of two JASCO PU-2080i plus intelligent HPLC inert pumps, JASCO CO-2060 plus intelligent column thermostat and a JASCO UV-2075 plus intelligent UV detector. Chromatographic separation was achieved on a Symmetry C8 column (250 mm × 4.6 mm, 5 μm) (Waters Corporation, USA) with a mobile flow rate of 1.0 mL $\min^{-1}$ under gradient conditions. The mobile phase used in the chromatographic separation consisted of acetonitrile (A) and 0.1% formic acid solution containing 0.01 mol L^{-1} TBAB (B). The FQs were separated with the following gradient program: maintaining 3% A for 15 min; followed by a linear gradient to 15% A in 1 min and maintained for 10 min, and returning linearly to 3% A in 1 min until the next injection. The column temperature was at 30 °C, the chromatographic data were acquired at 280 nm. The injection volume of sample was 20 μL. JASCO Chrompass Chromatography Data System was used to control the chromatographic units, acquire and process chromatographic data.

2.4. Water samples

In the present study, three environmental water samples including tap water sample, river water sample and wastewater sample were selected for investigation. Tap water, river water, and wastewater samples were taken from our lab, the Chongqing section of the Jialingjiang River and the effluent of one constructed wetland system (Yongchuan, Chongqing, China), respectively. Before analysis, all the environmental water samples were filtered through 0.45 μm micropore membranes (Tianjin Automatic Science Instrument Co., Ltd., China) and stored in brown glass bottoms at 4 °C in a refrigerator.

3. Results and discussion

3.1. Optimization of the solid-phase extraction procedures

In the present work, the cigarette filter was employed as the adsorbent for simultaneous preconcentration of the target FQs because the cigarette filter adsorbent is much cheaper and more easily available. The results of FT-IR spectra indicated that the used CFs are composed of cellulose acetate (CA) tows (Fig. S1, Supplementary information). As can be seen from Fig. S1, the presence of hydroxyl groups and ester groups in the CFs was found, exhibiting significant peaks at 3445 cm^{-1} (attributed to O–H stretching mode), 1754 cm^{-1} (attributed to O–C=O stretching mode) and 1243 cm^{-1} (attributed to C–O stretching mode). The large quantities of oxygen-containing functional groups such as hydroxyl groups and ester groups played an important role in the adsorption of FQs due to the polarity property of the target analytes. Our preliminary experiments demonstrated that the adsorbent favored the adsorption of FLE, LEV, NOR, CIP, GAT and MOX. For solid-phase extraction (SPE), the pretreatment efficiency could be influenced by several factors such as the type and volume of elution solvents, pH of sample solution, flow rate of sample solution, ionic strength and volume of sample solution. To obtain appropriate extraction performance with CFs as SPE adsorbent, these mentioned factors were optimized systematically in this experiment.

3.1.1. Effect of the elution solvent

As far as SPE method is concerned, the selection of elution solvent plays the most important role in desorption of analytes retained on the SPE cartridge. In order to efficiently elute the selected targets retained on the solid-phase extraction cartridge, different organic solvents, such as acetonitrile, methanol, acetone, dichloromethane, hexane and ethyl acetate, were used to elute the analytes from CFs packed cartridge. The experimental results indicated that acetonitrile, acetone, dichloromethane, hexane and ethyl acetate can make the packed CFs gradual deformation, hence, they are not suitable for desorption of FQs. Although methanol can be used for desorption of the retained FQs, only about 25% recoveries could be obtained for the studied FQs. In order to obtain quantitative elution of the analytes, ammonia was selected and added into methanol. The effect of ammonia on extraction recovery was investigated and the results are shown in Fig. 2. As can be seen, the recoveries of FQs showed ammonia concentration level dependence, and they increased with increasing of ammonia concentration up to 20% ammonia, above which they decreased. So, 20% ammonia was recommended for experimental work. Our experimental results clearly demonstrated that the addition of ammonia to elution methanol was in favor of FQs desorption from CFs adsorbents. This may be due to its ability to adjust apparent pH of methanol [40]. These results indicate that analyte–CFs interactions may be mostly of the polar or dipole–dipole type rather than ionic type since adsorption in the aqueous medium was maximal near the isoelectric point (see Section 3.1.2), and once the analytes were charged, their solubility in the mobile phase increased and their adsorption decreased as a result. Finally, the volume of eluent was studied over range of 1–5 mL of methanol in order to get a higher enrichment factor. The experimental results demonstrated that the recoveries of FQs showed elutent volume dependence. The recoveries of FQs increased with the eluent volume up to 2 mL, after which the recoveries remained stable. Finally, 4 mL methanol containing 20% ammonia was selected as optimal eluent to obtain the quantitative results.

