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An anionic exchange stir rod sorptive extraction based on monolithic material for the extraction of non-steroidal anti-inflammatory drugs in environmental aqueous samples

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ABSTRACT

In this study, a stir rod sorptive extraction (SRSE) adsorbent material was prepared by coating poly(4-vinylpyridine-co-ethylene glycol dimethacrylate) [poly(VP-co-EDMA)] monolithic polymer on stir rod, and then applied to the extraction of three non-steroidal anti-inflammatory drugs (NSAIDs) in environmental aqueous samples. The preparation conditions of monolithic material such as the amount of porogen and the ratio of functional monomer to cross-linker were investigated. To achieve the best extraction efficiency, several parameters, including pH value of sample solution, salt concentration in sample matrix, desorption solvent, extraction time, and desorption time, were optimized. By combining SRSE and high performance liquid chromatography with ultraviolet detector, a SRSE–HPLC/UV method for the determination of NSAIDs in environmental aqueous samples was proposed successfully. The limits of detection (LODs) of the developed method for three NSAIDs ranged between 0.09 and 0.25 ng/mL. Good method reproducibility presented as intra- and inter-day precisions were also obtained with the relative standard deviations (RSDs) less than 8.7% and 9.8%, respectively.

1. Introduction

Pharmaceuticals have been emerged as environmental pollutants due to the continually discharging into the sewer system and disposal of medicines [1,2]. Recent researches confirmed that these compounds in environmental aqueous samples have potential long-term adverse effects to both humans and aquatic organisms [1,3,4]. Non-steroidal anti-inflammatory drugs (NSAIDs) are widely applied in the treatment of pain and inflammation. Among them, ketoprofen (KEP), fenbufen (FBF), and ibuprofen (IBP) are customarily prescribed NSAIDs [5]. If the NSAIDs residues were released into environmental aqueous, it would be toxic to many animal species and human beings. So it is essential to monitor the levels of NSAIDs in environmental aqueous.

Several analysis methods for the determination of NSAIDs in environmental samples have been developed, such as gas chromatography (GC) [2,6], high-performance liquid chromatography (HPLC) [7], and capillary electrophoresis (CE) [8] with conventional detectors [4,9–11] or mass spectrometry (MS) [12,13]. Since most of NSAIDs are polar and relatively non-volatile, a prior derivatization reaction is essential when using GC detection [5,6,14], which is time-consuming and labor-intensive. CE is a high-efficiency separation technique but with low sensitivity [8,15]. Therefore, HPLC is the most popular method for NSAIDs analysis.

Generally, the NSAIDs residues are present in diverse aquatic environments (such as sewage water, drinking water, and surface water) with trace levels [16]. Thus, an effective sample preparation procedure is required prior to the instrumental analysis. A number of sample preparation methods, such as liquid–liquid extraction [9,17], solid phase extraction (SPE) [18–20], and solid phase micro-extraction (SPME) [7,21,22], have been employed for the enrichment and purification of NSAIDs in environmental aqueous samples. Recently, an environmentally friendly extraction technique, stir bar sorptive extraction (SBSE), has been successfully developed into an efficient method for the pretreatment of environmental and biological contaminants [3,10,23]. Noticeably, SBSE has many distinct advantages such as low consumption of toxic solvent and convenience compared with conventional extraction techniques. Furthermore, the volume of adsorbent material coated on stir bar was larger than SPME [23], achieving the higher extraction capacity when dealing with the large volume sample. However, in the traditional SBSE procedure, the non-polar polydimethylsiloxane coating has low extraction capacity for polar compounds such as NSAIDs. A derivatization reaction with the polar compound

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is a possible solution to the problem [24–26]. But the derivatization reaction was tedious and time-consuming. To avoid the derivatization reaction, a polar material, poly(4-vinylpyridine-co-ethylene glycol dimethacrylate) [poly(VP-co-EDMA)] monolithic material was synthesized and used as the SBSE coating [27,28]. Although it has excellent performance in the extraction of polar compounds such as phenols and steroid sex hormones [27,28], the coating may suffer from cracking due to the continually friction between stir bar and sample vessel. To overcome this problem, in our previous work [29], a stir rod sorptive extraction (SRSE) device was proposed, which widens the application of SBSE. Different monolithic materials have been used as SRSE coating to extract various compounds from honey or environmental aqueous samples [29,30].

