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# A simple extraction method for Norfloxacin from Pharmaceutical wastewater with Magnetic Core-shell Molecularly imprinted polymer under the aid of Computer simulation

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**Appendix S1**

**TableS1 Energies found of individual structures and interaction energy （ΔE） of complexes supposed to be formed between molecule**

| Structures | Best riatio | E(kal/mol) | ΔE(kal/mol) |
|---|---|---|---|
| norfloxacin | | 44.06 | |
| MAA | | -16.98 | |
| AA | | -29.20 | |
| MAM | | -29.84 | |
| AM | | -30.76 | |
| N-isoacryamide | | -28.88 | |
| 4-VP | | 2.63 | |
| AM- norfloxacin | 1:5 | -198.53 | 19.65 |
| AA- norfloxacin | 1:6 | -179.03 | 12.97 |
| MAM- norfloxacin | 1:6 | -186.75 | 14.09 |
| MAA- norfloxacin | 1:3 | -47.86 | 23.98 |
| N-isoacryamide-norfloxacin | 1:4 | -110.74 | 14.59 |

| | | | |
|---|---|---|---|
| 4-VP- norfloxacin | 1:6 | 23.59 | 18.24 |

**Appendix S2 The synthesis steps of magnetic cores**

0.02 mol $Fe^{2+}$ and 0.04 mol $Fe^{3+}$ was dissolved in 50 mL deionized water firstly, when the mixture under ultrasonication change into a clear solution , transfer the mixture into a 250 mL three neck round bottom flask and heat the solution until 80℃. 50 mL amino solution was added drop by drop under the atmosphere of $N_2$ and magnetic stirring until getting 10-11 of pH. The color of solution changed into black quickly after the amino solution added, which indicate the formation of magnetic particles. The whole synthesis process should sustain for 2 hours. The final magnetic particles were separated in the exist of applied magnetic field. After the magnetic particles were washed with deionized water for a few times, dry the magnetic particles to powder in vacuum under 40℃.

**Appendix S3. FTIR spectrogram (Fig S3) and explanation**

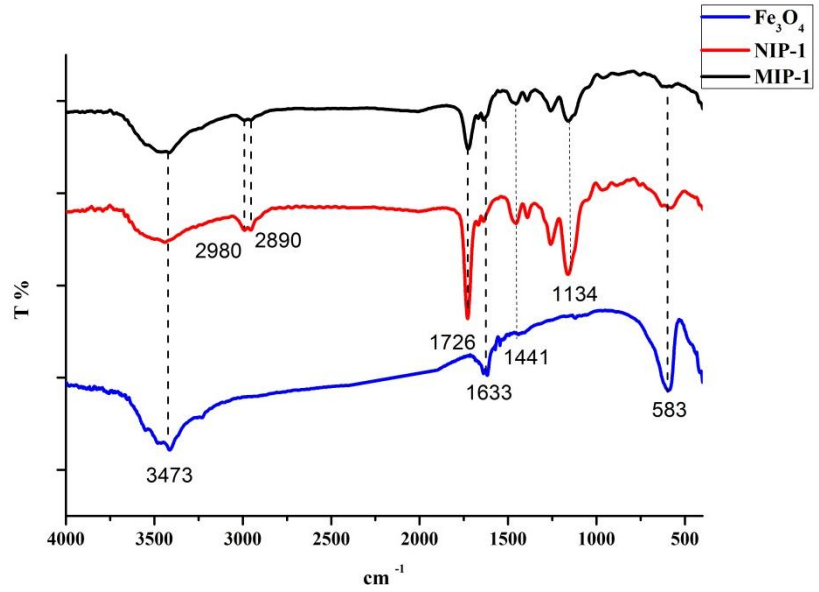


**Fig S1 FT-IR spectrogram of $Fe_3O_4$, MIP-1 and NIP-1**

As Fig S3 shows, 3473 $cm^{-1}$ is the special peak of O-H vibration, which proved the existance of $Fe(OH)_3$,$Fe(OH)_2$ and FeOOH. 583, 1134, 1441 $cm^{-1}$ exist in the three lines, which proved existance of $Fe_3O_4$. Different intensity of peak indicate that the amount of iron oxide substance is different. MMIP and MNIP possess a special C-H peak at 2890 $cm^{-1}$ and 2980$cm^{-1}$,the poignant peak at 1726 $cm^{-1}$ is resulted by C=O vibration and proved the exist of MAA in both MMIP-1 and $MNIP^{-1}$. All these special peaks proved that the MIP shell already coated on the surface of magnetic cores**.**

**Appendix S4. Pseudo-first-order model and pseudo-second-order model**

Pseudo-first-order model and pseudo-second-order model were utilized to explain the adsorption process of MMIP-1 for norfloxcin.

The equation of pseudo-first-order model is：

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \qquad (1)$$

$Q_e$ and $Q_t$（μg·mg$^{-1}$）means the equilibrate adsorption of norfloxcin and adsorption amount at $t$（min）respectively; $K_1$ is the equilibrate rate constant of pseudo-first-order model.

The equation of pseudo-second-order model is：

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2} \qquad (2)$$

$Q_e$ and $Q_t$（μg·mg$^{-1}$）means the equilibrate adsorption of norfloxcin and adsorption amount at $t$（min）respectively; $K_2$ is the equilibrate rate constant pseudo-second-order model.

According to the data of adsorption kinetic, the Table S2 can be get below.

**Table S2 Pseudo-first-order model and pseudo-second-order model results**

| Material | pseudo-first-order model | | | pseudo-second-order model | | |
|---|---|---|---|---|---|---|
| | Qe,cal (μg mg$^{-1}$) | $k_1$ (min$^{-1}$) | $R^2$ | Qe,cal (μg mg$^{-1}$) | $k_2$ (μg mg$^{-1}$ min$^{-1}$) | $R^2$ |
| MMIP-1 | 52.59 | 0.029 | 0.864 | 165.28 | 0.003 | 0.999 |
| MNIP-1 | 17.16 | 0.019 | 0.979 | 50.73 | 0.003 | 0.998 |

Pseudo-second-order model is much more suitable for MMIP-1 and MNIP-1 due to a higher $R^2$ and a more approximate equilibrate adsorption amount. Combined with rate controlling study, pseudo-order model verified further that the whole rate of adsorption influenced by chemical adsorption due to higher strength and specificity of hydrogen bond.

**Appendix S5.**

**Fig S2** Optimization of SPE process (Amount of MMIP-1 (Fig S2A)  extraction time (Fig S2B) elution solvents (Fig S2C), elution time (Fig S2D).)