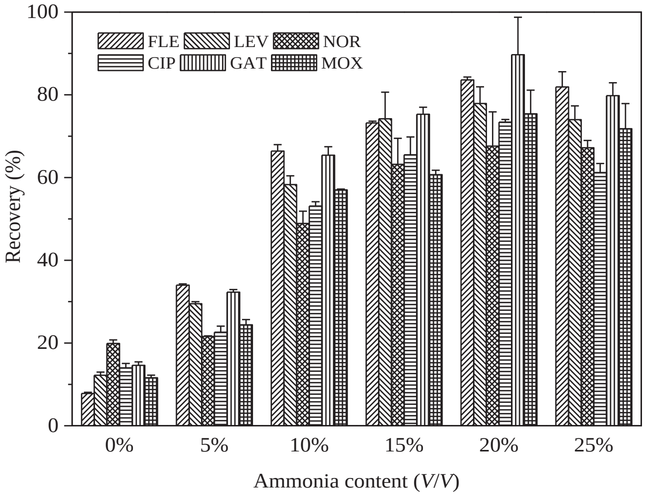

Fig. 2. Effect of the ammonia content in methanol solution on recoveries of FQs. FQs concentration: 2.5 μg L^{-1}; sample solution volume: 100 mL (pH 3.5); sample flow rate: 3.5 mL min^{-1}; NaCl content in sample solution: 0% (w/v); eluent: 5 mL methanol solution. Error bars represent one standard deviation for three measurements.

3.1.2. Effect of the pH of sample solution

Various studies have demonstrated that pH value of sample solution plays an important role in the extraction of organic compounds from environmental water samples because it determined the existing state of analytes (targets) as ionic or molecular state as well as the surface properties of the as-used sorption materials. Therefore, pH of sample solution determined the extraction efficiency of the target compounds. In order to investigate the pH effect, the isoelectric point (IEP) of CFs was measured in the present study (Fig. 3), and it was found to be about 2.50. As can be seen from Fig. 3, the surface charge of the CFs is dependant on pH. Since FQs are zwitterionic compounds showing two pK_a value (pK_{a1} = 5.2–6.3; pK_{a2} = 7.4–8.9) [41], all the studied FQs are presented as their cationic forms when pH value of sample solution was below 5. As can be seen from Fig. 4, adsorption of FQs onto CFs

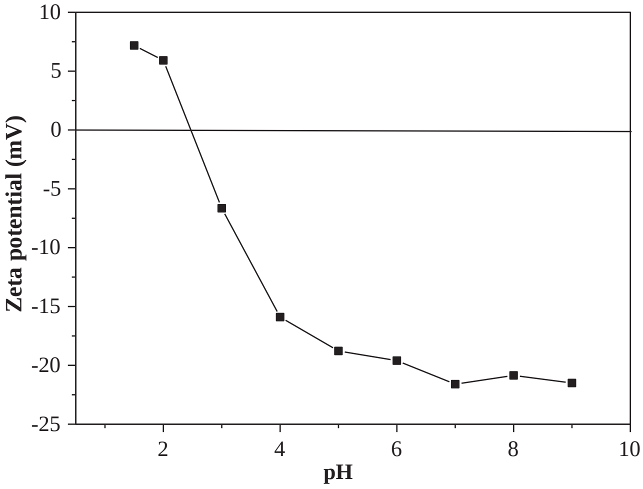

Fig. 3. Effect of pH value on the zeta potential of CFs.