In this study, a new monolithic material was prepared by polymerizing VP and EDMA on stir rod and further used as SRSE coating to extract three NSAIDs in environmental aqueous samples. The preparation conditions for monolithic coating were optimized and the parameters that influenced extraction efficiency were investigated. By combining SRSE and HPLC with UV detector, a convenient and low-cost analytical method for the determination of the NSAIDs residues in environment aqueous samples was established. Compared with other methods for the determination of NSAIDs, our method can obtain lower limits of detection [31].

2. Experimental

2.1. Chemicals and materials

4-Vinylpyridine (VP) and ethylene glycol dimethacrylate (98%, EDMA) were obtained from Acros (New Jersey, USA). γ-Methacryloxypropyltrimethoxysilane (γ-MAPS) was purchased from the Chemical Plant of Wuhan University (Wuhan, China), which was used directly without further purification. Azobisisobutyronitrile (AIBN), dodecanol, and toluene of analytical reagent grade were bought from Shanghai Chemical Co. Ltd. (Shanghai, China). Analytical-grade methanol (MeOH) and acetonitrile (ACN) were bought from Concord Technology (Tianjin, China). Deionized water was purified using an Aike apparatus (Chengdu, China).

Ketoprofen (KEP), fenbufen (FBF), and ibuprofen (IBP) were purchased from Sigma–Aldrich (Missouri, USA). Individual stock solutions of three NSAIDs were prepared at a concentration of 1 mg/mL in methanol and kept at 4 °C in the dark. A mixed working solution of all standards was prepared in deionized water.

2.2. Preparation of monolithic material coated stir rod

The pretreatment and chemical modifications of the vial glass insert were described in our previous work [29,30]. The preparation of monolithic materials coating for SRSE was similar to the procedure described previously [29,30]. In brief, the monomer VP (88 mg), cross-linker EDMA (336 mg), binary porogens dodecanol (400 mg) and toluene (150 mg), and initiator AIBN (5.5 mg) were mixed ultrasonically into a homogenous solution. Subsequently, 150 μL of the pre-polymerization mixture was moved into a cleaned Eppendorf vial (0.6 mL). After the removal of air bubbles in the Eppendorf vial, a vial glass insert was inserted into the Eppendorf vial and sealed with parafilm. The polymerization reaction took place at 60 °C for 20 h. The glass insert with monolithic material coating was taken out from Eppendorf vial, and then washed with methanol/pure water (1/1, v/v) to remove the residue monomers, porogen, and initiator. The stir rod was kept in phosphate buffer solution (PBS, 20 mM, pH 4.0) before use.

2.3. Instrument and analytical conditions

The morphology was examined using the scanning electron microscopy (SEM, Quanta 200, FEI, Holland). Autopore IV 9500 mercury intrusion porosimeter (MIP) (Micromeritics Norcross, USA) was used to measure the mesopores and macropores of the monolithic coating. Nitrogen sorption experiments were carried out at 77 K by using JW-BK surface area and pore size analyzer (JWGB Sci. & Tech., Beijing, China).

The HPLC system was LC-20A (Shimadzu, Japan) which consists of binary LC-20AD pumps, a DGU-20A_3 degasser, a SPD-20A ultraviolet visible detector, a SIL-20A autosampler, and a CTO-20AC column oven. A LC-solution workstation (Shimadzu, Japan) was utilized to control the system and also for data processing. The analytical column was Agilent Eclipse XDB-C18 (4.6 mm × 150 mm, 5 μm). The column oven temperature was maintained at 30 °C. The optimized mobile phase was methanol–sodium acetate buffer solution (25 mM, pH 5) (65/35, v/v) and the flow rate was 1.0 mL/min. The UV detection was set at 223 nm and the sample injection volume was 20 μL.

