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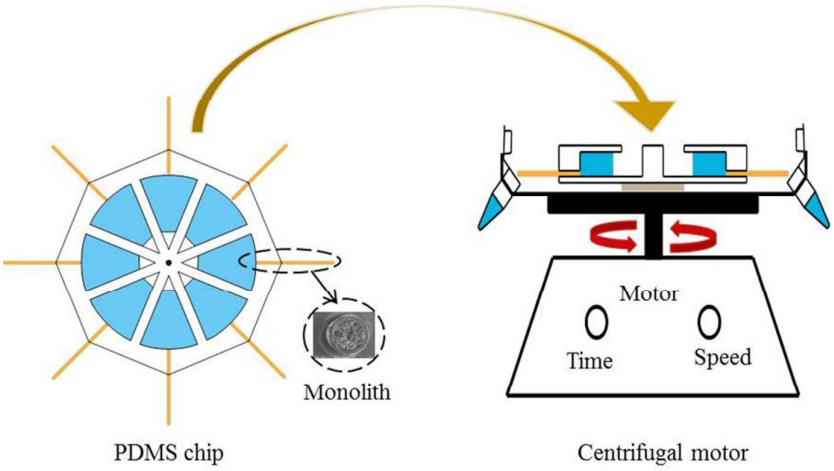

Cr(VI) and Cr(III) species were separated with high throughput.

A centrifugal microfluidic platform integrating monolithic capillary columns for high-throughput speciation of chromium

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Abstract

In this work, a centrifugal microfluidic platform with multiple solid phase extraction (SPE) units has been developed and successfully applied to separate Cr(VI) and Cr(III) with high throughput, followed by inductively coupled plasma mass spectrometry (ICP-MS) detection. Monolithic capillary columns, prepared by polymerization of N-(β-aminoethyl)-γ-aminopropyltriethoxysilane (AEAPTES) and tetraethoxysilane (TEOS), were integrated on a PDMS chip and used as the mediums for the selective extraction of Cr(VI). The aqueous solutions on the chip were driven

by centrifugal force produced by a centrifugal motor, so that high-throughput SPE was achieved by processing multiple samples simultaneously. The adsorption and elution conditions of Cr(VI) onto the monolithic capillary column, and the rotation speed of the centrifugal motor were well studied. The feasibility of the proposed protocol was validated by certified reference materials and real water samples. Contrast with traditional speciation analysis procedure, the species separation of eight samples can be finished within 10 min on the established centrifugal microfluidic platform. The device possessing the advantages such as portability and simplicity provides a potential application for field sampling and pretreatment.

Key words: Speciation of chromium; microfluidic chip; centrifugal force; monolithic capillary column; Inductively coupled plasma mass spectrometry

1. Introduction

Chromium, which was widely used in industrial processes such as steel manufacturing and tannery, is found in natural waters predominantly in its Cr(III) and Cr(VI) oxidation states. The toxicological studies have indicated that the role and impact of Cr on the environment and living organisms depend primarily on its chemical form. Cr(III) is considered as an essential micronutrient for mammals, while Cr(VI) is highly toxic due to its mutagenic and carcinogenic properties.[1-4] The

allowed limit of Cr(VI) discharge into inland surface water is 0.1 mg L^{-1}, but the guidelines for drinking water prescribed by World Health Organization (WHO) recommends even lower, i.e., 0.05 mg L^{-1}.[5,6] Therefore, species separation of Cr(III) and Cr(VI) is of great significance to Cr analysis.

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most powerful determination techniques for trace elements because of its high sensitivity, wide dynamic linear range, multi-element capability *etc*.[7] With preliminary separation techniques, e.g. liquid chromatography (LC) and capillary electrophoresis (CE), ICP-MS can realize the speciation analysis of an element.[8-10] Although these hyphenated technique showed a great success in speciation of Cr, they still face the great consumption of instrument, mobile phase, and analysis time. Solid phase extraction (SPE) is another important strategy for the species separation and concentration prior to analysis.[11,12] Based on the principle of selective adsorption for one species on adsorbents, various packed microcolumns containing adsorbents have been developed for the speciation of Cr, e.g., NH_2-SBA-15, TiO_2 and chelating resin packed microcolumns and so on.[13-16] In these microcolumn systems, because fluids were generally driven by mechanical pumps, the system can only handle one sample at a time. As a result, it will take a long time to finish sample pretreatment.