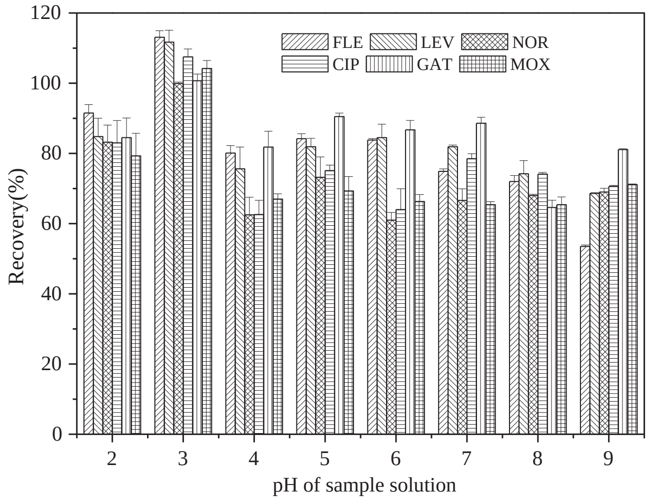

Fig. 4. Effect of sample solution pH on recoveries of FQs. Eluent: 4 mL methanol solution containing 20% ammonia; sample flow rate: 3.5 mL min^{-1}. Other conditions were same as in Fig. 2. Error bars represent one standard deviation for three measurements.

peaked near pH 3.0, which was near the isoelectric point of CFs. As indicated in previous section, the organic solvent was capable of eluting only partial of the analytes from the CFs. This suggests the importance of the polar or dipole–dipole type rather than ionic type interactions between analyte and CFs since adsorption in the aqueous medium was maximal near the isoelectric point, and once the analytes were charged, their solubility in the mobile phase increased and their adsorption decreased as a result. Hence, lower or above pH 3 would lead to decrease the recoveries of FQs. Therefore, pH 3 was selected in the following experiments.

3.1.3. Effect of the ionic strength and other co-existing substances

Further experiments were conducted to investigate the effect of ionic strength on the extraction of FQs. Sodium chloride was selected to investigate ionic strength effect in this study. The examined NaCl amount ranged from 0 to 2.0% (w/v). The experimental results suggested that addition of sodium chloride decreased retention of all analytes on CFs rather than enhancing them (Fig. 5). And the extraction recoveries of the target compounds decreased sharply from about 100% to below 40% with the increasing of sodium chloride from 0 to 2% (w/v). It is also observed that the recovery of FQs was lower than 95% at the sodium chloride concentration above 0.1% (w/v), corresponding to 393 mg L^{-1} and 607 mg L^{-1} for Na^+ and Cl^-, respectively. The effect of electrolytes on retention of FQs is related to the effects of NaCl addition to the sample solution. Generally, addition of NaCl to the sample solution increases the ionic strength of solution as well as changes the physical properties of the Nernst diffusion layer. It is well known that addition of salt can decrease the solubility of analytes in the aqueous sample [42,43], which is beneficial to extraction of target analytes. However, addition of sodium chloride also reduces mass transfer by changing the Nernst diffusion layer, probably leading to the decreased diffusion rate of the target FQs to the surface of the cigarette filter, therefore decreasing the extraction efficiency. Results shown in Fig. 5 clearly suggest that the higher the concentration of NaCl is, the lower the diffusion rate of the target FQs to the surface of the cigarette filter is. On the basis of above experimental results, sodium chloride was not added to the aqueous sample in the subsequent experiments. Also, the effect of other commonly co-existing substances such as NO_3^-, SO_4^{2-}, PO_4^{3-}, K^+, Na^+, Ca^{2+}, Mg^{2+} ions in water samples were investigated under the optimized conditions. The effect of co-existing substances was tested by enrichment a standard solution of FQs (2 μg L^{-1}) according to SPE procedure described in experimental section to which increasing amounts of interfering substances were added. The results shown in Table S1, Supplementary information demonstrated that commonly co-existing cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) had little effect on FQs extraction.