2.4. Sample preparation

For the optimization of extraction conditions of SRSE, aqueous samples were prepared by spiking analytes in PBS (20 mM) at a known concentration (100 ng/mL).

Environmental aqueous samples were collected from East Lake (Wuhan, China) and sewage outfall of a hospital. Before experiment, all the environmental aqueous samples were filtered through 0.45 μm microporous membranes and stored in brown glasses at 4 °C in the refrigerator.

3. Results and discussion

3.1. Optimization of preparation condition of the monolithic material coating for SRSE

In this study, KEP was selected as testing analyte to investigate the effects of preparation conditions on extraction efficiency. As shown in Table 1, the best extraction efficiency can be obtained under the optimized preparation conditions (rod 8). Meanwhile, no cracking of the monolithic coating was observed during stirring process, which indicated that the monolithic coating under this condition was acceptable for a SRSE coating. Therefore, the polymerization parameters were adopted to prepare the coating for the further experiments.

3.2. Characterization of the monolithic coating

The monolithic polymer coating under the optimal condition was characterized by SEM, MIP, surface area and pore size analyzer. Fig. 1 is a SEM image of the poly(VP-co-EDMA) monolithic polymer coating, showing the interconnected skeletons and textural pores of the monolithic polymer coating. The skeletons and the pores were distributed evenly in the monolith and formed a continuous network. The pore size distribution plot determined by mercury intrusion porosimeter is also shown in Fig. 1. The monolithic polymer coating had a large quantity of mesopores and meanwhile some macropores which contributed to mass transfer during extraction. The total surface area of the monolithic polymer was 234 m^2/g through Brunauer–Emmett–Teller (BET) method. The existence of mesopore and large surface area ensured the high extraction capacity of monolithic polymer coating.

Table 1
Extraction efficiency of KEP under different preparation conditions for the monolithic polymer coating.

Rod No.	VP (mg)	EDMA (mg)	Toluene (mg)	Dodecanol (mg)	AIBN (mg)	Extraction efficiency[a] (%)
1	110	420	105	280	5.5	5.7
2	110	420	120	320	5.5	11.2
3	110	420	135	360	5.5	10.4
4	110	420	165	490	5.5	11.4
5	110	420	180	480	5.5	9.4
6	110	420	195	520	5.5	12.3
7	77	294	150	400	5.5	10.7
8	88	336	150	400	5.5	12.9
9	99	378	150	400	5.5	11.2
10	121	462	150	400	5.5	9.6
11	132	504	150	400	5.5	10.5

[a] The extraction efficiency is calculated from the equation: $E = Pd/Ps \times 100\%$, where E is the extraction efficiency, and Pd and Ps are the peak area of KEP obtained by SRSE process and the direct injection of standard sample solution without SRSE process (the KEP concentration was 50 μg/mL), respectively. The SRSE method is following: the sample solutions pH was 5, no additional inorganic salt was used, extraction time was 60 min, desorption time was 20 min, methanol containing 5% (v/v) ammonium hydroxide was used as the desorption solution in the experiments.

3.3. Optimization of the extraction parameters

In this study, an anionic exchange monolithic material, poly(VP-co-EDMA), was prepared as an extraction coating of stir rod sorptive extraction. Three NSAIDs were selected as model analytes to evaluate the extraction efficiency. In order to achieve the best extraction efficiency of the coating for three NSAIDs, a variety of parameters, including desorption conditions, salt concentration in sample matrix, pH value of sample solution, and extraction time, were optimized in detail.

3.3.1. Investigation of desorption conditions

In this work, the extraction and desorption mode were the same as described previously [29,30]. The desorption solution was evaporated to dryness under a gentle stream of nitrogen at 35 °C, and the residue was reconstituted with 0.1 mL mobile phase for the subsequent HPLC/UV analysis. To obtain the optimal desorption condition we optimized several parameters like desorption solution, desorption time, and desorption temperature.