Centrifugal force derived from rotation has been utilized to drive the mobile phase for fluid based analysis since 1964.[17] With the help of centrifugal force, centrifugal devices such as centrifugal chromatography or centrifugal microfluidic discs have shown a very high potential for miniaturization and the processing of multiple

samples in parallel.[18-20] Salin et al reported a centrifugal SPE platform with eight C18-bonded silica packing channels for on-site pre-concentration of trace metals, followed by Laser ablation (LA) ICP-MS determination.[21] However, in their system, quartz wool frits are necessary at the ends of the packed channels, which make the device fabrication a bit tedious and time consuming, and the SPE adsorbents in the channels not uniform.

Monolithic capillary column is a continuous piece of highly porous material usually formed by in situ polymerization of a monomeric solution in a fused-silica capillary, and has grown in interest because of their characteristic enhanced mass transfer and simple preparation.[22] Since the monolithic skeleton is covalently bonded to the inner walls of the fused-silica capillary, monolithic capillary columns do not require retaining frits that is difficult to reproducibly fabricate for packed capillary columns, and could be assembled well with other units. For these novel characteristics, it has been demonstrated that monolithic capillary columns are very useful in extraction and separation for organic substances.[23,24] However, only a few applications of these columns have been reported on the analysis of trace elements and their speciation.[25,26]

A past research suggests that the main difficulty in Cr speciation analysis arises from the redox equilibrium between Cr(III) and Cr(VI) species, which is prone to changes in pH and the presence of oxidizing and/or reducing agents in the sample.[1] So it would be desirable that preliminary separation techniques being developed are high efficient to avoid the potential change of Cr species in sample transportation and storage, moreover, improve the utilization efficiency of the instruments used, like

ICP-MS, and save analysis time. Considering above, we report here a miniaturized centrifugal microfluidic platform for rapid speciation analysis of Cr in environmental waters, basing on the centrifugal force operated SPE procedures. An organic-inorganic hybrid monolithic capillary column was prepared and integrated onto a centrifugal microfluidic platform used as a selective extraction medium for Cr(VI) under controlled pH condition. With the help of centrifugal microfluidic platform, multiple samples can be handled simultaneously, giving a high throughput of eight samples in 10 min.

2. Experimental

2.1 Instrument

The determination of different chromium species was performed on a Model ELAN 9000 quadrupole (Q) ICP-MS (PerkinElmer, Boston, MA, USA) equipped with a 7725i six-port injection valve (Rheodyne, Cotati, CA, USA) with a 20 μL loop as a flow injection (FI) system. The optimum operation conditions are summarized in Table 1. The scanning electron microscopy (SEM) images of the monolithic column were obtained using a S-3400N scanning electron microscope (Hitachi, Tokyo, Japan). Fourier transform infrared (FT-IR) spectra (4000-400 cm^{-1}) in KBr were recorded on a

NEXUS870 spectrometer (Nicolet, Madison, WI, USA). The pH values of solutions were controlled by a SevenMulti pH meter (Mettler-Toledo, Shanghai, China).

Table 1

2.2 Reagents and samples

Cetyltrimethylammonium bromide (CTAB) was purchased from TCI (Tokyo, Japan). AEAPTES and TEOS were purchased from Ourchem (Shanghai, China) and Alfa Aesar (Tianjing, China), respectively. HNO_3 was of guarantee reagent, and all other chemicals were at least of analytical grade. Stock standard solutions of Cr(III) and Cr(VI), 1000.0 mg L^{-1}, were prepared by respectively dissolving appropriate amounts of $Cr(NO_3)_3$ and $K_2Cr_2O_7$ (purchased from Sigma-Aldrich, USA) in deionized water. Lower concentration standard solutions were prepared daily by appropriate dilutions from their stock solutions. A set of silicon elastomer and curing agent (Sylgard 184) obtained from Dow Corning Corporation (Midland, USA) was used for the fabrication of polydimethysiloxane (PDMS) chip. Deionized water (DIW, 18.25 MΩ cm) obtained from a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout the experiment.