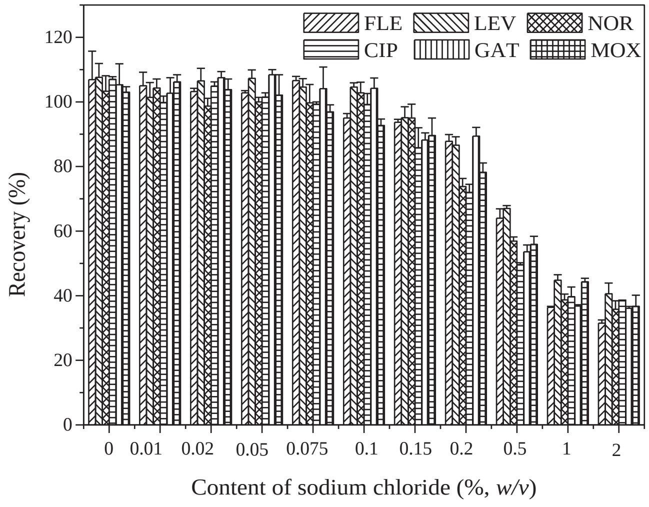

Fig. 5. Effect of sodium chloride content on recoveries of FQs. Sample solution pH: 3.0. Other conditions were same as in Fig. 4. Error bars represent one standard deviation for three measurements.

3.1.4. Effect of the flow rate

The effect of the sample flow rate was investigated over the range from 3 to 8 mL min^{-1}. The experimental results demonstrated that the recoveries remain stable over 99% when the flow rate of sample solutions was below 6 mL min^{-1}. For flow rate above 6 mL min^{-1}, the increase in flow rate induced a general decrease in recovery. Hence, 6 mL min^{-1} was chose as the optimal flow rate for further experiment.

3.1.5. Effect of the volume of sample solution

The optimal sample volume was investigated in order to obtain an enrichment factor as high as possible. Experiments were done by using different sample volumes (100, 250, 500, 750 and 1000 mL) with the same FQs concentration of 2.5 μg L^{-1}. The results indicated that the quantitative retention of FQs was observed when the sample volumes ranged from 100 to 500 mL. However, the recoveries decreased when the sample volume increased to 750 mL. Considering the packed amount of CFs in cartridge (about 400 mg) used in present study, finally, sample volume of 500 mL was selected for further investigation to achieve the reliable experimental results and a high enrichment factor because the recoveries for all the analytes were satisfactory.

3.2. Effect of humic acid

The natural organic matter (NOM) such as humic acid is commonly present in environmental water samples. And there may be competitive adsorption between targets and NOM onto CFs sorbents, thus affecting the extraction of FQs in real samples. In order to evaluate the effect of NOM (with Aldrich humic acid as model) on extraction of FQs from sample solution using CFs as sorbents, sample solutions contained different amount of humic acid were extracted by the proposed CFs-based SPE method. As can be seen from results shown in Fig. 6, no obvious changes of recoveries of all target FQs were observed when the concentration of humic acid was lower than 5 mg L^{-1} dissolved total organic carbon (TOC). The TOC contents in the water samples investigated in the present study