The effect of different kinds of desorption solution such as methanol and acetone on the desorption efficiencies was investigated. The result showed that methanol containing 0.5% (v/v) formic acid was the best desorption solution. Therefore, it was used as the desorption solution in the following experiments. We also investigated the desorption time from 10 to 30 min, which showed that the three NSAIDs could be completely eluted from stir rod in 20 min. Thus, 20 min was chosen as the desorption time. And the desorption temperature was studied from 25 to 45 °C. It was found that 35 °C was suitable for desorption of the target analytes from stir rod.

3.3.2. pH value of sample solution

Before the optimization of pH value of sample solution, the effect of stirring rate on extraction efficiencies was investigated in the range of 80–190 rpm. It was found that the stirring rate has no obvious influence on the extraction efficiencies of the target compounds, so the stirring rate was kept at a moderate stirring rate (about 130 rpm) in the following experiments.

The analytes and the extraction coating can have specific charge status at different pH values, which in turn affect the interaction between them. Therefore, the extraction efficiencies of three studied NSAIDs are expected to be pH-dependent. The pH investigation was performed in 20 mM phosphate buffer solution from 2.0 to 11. As shown in Fig. 2, the satisfactory extraction efficiencies were obtained at the pH values from 3.0 to 5.0. The pKa values of studied NSAIDs were reported to be 4.45 for KEP, 4.43 for FBF, and 4.91 for IBP [19,32]. The pKa value of pyridine group of the functional monomer was reported to be 5.39 [33]. Under this condition, the three NSAIDs mostly existed in deprotonated forms and small in the neutral forms; while the functional pyridine groups were present in their protonated forms, which resulted in hydrophobic interaction and anionic exchange interaction were coexisted between

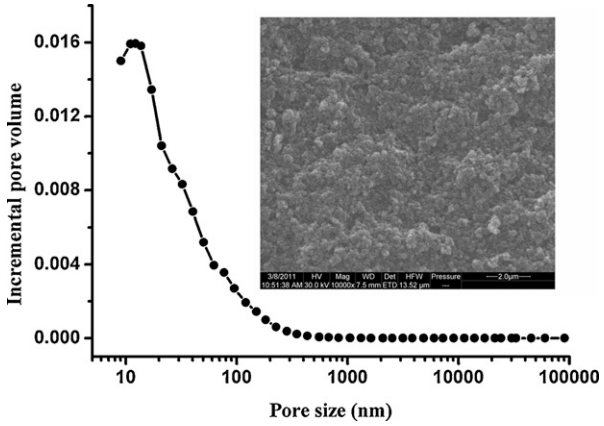

Fig. 1. Incremental pore size distribution profile of coating measured by mercury intrusion porosimeter. The inset shows scanning electron microscope image of graphene-polymer composite with a magnification 10,000×.

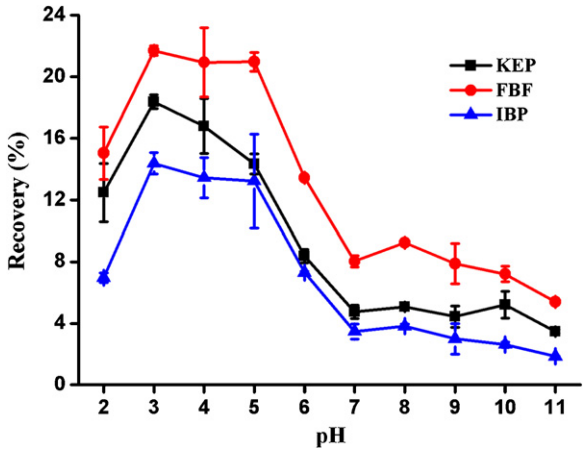

Fig. 2. Optimization of the pH value of sample solution. Sample solutions with NSAIDs spiked at 100 ng/mL were prepared with PBS (20 mM). The sample solutions pH was adjusted by phosphoric acid, extraction time was 60 min, desorption time was 20 min, methanol containing 0.5% (v/v) formic acid was used as the desorption solution, no additional inorganic salt was used in the experiments.