Certified Reference Material of Environment Water (GBW08607) was supplied by China National Measuring Science Research Institute (Beijing, China). Bottled drinking water (Wahaha Purified Water, Wahaha Group Ltd., Hangzhou, China) was

purchased from a local supermarket in Nanjing. Waste water was collected from a dormitory sewer in our downtown campus in Gulou District, Nanjing. All water samples were filtered through 0.45 μm cellulose acetate membranes and analyzed immediately. The pH of samples was adjusted to the desired value with diluted HNO_3 prior to analysis.

2.3 Preparation of monolithic capillary columns

The fused-silica capillary (Reafine Chromatography Ltd., Hebei, China) with 530 μm i.d. and 690 μm o.d. was used to prepare the monolithic capillary column. Prior to preparation, the capillary was activated at ambient temperature by rinsing sequentially with 1.0 M sodium hydroxide for 4 h, water for 30 min, 1.0 M hydrochloric acid for 4 h, water for 30 min and methanol for 30 min, and dried at 160 °C while being purged with nitrogen for 3 h.

The monolithic capillary column was prepared by the following procedures based on the previously reported method[27] with minor modifications. Briefly, 225 μL ethanol, 75 μL water and 22.2 mg CTAB were mixed together, and then 160 μL TEOS and 40 μL AEAPTES were added to above solution, and the mixture was vortexed at room temperature for 30 s and subsequently ultrasonicated at 0 °C for 30 s before being introduced into the pre-activated capillary of 100 cm length. After sealed at both ends with rubber stoppers, the capillary was placed at 40 °C for 20 h and then rinsed

with HNO_3/ethanol (v/v = 1/200) and water, respectively. After preparation, the long capillaries containing continuous monolith were cut into short pieces of 2 cm length.

2.4 Fabrication of centrifugal microfluidic platform

Fig. 1 is the schematic diagram of the centrifugal microfluidic platform. A PDMS chip of eight reservoirs was the basic component, and monolithic capillary columns were inserted into the PDMS chip for SPE. The PDMS chip was fabricated using replicating techniques and the fabrication procedures are described as follows. A poly(methylmethacrylate) (PMMA) mold of eight fan-shaped positive reliefs (15 mm radius, 3.5 mm thickness and $2\pi/8$ angle) was used as a positive mold. Eight stainless steel tubes (650 μm diameter, 10 mm length) were used as a mold of the insertion holes on the chip for monolithic capillary columns insertion. Each stainless steel tube was fixed along the centerline of the fan-shaped positive relief, and the head of the tube was clung to the edge of the sector. The resulting mold was placed in a glass tray, and a mixture of 10:1 w/w of silicon elastomer and curing agent was then poured into the glass tray and cover the PMMA mold. The polymer mixture was incubated at 80 °C for 2 h to complete the polymerization.

After the cured PDMS piece was peeled off the mold, holes were punched to form sample inlets. The replica and a flat PDMS substrate were then treated with oxygen plasma for irreversible sealing, and the volume of each formed reservoir was 300 μL. Finally, the PDMS chip was cut into the required size, and monolithic capillary

columns were inserted directly into the reserved insertion holes. Since the elastic property of PDMS, the interface between monolithic capillary column and reservoir was hermetically sealed without any leakage.

The integrated PDMS chip with monolithic capillary columns were mounted on a stage built in-house which driven by a centrifugal motor (Institute of Microelectronics of Chinese Academy of Sciences, Beijing, China) to rotate. The stage was designed that eppendorf tube (0.2 mL) was locked at an angel of 45° to the plane, so the effluent of the column could be collected by the eppendorf tube. The magnetic force between the magnet pasted in the bottom of the chip and the stage can fix the chip on the stage well in the rotation process.

Fig. 1

2.5 General procedures for speciation analysis

Separation of Cr(VI) and Cr(III) was based on the selective extraction of Cr(VI) under specific pH condition. The rotation speed of the centrifugal motor selected was 1600 rpm, and rotation time was set to 2 min for each step. A portion of aqueous sample solution containing Cr(III) and Cr(VI) species was used as the test sample, which pH was adjusted to 2.5 with diluted HNO_3. Prior to the extraction, 200 μL DIW (pH 2.5, adjusted by diluted HNO_3) was pipetted into the reservoir and the motor was activated to rotate to precondition the monolithic capillary column. In the extraction

step, 200 μL of sample solution was pipetted into the reservoir, and then the motor was activated. Cr(VI) species was retained on the column, while Cr(III) species passed through the column and was collected by eppendorf tube. In the elution step, after centrifuging 200 μL DIW (pH 2.5, adjusted by diluted HNO_3) for a rinse, the retained Cr(VI) was eluted by 200 μL 0.1 M $NH_3 \cdot H_2O$, and the effluent was collected. The collected effluent containing Cr(III) in the extraction step, and Cr(VI) in the elution step was subsequently determined by FI-ICP-MS under the optimum operation conditions, respectively.