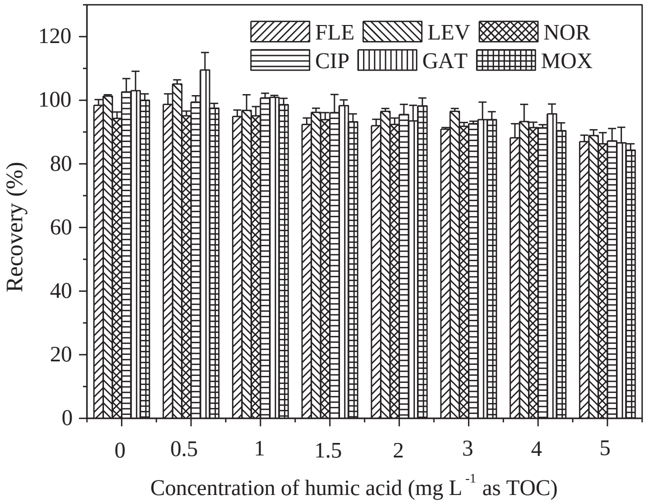

Fig. 6. Effect of humic acid concentration on recoveries of FQs. Other conditions were same as in Fig. 4. Error bars represent one standard deviation for three measurements.

are less than 3.50 mg L^{-1} for river water samples [44], hence humic acid did not interfere with FQs determination, showing the good anti-interference ability of the CFs sorbent to NOM.

3.3. Analytical performance

On the basis of the experimental results shown above, the optimized SPE conditions of CFs packed cartridge are as follows: 6 mL min^{-1} of sample flow rate, sample solution pH 3, 4 mL methanol eluent containing 20% ammonia, and 500 mL of sample volume. Then the optimized extraction conditions were applied to evaluate the analytical performances such as linearity, detection limits and precision of the CFs SPE method in combination with HPLC. The calibration plots for FQs determination were linear in the range of 0.017–20 μg L^{-1} for NOR, 0.05–20 μg L^{-1} for LEV, FLE, CIP, GAT, and MOX under the optimum experimental conditions, respectively, demonstrating the applicability of the optimized method for fluoroquinolone analysis in environmental samples at the ng L^{-1} concentration level. The correlation coefficients ranged between 0.9947 and 0.9996. The detection limits were 2–5 ng L^{-1} at a signal-to-noise ratio of 3. The relative standard deviations (RSDs) were 4.1–6.3% for nine replicate determinations of 2.5 μg L^{-1} FQs. The enrichment factors for FLE, LEV, NOR, CIP, GAT, and MOX were 483, 562, 507, 514, 476, and 554, respectively. The present method was compared to the analytical methods previously published in literatures [1,5,23,34,41,45] using solid-phase extraction for FQs analysis in terms of the detection limits (LODs). And the LODs were listed in Table 1. Generally speaking, the cigarette filter gave lower detection limits than C18, Oasis WCX, and MIPs. These excellent analytical performances of the proposed method suggest that the proposed method has a tremendous potential to be used for the analysis of the selected compounds at trace levels in real water samples, and CFs is a kind of promising adsorbents for effective extraction of FQs in environmental water samples.

Table 1
Comparison LOD of this work with some established methods using solid-phase extraction for FQs.

Sorbent material	Analytical method	Detection limit (ng L^{-1})	Reference
C18	HPLC–UV	10–11	[1]
Oasis HLB	LC–MS/MS	3.1–18	[5]
Oasis WCX	HPLC–FLD HPLC–MS/MS	10	[23]
MIPs	HPLC–FLD	110–140	[34]
Magnetic MIPs	LC–MS/MS	5.5–6.2	[41]
Online-MIPSPE	HPLC–UV	5–12	[45]
Cigarette filters	HPLC–UV	2–5	This paper

Table 2
The results of FQs determination in tap water and river water samples ($n = 3$).

