

## Supporting Information (SI)

### Development of molecularly imprinted polymers (MIPs) as solid phase extraction (SPE) sorbent for determination of ibuprofen in water

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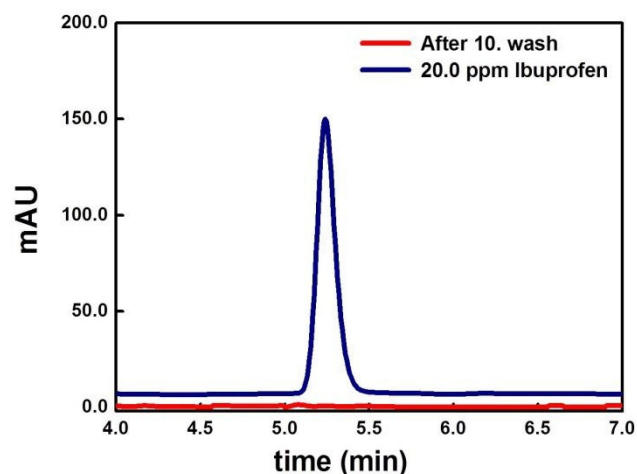
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## 3. Results and discussion

### 3.2 Synthesis of MIP and NIP

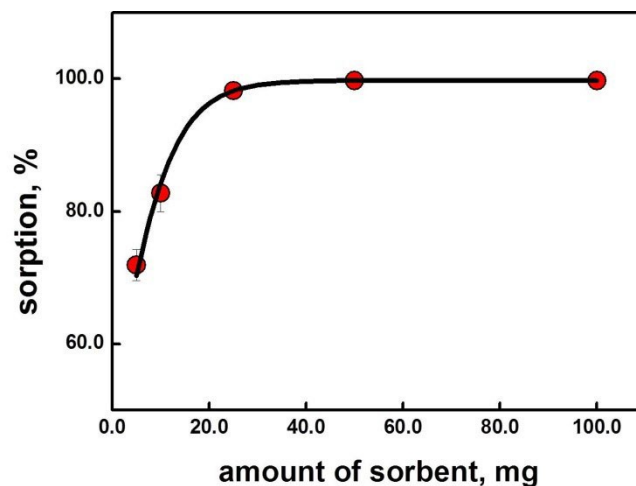
After the synthesis of MIP, the template (ibuprofen) was removed by washing out with MeOH. Ten consecutive wash cycles were shown to be sufficient for complete removal (Fig. S-1).



**Figure S-1:** Chromatogram of ibuprofen before and after washing steps. (Agilent 1200 Series HPLC-DAD system, Supelco C18 (Lichrosphere RP 18-5, 25cm×4.6mm) column, 80:20 MeOH:H<sub>2</sub>O (pH 3.0) mobile phase, 0.8 mLmin<sup>-1</sup> flow rate, 220 nm).

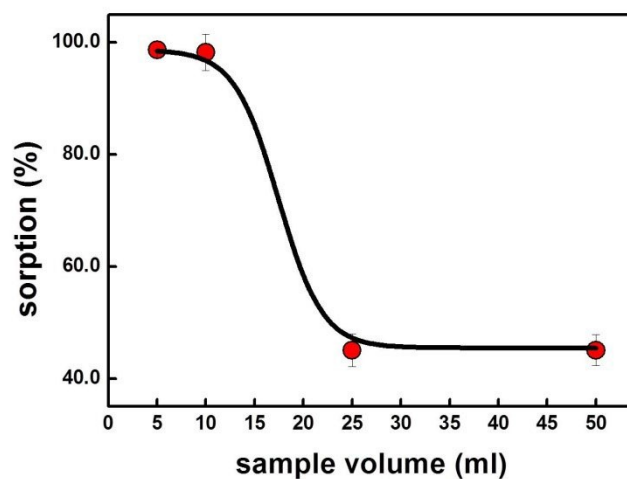
### 3.4 Optimization of working parameters

MISPE procedure was also applied with different amounts of MIP100. There is a linear increase in sorption with respect to sorbent amount up to 25.0 mg of MIP100 (Fig. S-2). Then, sorption levels off and remains unchanged at (98.5 %,  $\pm 0.7251$ ,  $n=3$ ). It is clear that the smaller values than 25.0 mg are not sufficient to have nearly complete sorption of  $1.0 \text{ mgL}^{-1}$  of ibuprofen. Therefore, it was decided to use 25.0 mg sorbent in the remaining experiments.