3. Results and discussion

3.1 Characterization of the monolithic capillary column

SEM was employed to characterize the micro-structure of the monolithic capillary column. From Fig. 1B, it can be seen that the formed monoliths attached well to the inner wall of capillary. This is because the pre-activating treatment resulted in abundant Si-OH groups on the inner wall of capillary, which provide effective binding sites between monolithic skeleton and capillary through condensation of Si-OH. Furthermore, there were many macropores and flow-through channels in the network skeleton of the monoliths, which offer large surface area and low flow resistance for SPE.

Besides, FT-IR spectrum of the prepared monolith was examined. Characteristic bands of C-H, C-N and N-H stretching vibrations of -NH-CH_2-CH_2-NH_2 functional group demonstrate the successful incorporation of AEAPTES in the matrix (data not shown), which endues the monolithic capillary column with selective adsorption for Cr(VI).

3.2 Effect of pH on the selective adsorption of Cr(VI)

pH plays an important role on the retention of trace metal ions including chromium species in SPE procedure because it influences not only the surface property of adsorbents but also the distribution of Cr species. In this work, the adsorption behaviors of Cr (III) and Cr(VI) on the monolithic capillary column were investigated separately with pH varying in the range of 1.0-8.0. As can be seen in Fig. 2, the adsorption percentage of Cr(VI) was sharply increased with the increase of sample pH from 1.0 to 2.5, remained constant in pH range of 2.5-4.0, then almost dropped down to nil at pH 6.0, and finally kept unchanged with the further increase of sample pH to 8.0, while the adsorption percentage of Cr(III) was gradually increased with the increase of sample pH from 1.0 to 8.0. The quantitative adsorption for Cr(VI) was achieved in the range of pH 2.5-4.0, whereas the adsorption for Cr(III) at corresponding pH range was rather low. Therefore, pH 2.5 was chosen for the extraction of Cr(VI) in the following study.

The adsorption behaviors of Cr(III) and Cr(VI) on the monolith can be explained by different mechanisms caused at specific pH. At pH 2.5-4.0 range, Cr(VI) exists mainly as anion $HCrO_4^-$, whereas Cr(III) exists as its kinetically inert aqua complex $Cr(H_2O)_6^{3+}$. Meanwhile, the surface of the monolith is positively charged owing to the protonated amino group. Therefore, Cr(VI) could be selectively adsorbed through electrostatic attraction. As pH increases, the protonation degree of amino group of the monolith is reduced, so the adsorption percentage of Cr(VI) was decreased. Whereas, Cr(III) tends to form a more labile form ($Cr(H_2O)(OH)^{2+}$, $Cr(H_2O)(OH)_2^+$) in pH range 4.0-8.0, which allows for better interaction with chelating group of $-NHCH_2CH_2NH_2$ on the surface of monolith, so a portion of Cr(III) was extracted.

Fig. 2

3.3 Effect of rotation speed

In the designed platform, aqueous solutions were driven by centrifugal force. The centrifugal force affects flow rate of solution passing through the capillary, and affects extraction efficiency further. Therefore, the influence of rotation speed of motor was evaluated in detail. The percentage adsorption results are shown in Fig. 3 together with the approximate flow rate generated by rotation as a function of the rotation speed. As can be seen, Cr(VI) could be quantitatively adsorbed when the rotation speed was in the range of 1000-1600 rpm. As the flow rate increases with the increase

of rotation speed, it could be suggested that the decrease in adsorption percentage of Cr(VI) is a consequence of the larger flow rate (e.g. 1800 rpm), which leads to insufficient interaction between Cr(VI) and the monolith. Accordingly, a rotation speed of 1600 rpm (equivalent to a flow rate of 102 μL min^{-1}) was selected for subsequent experiments, and the centrifugal time was set to 2 min for 200 μL sample solution. In addition, the effect of the same flow rate on the adsorption of Cr(VI) onto the monolithic capillary column was investigated by a syringe pump (Baoding Longer, Hebei). The sample flow rate of pump was set to the corresponding flow rate generated by centrifugal rotation. The results are shown as a bar graph in Fig. 3. Compared the results obtained by rotation and syringe pump, it can be seen that these two driving modes had similar influence on the adsorption percentage of Cr(VI), indicating the centrifugal force can be successfully utilized in driving solution.