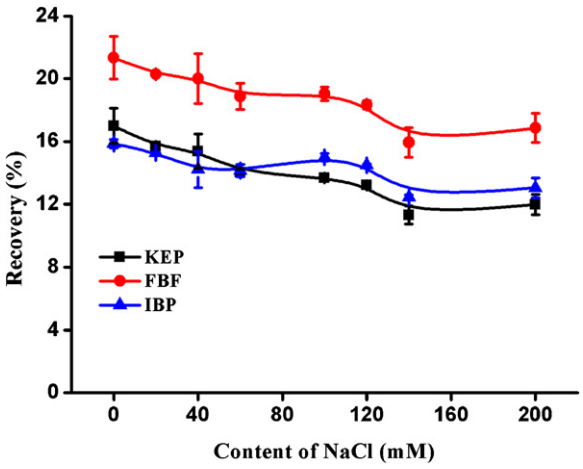

Fig. 3. Optimization of the salt concentration. Sample solutions with NSAIDs spiked at 100 ng/mL were prepared with PBS (20 mM). The sample solutions pH was 4, extraction time was 60 min, desorption time was 20 min, methanol containing 0.5% (v/v) formic acid was used as the desorption solution.

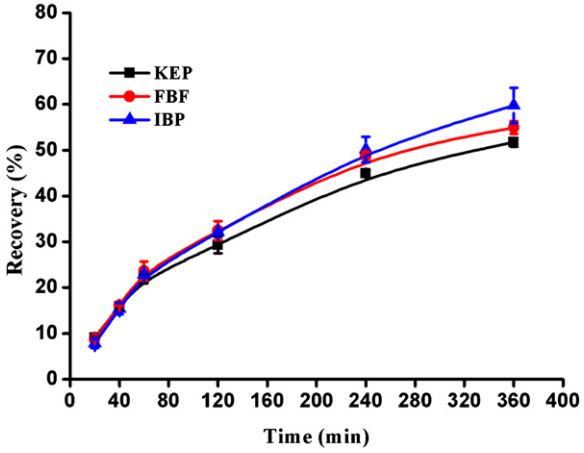

Fig. 4. Extraction time profiles of the three NSAIDs. Sample solutions with each NSAID spiked at 100 ng/mL were prepared with PBS (20 mM, pH 4.0). Extraction time was from 20 min to 6 h. Desorption time was 20 min, methanol containing 0.5% (v/v) formic acid was used as the desorption solution, no additional inorganic salt was used in the experiments.

analytes and monolithic coating, and higher extraction efficiencies were obtained. When pH is below 3.0, the NSAIDs molecules are mostly transformed into neutral forms, while the pyridine groups on monolithic coating were existed in protonated forms. Thus only hydrophobic interaction between monolithic skeleton and analytes was existed, which resulted in the relatively lower extraction efficiencies. When pH value is above 5.0, the NSAIDs molecules are gradually transformed into anionic forms, while the adsorbent was presented in neutral forms, and the interactions between them were severely weakened, leading to the low extraction efficiencies for targeted analytes. Considering the extraction efficiency and stability of the extraction procedure, the sample matrix was adjusted to pH 4.0 using 20 mM phosphate buffer solution in the following experiments.

3.3.3. Salt concentration

Since anionic exchange interaction contributed to the extraction of the targeted analytes on the monolithic polymer coating, the effect of inorganic salt concentration on the extraction efficiency was also investigated. In our experiment, sodium chloride was added to the sample solution in the range of 0–200 mM. As shown in Fig. 3, an initial decrease and then a slightly increase in extraction efficiency with the increase of salt concentration in sample solution was observed. It is known that the addition of inorganic salt may decrease the ion-exchange interaction between the analytes and monolithic coating. As a result, the extraction efficiency decreased as the inorganic salt concentration increased from 0 to 140 mM. When the salt concentration was further increased from 140 to 200 mM, a slight increase in extraction efficiency was observed. This was because the relatively high salt concentration could result in 'salting out' effect, which directly leaded to the small increase of extraction performance. To simplify the sample preparation process, no additional sodium chloride was added in the further experiments.