Targets	Tap water samples			River water samples		
	Added (μg L^{-1})	Found (μg L^{-1})	Recovery[a] (%)	Added (μg L^{-1})	Found (μg L^{-1})	Recovery[a] (%)
FLE	0	n.d.[b]	–	0	n.d.	–
	0.50	0.48	96.6 ± 2.6	0.50	0.47	94.1 ± 2.4
	1.00	1.02	102.2 ± 4.1	1.00	0.96	95.5 ± 0.9
	2.00	2.13	106.6 ± 8.0	2.00	1.79	89.5 ± 1.5
LEV	0	n.d.	–	0	n.d.	–
	0.50	0.56	112.2 ± 1.9	0.50	0.50	100.5 ± 4.7
	1.00	1.00	100.4 ± 4.1	1.00	0.98	97.9 ± 0.3
	2.00	1.98	98.8 ± 7.2	2.00	1.94	97.1 ± 5.6
NOR	0	n.d.	–	0	n.d.	–
	0.50	0.51	101.5 ± 6.3	0.50	0.45	90.4 ± 1.6
	1.00	0.96	96.4 ± 4.5	1.00	0.91	90.6 ± 1.1
	2.00	1.82	91.1 ± 7.3	2.00	1.77	88.4 ± 1.6
CIP	0	n.d.	–	0	n.d.	–
	0.50	0.51	102.8 ± 9.2	0.50	0.46	91.2 ± 6.9
	1.00	0.97	97.4 ± 1.7	1.00	0.97	96.9 ± 0.5
	2.00	1.92	96.2 ± 1.9	2.00	1.93	96.4 ± 0.9
GAT	0	n.d.	–	0	n.d.	–
	0.50	0.48	95.1 ± 7.4	0.50	0.49	98.5 ± 5.6
	1.00	1.00	100.4 ± 1.5	1.00	0.99	99.2 ± 0.4
	2.00	1.99	99.3 ± 3.9	2.00	1.93	96.6 ± 2.1
MOX	0	n.d.	–	0	n.d.	–
	0.50	0.55	110.8 ± 4.2	0.50	0.46	92.4 ± 4.7
	1.00	1.03	102.6 ± 6.0	1.00	0.97	97.2 ± 0.1
	2.00	1.94	97.0 ± 7.5	2.00	1.80	89.9 ± 1.2

[a] Average ± standard deviation.
[b] Not detected.

Table 3
Results of recoveries of the constructed wetland wastewater samples spiked with six FQs ($n = 3$).

Targets	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery[a] (%)
FLE	0	n.d.[b]	–
	0.50	0.40	79.5 ± 3.3
	1.00	0.86	85.6 ± 6.4
	5.00	4.34	86.7 ± 1.6
LEV	0	n.d.	–
	1.00	0.42	83.9 ± 3.9
	2.00	1.64	85.6 ± 6.4
	10.00	9.00	90.0 ± 1.2
NOR	0	n.d.	–
	0.50	0.41	82.3 ± 6.5
	1.00	0.71	80.6 ± 4.1
	5.00	4.34	86.8 ± 5.2
CIP	0	n.d.	–
	0.50	0.38	75.5 ± 4.6
	1.00	0.79	78.7 ± 5.7
	5.00	4.27	85.3 ± 1.4
GAT	0	n.d.	–
	0.50	0.47	94.6 ± 5.2
	1.00	0.87	87.3 ± 4.6
	5.00	4.44	88.8 ± 1.2
MOX	0	n.d.	–
	0.50	0.45	89.3 ± 4.1
	1.00	0.87	87.3 ± 3.9
	5.00	4.47	89.4 ± 4.4

[a] Average ± standard deviation.
[b] Not detected.

Three replicate determinations at 5 $\mu g\,L^{-1}$ level were carried out to test the reproducibility among three columns. The results demonstrated that the RSD (precision) of inter-column and intra-column is less than 7%, suggesting the reproducibility among columns is satisfactory.