Fig. 3

3.4 Effect of the eluent

Above results showed that the monolith can adsorb Cr(VI) under acidic conditions. In addition, diluted $NH_3 \cdot H_2O$ solution have no interference for ^{52}Cr or ^{53}Cr detection by ICP-MS. Therefore, diluted $NH_3 \cdot H_2O$ was selected as the eluent for Cr(VI). The systematic experiments indicated that Cr(VI) can be quantitatively desorbed by 100 μL 0.1 M $NH_3 \cdot H_2O$ at a rotation speed of 1600 rpm. To ensure the complete elution

and taking no care of enrichment, a volume of 200 μL of 0.1 M $NH_3 \cdot H_2O$ was used for elution of Cr(VI).

3.5 Interference study

Generally, the coexisting ions in sample solution may compete with analyte for active sites of monolith. To study the effects of cations and anions on determination of Cr(VI), 200 μL sample solution containing 20 μg L^{-1} Cr(VI) and a certain amount of individual interfering ion were tested under the general procedure. Taking the deviation of the recovery out of 90%-110% as the criterion for interference, the highest amounts of coexisting ions are summarized in Table 2. The achieved tolerance limits indicated that the proposed method could be applied for speciation analysis of Cr in environmental waters.

Table 2

3.6 Reproducibility and reusability of the monolithic capillary column

In order to study the preparation reproducibility of the monolithic capillary columns, columns prepared within batch (n = 4) and between different batches (n = 4) were examined by measuring the recoveries of the same solution containing 10 μg L^{-1} Cr(VI) under the optimized conditions. It was found that the relative standard

deviations (RSDs) for eluted Cr(VI) were 4.2% and 4.7% for intra- and inter-batch, respectively. Moreover, the monolithic columns could be reused at least 10 times without decreasing extraction efficiency for Cr(VI), and consecutive use of the columns did not result in any visible bleeding of the monolith. If necessary, the used column could be easily replaced by inserting a new one directly into the PDMS chip, owing to the freely pluggable design and the uniform monolith structure.

3.7 Analytical application

The differences in retention of Cr(VI) and Cr(III) in the centrifugal microfluidic platform make it possible to develop a simple and sensitive speciation method. Selective retention of Cr(VI) on the monolithic capillary column under acidic conditions could be applied for separation of Cr(VI) from Cr(III) present in the aqueous sample. The concentration of Cr(III) in the aqueous phase can be determined by ICP-MS after separation of Cr(VI) using the designed platform, and the concentration of Cr(VI) can be determined after desorbing it from the column with 0.1 M $NH_3 \cdot H_2O$.

By using the proposed procedure, calibration curves were established in the range of 0-100 μg L^{-1} Cr(VI) and Cr(III) with linear equation of $y = 12996.1\ x + 3342.4$ ($R^2 = 0.9987$) and $y = 11410.3\ x - 71.0$ ($R^2 = 0.9991$), respectively. It should be noted that breakthrough curve experiment of 500 μg L^{-1} Cr(VI) revealed that the adsorption capacity of 2 cm monolithic capillary column is 4.3 μg at 5% breakthrough volume,

indicating that much higher concentration of Cr could be suitable for this system. The precisions (RSDs) for six replicate measurements of 10 μg L^{-1} Cr(VI) and Cr(III) were 4.6% and 3.7%, respectively. The limits of detection (LODs) of the proposed method achieved by the described procedure in combination with FI-ICP-MS determination were estimated to be 1.2 μg L^{-1} and 0.9 μg L^{-1}, respectively, for Cr(VI) and Cr(III) as three times the standard deviation of the background.