3.3.4. Extraction time

In this study, the effect of extraction time from 20 min to 6 h on the extraction efficiency for the three NSAIDs was also investigated. As shown in Fig. 4, increasing extraction time could remarkably improve the extraction efficiency, implying the excellent enrichment ability of the monolithic polymer coating towards the studied NSAIDs. Considering the detection sensitivity and the time consumed of proposed method, 2 h was adopted as the extraction time in the following experiments.

From the above experimental results, the optimized parameters for extraction of NSAIDs from water sample with SRSE were as follows: the pH value of sample solution was 4.0; extraction and desorption time were 2.0 h and 20 min, respectively; methanol containing 0.5% (v/v) formic acid was used as desorption solvent; no inorganic salt was added to the sample solution.

Under these optimal experimental conditions, the three NSAIDs were analyzed. Fig. 5 showed the chromatograms obtained by direct HPLC/UV analysis without SRSE process and the SRSE–HPLC/UV analysis. In comparison with the chromatogram of direct injection, an obvious enhancement of each peak height was observed after extraction, indicating the remarkable preconcentration ability of the polymer coating to the three NSAIDs.

3.4. Validation of the SRSE–HPLC/UV method

Under the above optimized conditions, blank water samples spiked with three target NSAIDs were prepared to evaluate the developed method. A serial of experiments with regard to the linearity, limit of detection (LOD), limit of quantification (LOQ),

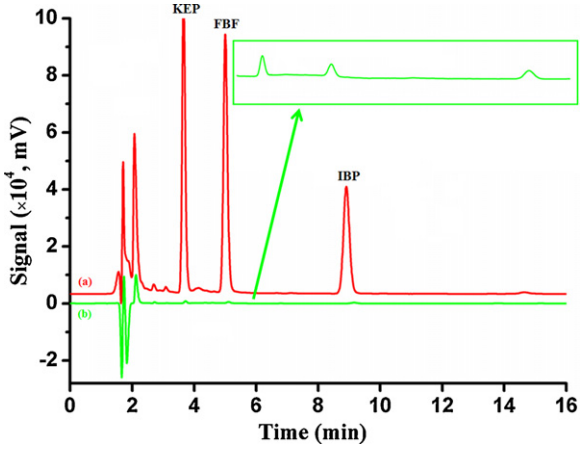

Fig. 5. Chromatograms of three NSAIDs obtained by SRSE–HPLC/UV (a) and direct injection (b) analysis. The sample solution was spiked at 100 ng/mL for each of the NSAIDs and the direct injection volume was 20 μL.

Table 2
The linear range, regression data, limits of detection (LODs), limits of quantification (LOQs) for the NSAIDs from aqueous samples.

Analytes	Linear range (ng/mL)	Calibration curves			LOD (ng/mL)	LOQ (ng/mL)
		Slope	Intercept	R^2 value		
KEP	1–200	11,457	25,273	0.9999	0.09	0.30
FBF	1–200	10,737	−8784	0.9999	0.11	0.37
IBP	1–200	8270	2656	0.9995	0.25	0.83

Table 3
Method precisions at three different concentrations for the extraction of the NSAIDs from aqueous samples.

Analytes	Intra-day precision (RSD%, $n = 3$)			Inter-day precision (RSD%, $n = 3$)		
	200 ng/mL	20 ng/mL	2 ng/mL	200 ng/mL	20 ng/mL	2 ng/mL
KEP	3.0	6.6	8.7	5.0	5.3	9.8
FBF	3.0	4.3	2.7	6.3	4.0	2.6
IBP	2.5	4.4	3.9	7.4	7.9	3.4

Table 4
Comparison of the limits of detection (ng/mL), times consumed and precisions of the proposed method in this study with other methods.