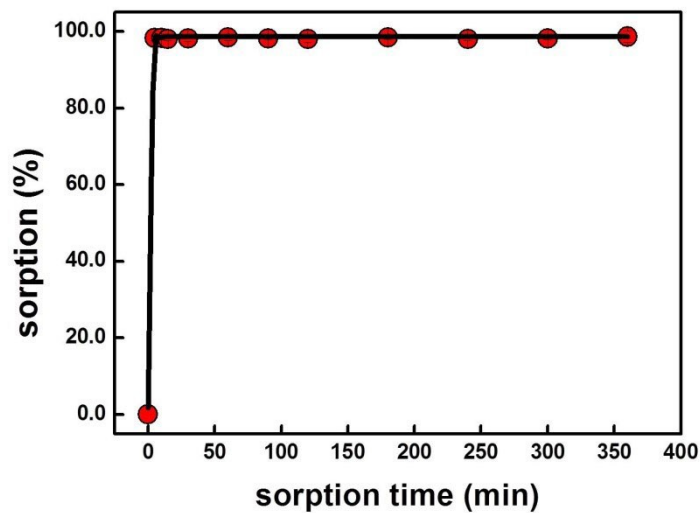
**Figure S-2:** Effect of sorbent amount for 10.0 mL,  $1.0 \text{ mgL}^{-1}$  of ibuprofen. (Agilent 1200 Series HPLC-DAD system, Supelco C18 (Lichrosphere RP 18-5, 25cm $\times$ 4.6mm) column, 80:20 MeOH:H<sub>2</sub>O (pH 3.0) mobile phase,  $0.8 \text{ mLmin}^{-1}$  flow rate, 220 nm,  $n=3$ ).

Effect of the sample volume on sorption percentage of MIP100 was examined with all the other parameters held constant. Ibuprofen solutions of 5.0 and 10.0 mL gave high sorption percentage (98.6% ( $\pm 3.5$ ),  $n=3$  and 98.5% ( $\pm 3.3$ ),  $n=3$ , respectively) and the percentage sorption decreased immediately after further increase in the sample volume (Fig. S-3). This might have been caused by two reasons; first, total number of moles of ibuprofen was higher than the available sorption sites and second, the mixing was inefficient when the volume was increased beyond 10.0 mL. The number of cavities in 25.0 mg of MIP100 may not be sufficient for this increase. In order to guarantee the quantitative sorption, 10.0 mL of 1.0 mgL<sup>-1</sup> ibuprofen solution was used in the remaining experiments.



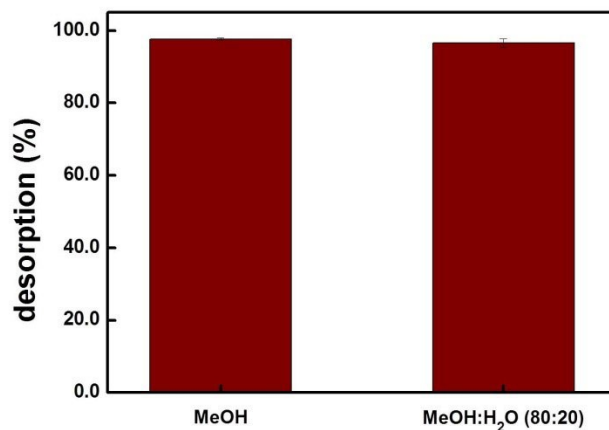
**Figure S-3:** Effect of sample volume for 1.0 mgL<sup>-1</sup> ibuprofen and 25.0 mg MIP100 sorbent. (Agilent 1200 Series HPLC-DAD system, Supelco C18 (Lichrosphere RP 18-5, 25cm×4.6mm) column, 80:20 MeOH:H<sub>2</sub>O (pH 3.0) mobile phase, 0.8 mLmin<sup>-1</sup> flow rate, 220 nm,  $n=3$ ).

By using the predetermined parameters, effect of shaking time on sorption was examined. The interaction time was not critical on sorption. Even 1 min was found to be sufficient for quantitative sorption (Fig. S-4). The reason may be the ability of the high diffusion rate of spherical MIP100 due to the homogenous binding sites. In order to be sure that the quantitative sorption is achieved, 30 min was chosen as sorption time in the remaining experiments.



**Figure S-4:** Effect of shaking time on the sorption of 10 mL 1.0 mgL<sup>-1</sup> of ibuprofen and 25.0 mg MIP100 sorbent. (Agilent 1200 Series HPLC-DAD system, Supelco C18 (Lichrosphere RP 18-5, 25cm×4.6mm) column, 80:20 MeOH:H<sub>2</sub>O (pH 3.0) mobile phase, 0.8 mLmin<sup>-1</sup> flow rate, 220 nm, n=3).

Desorption is equally important part of the SPE process as the sorption. Therefore, the analyte sorbed by MIP should be recovered from the sorbent with a proper eluent and desorption percentage should be calculated to understand the analyte concentration in an unknown sample. Two different eluents, namely, MeOH and MeOH:H<sub>2</sub>O (acetic acid, pH 3) (80:20), were tried for the desorption process. Both of the solutions have the ability of making hydrogen bond stronger than analyte molecule, ibuprofen. These solvents disturb the hydrogen bonding between the analyte and the solid sorbent. Although both of the eluents gave >97 % (97.2 %, ±0.8, n=3) desorption (Fig. S-5), MeOH:H<sub>2</sub>O (acetic acid, pH 3) (80:20) solution was decided to be used in the remaining experiments since it was the mobile phase employed in HPLC-DAD determinations.



**Figure S-5:** Effect of eluent type. (Agilent 1200 Series HPLC-DAD system, Supelco C18 (Lichrosphere RP 18-5, 25cm×4.6mm) column, 80:20 MeOH:H<sub>2</sub>O (pH 3.0) mobile phase, 0.8 mLmin<sup>-1</sup> flow rate, 220 nm).