The proposed method was applied to the determination of Cr(VI) and Cr(III) in certified reference material (GBW08607) and two water samples including bottled drinking water and sewage water. The analytical results and the recoveries in the spiked samples are given in Table 3. It can be seen that Cr in GBW08607 environmental water is mainly existed in Cr(III), but after Cr(III) was oxidized by hydrogen peroxide in concentrated $NH_3 \cdot H_2O$ medium, Cr is primary in the form of Cr(VI). The values of Cr(III) and Cr(VI) determined is in good agreement with the certified value of 0.520±0.010 μg mL^{-1}.[11] Furthermore, the recoveries of 91-108% were obtained for the spiked water samples. These results validated that the method was suitable to analyze Cr(VI) and Cr(III) in environmental waters.

Table 3

4. Conclusions

A novel centrifugal microfluidic platform containing monolithic capillary columns synthesized by AEAPTES and TEOS was successfully implemented to separate Cr(VI) and Cr(III), based on the selective extraction of Cr(VI) onto the monolith under different pH. This is the first report that the monolithic capillary columns was employed as an adsorbent and integrated onto a centrifugal microfluidic platform for Cr speciation. Due to its stable structure and no needs for any frits or plugs, the monolithic capillary column can be easily installed on and removed from the microfluidic platform, which make the fabrication of the device very convenient. Compared with traditional speciation procedure, the design of the platform is user-friendly and it considerably reduced the time required for multiple measurements. Besides, the throughput can be further improved by increasing the SPE units on the chip.

Acknowledgments

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Table legends

Table 1 Instrumental parameters for determination of Cr by FI-ICP-MS

Table 2 Tolerance limits of coexisting ions

Table 3 Analytical results of Cr(III) and Cr(VI) in certified reference material and water samples (mean ± sd, n = 3)

Figure captions

Fig. 1 Schematic diagram of the centrifugal microfluidic platform. A. Top view of PDMS chip; B. SEM of monolithic capillary column; C. Side view of the centrifugal microfluidic platform; D. Real model used in this work.

Fig. 2 Effect of pH on the adsorption percentage (%) of Cr(III) and Cr(VI).

Fig. 3 Effect of rotation speed on the adsorption percentage (%) of 50 μg L^{-1} Cr(VI) (pH 2.5), and the flow rate of the solution. Inset: The comparison between adsorption percentages (%) of Cr(VI) solution driven by rotation and syringe pump.

Tables

Table 1 Instrumental parameters for determination of Cr by FI-ICP-MS

Parameter	Settings
Rf power	1000 W
Carrier gas flow rate	0.85 L min^{-1}
Auxiliary gas flow rate	1.20 L min^{-1}
Plasma gas flow rate	15 L min^{-1}
Sampling cone	Ni / 1.1 mm
Skimmer cone	Ni / 0.9 mm
Acquisition mode	Time-resolved data acquisition
Scanning mode	Peak-hopping
Dwell mode	250 ms
Integration mode	Peak area
Isotope monitored	^{52}Cr

Table 2 Tolerance limits of coexisting ions

Coexisting ions	Tolerance limit of ions / mg L^{-1}
Na^{+}, K^{+}	500
Mg^{2+}, Ca^{2+}	100
Al^{3+}	10
Fe^{3+}	5
Zn^{2+}	10
PO_4^{3-}	100
SO_4^{2-}	100
Cl^{-}	500

Table 3 Analytical results of Cr(III) and Cr(VI) in certified reference material and water samples (mean ± sd, n = 3)

Sample	Cr(VI)			Cr(III)		
	Spiked / μg L^{-1}	Determined / μg L^{-1}	Recovery / %	Spiked / μg L^{-1}	Determined / μg L^{-1}	Recovery / %
GBW08607	0	ND	--	0	500±11	96
GBW08607 (Oxidation)	0	496±14	95	0	ND	--
	0	ND	--	0	ND	--
Drinking water	50.0	47.2±1.1	94	5.0	5.4±0.1	108
	5.0	5.1±0.1	103	50.0	47.6±2.1	95
	0	ND	--	0	ND	--
Sewage water	20.0	18.8±2.0	94	2.0	1.9±0.2	97
	2.0	2.1±0.1	104	20.0	18.1±1.4	91