3.4. *Analysis of fluoroquinolone antibiotics in real environmental water samples*

As an illustration of analytical application, the proposed method was used to determine FQs in the environmental water samples under the optimal experimental conditions shown above. Prior to spiked water samples preconcentration, the blank experiments were done and the extraction of each spiked water sample should be carried out for three times. Fig. 7 shows typical chromatograms obtained after the application of the off-line CFs SPE-LC–UV method for the analysis of a blank river water sample and the same sample spiked with target FQs, respectively.

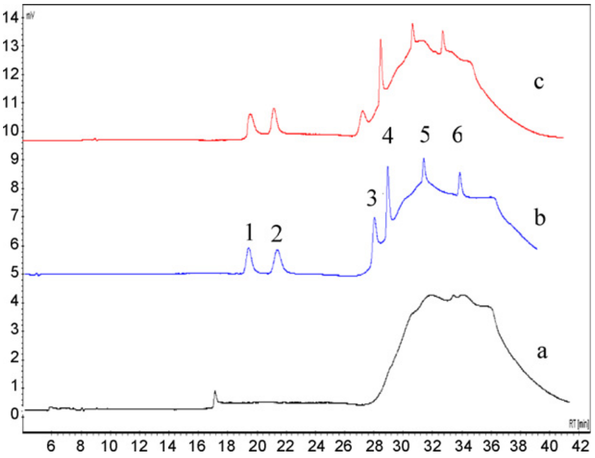

Fig. 7. Typical chromatograms obtained after the analysis of (a) a blank river water sample, (b) a blank river water sample spiked with the target FQs in the range from 0.5 to 1 $\mu g\,L^{-1}$ (FLE: 0.5 $\mu g\,L^{-1}$; LEV: 1 $\mu g\,L^{-1}$; NOR: 0.5 $\mu g\,L^{-1}$; CIP: 0.5 $\mu g\,L^{-1}$; GAT: 0.5 $\mu g\,L^{-1}$; MOX: 0.5 $\mu g\,L^{-1}$), and (c) ultra pure water spiked with the target FQs in the range from 0.5 to 1 $\mu g\,L^{-1}$ (FLE: 0.5 $\mu g\,L^{-1}$; LEV: 1 $\mu g\,L^{-1}$; NOR: 0.5 $\mu g\,L^{-1}$; CIP: 0.5 $\mu g\,L^{-1}$; GAT: 0.5 $\mu g\,L^{-1}$; MOX: 0.5 $\mu g\,L^{-1}$). Peak identification: (1) FLE; (2) LEV; (3) NOR; (4) CIP; (5) GAT; and (6) MOX.

The results for FQs determination for unspiked and spiked tap water, river water and wastewater samples were shown in Tables 2 and 3, respectively. As can be seen, the recoveries of FQs in the spiked tap water and river water samples ranged from 88.4 to 112.2% when 500 mL water sample at three spiked concentration levels (0.5, 1 and 2 $\mu g\,L^{-1}$ FQs) were tested (Table 2). The recoveries of FQs in the spiked wastewater samples ranged from 76 to 95% at three spiked concentration levels (0.5, 1 and 5 $\mu g\,L^{-1}$ FQs) were tested (Table 3). Good recovery (>75%) and precision (RSDs < 10%) were obtained for all the analyzed samples in the evaluated range. It can be concluded that the CFs can be an excellent SPE adsorbents for extraction of trace FQs from real water samples.

4. Conclusions

In conclusion, the CFs adsorbent exhibit good extraction performance to FQs, and the application of CFs as SPE adsorbents to extraction of fluoroquinolone antibiotics is reported for the first time. The results demonstrated well the potential of the cigarette filter as SPE adsorbent for enriching of trace FQs in environmental water samples. Compared with other commercially available packing materials, CFs are much cheaper and more easily available. The proposed CFs based SPE method was successfully used for FQs enrichment in environmental water samples with good recoveries and precision. Furthermore, the adsorbent could extract trace target analytes efficiently from wastewater samples with relatively complex matrixes. It is believed that the CFs may be useful SPE adsorbents for other organic pollutants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.09.066.

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