Methods	Matrix	Analytes	LOD	Time consumed	Precision (RSD%)	Reference
SPE–LC/MS/MS	Water	KEP, IBP	0.003, 0.021	2 h	1–13	[19]
LPME–LC/MS	Sewage sludge	KEP, IBP	10, 10	21 h	6.8–10.7	[34]
LPME–HPLC/DAD/FLD	Human urine	IBP	40.6 for DAD; 1.9 for FLD	30 min	0.8–1.8	[9]
SPME–HPLC/DAD	Water	KEP, IBP	0.5, 12	100 min	7–14	[21]
SPME–GC/MS	Water	IBP	0.2	70 min	10	[22]
SBSE–HPLC/DAD	Water	IBP	1.1	7 h	7.2	[10]
SRSE–HPLC/UV	Water	KEP, FBF, IBP	0.09, 0.11, 0.25	3 h	2.5–9.8	This work

and reproducibility were performed. The linear regression analysis was performed using peak areas against the concentrations of the respective analytes. The LOD and LOQ were calculated as the concentration corresponding to the signals of 3 and 10 times the standard deviation of the baseline noise, respectively.

The linear regression, the LOD, and LOQ data were listed in Table 2. The LOD and LOQ for three NSAIDs were found to be 0.09–0.25 ng/mL and 0.30–0.83 ng/mL, respectively. The linear dynamic range was 1–200 ng/mL for three NSAIDs, and the linear correlation coefficients (R^2) were above 0.9995, showing a high degree of correlation between concentration and peak area.

In this study, the reproducibility of the method was determined by the intra- and inter-day precisions. The intra- and inter-day relative standard deviations (RSDs) were calculated with the NSAIDs spiked at three different concentration levels in water sample. Three parallel extractions of sample solution over a day gave the intra-day RSDs, and the inter-day RSDs were determined by extracting sample solutions that had been independently prepared for three continuous days. The results were summarized in Table 3. The intra- and inter-day RSDs were less than 8.7% and 9.8%, illustrating the acceptable reproducibility achieved by the proposed method.

Table 4 listed the comparison of the limits of detection, times and precisions of our developed method with other methods. As illustrated in Table 4, our proposed method has a moderate analysis time and satisfactory precision, and our method showed better sensitivity than most of them. Determination of NSAIDs by GC or HPLC with mass spectrometry (MS) detector was more sensitive than that with UV detector. However, our proposed method exhibited a greater sensitivity than LPME–LC/MS method with MS detector [34]. The experimental and comparative results well indicated that the SRSE–HPLC/UV method may be used to effectively monitor NSAIDs in aqueous matrices or other complex aqueous matrix with modification such as using more selective and sensitive MS detector.

3.5. Application to environmental aqueous samples

Under the optimized conditions, the proposed SRSE–HPLC/UV method was successfully applied to the analysis of the NSAIDs in two kinds of environmental aqueous samples including lake water and sewage outfall of a hospital. The recoveries were determined by comparing the calculated amounts of NSAIDs from the spiked environmental samples with the total spiking amounts (20 ng/mL). As listed in Table 5, the recoveries of the three NSAIDs from two environmental aqueous samples were in the range from 75.6% to 112.3% with the RSDs less than 9.3%. Compared to sewage water, higher inorganic salt concentration in East Lake water caused the lower precisions. Meanwhile, high salt concentration caused KEP has lowest recoveries (76 and 82%) among target analytes. The results demonstrated that the precision and accuracy of the present method were acceptable.

Table 5
Recoveries and precisions of the NSAIDs in the analysis of environmental aqueous samples.[a]

Sample	Analytes	Founded (ng/mL)	Recovery (%)	RSD (%, $n = 3$)
The East Lake water	KEP	15.12	75.6	6.8
	FBF	20.42	102.1	9.3
	IBP	18.44	92.2	9.1
Sewage outfall of a hospital	KEP	16.48	82.4	1.1
	FBF	22.46	112.3	3.7
	IBP	20.02	100.1	6.2

[a] Real aqueous samples were spiked at 20 ng/mL.

4. Conclusion

In this work, a poly(VP-co-EDMA) monolithic polymer was prepared and used as SRSE coating, and this anionic exchange monolithic material was applied to extract three non-steroidal anti-inflammatory drugs in environmental aqueous samples. The polymerization conditions were optimized by measuring the surface area and pore size analyzer, SEM, and MIP to characterize the monolithic material. Under the optimized extraction condition, the method for the determination of NSAIDs in environmental aqueous samples was established based on the combination of high performance liquid chromatography with ultraviolet detector (SRSE–HPLC/UV).

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