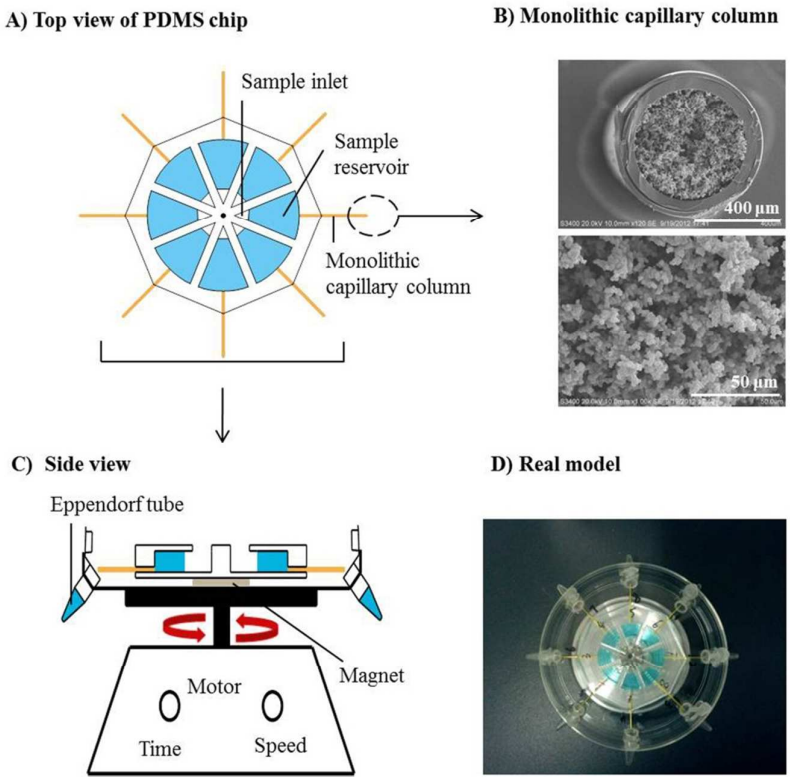

Fig. 1

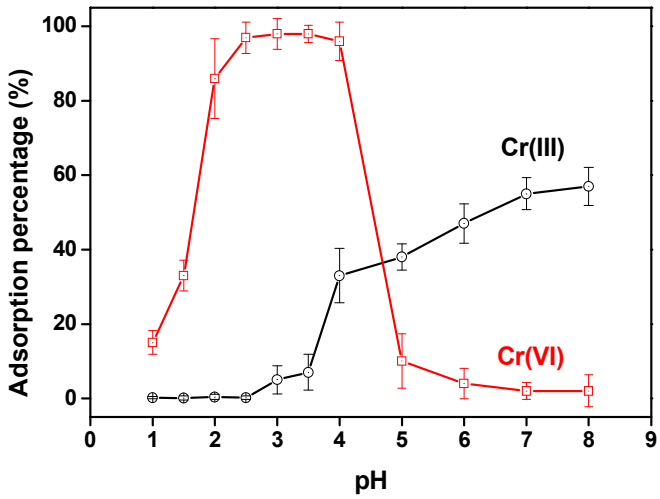

Fig. 2

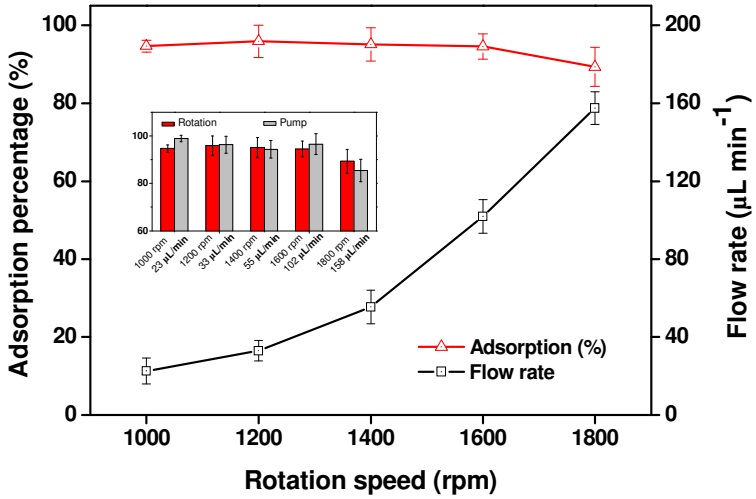

Fig. 3