Adsorption and Co-precipitation of Metoprolol with Struvite Recovered from Synthetic Source Separated Black Wastewater

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Abstract. Due to the residues of metoprolol (MET) in black wastewater, recovering phosphate as struvite (MgNH4PO4·6H2O) from black wastewater may pose threats to the utilization of struvite in the agricultural planting and human health. In this study, the adsorption and co-precipitation experiments of MET in the formation of struvite from synthetic black wastewater will be performed and some factors like initial MET concentration, pH values, temperatures were investigated. Results revealed that the adsorption process can be divided into rapid adsorption, fluctuation stage and steady stage, and the maximum MET adsorption quantity was 0.05029 mg/g under 80 ppb, 20 °C. Chemical adsorption and pseudo second-order kinetics were evident at the low concentration level. Neither Langmuir nor Freundlich isotherms fitted for the adsorption. The presence of Mg[H2O]62+ (Hexahydrate and magnesium ions) interfered with MET adsorption through recombining with MET, which was also determined by pH variation. The existence of MET in black wastewater would not obstruct the formation of struvite in alkaline condition generally and serious terrible influences would not be generated when using struvite as fertilizer. A vast majority of MET will stay in the solution after 3 hours’ reaction.

1. Introduction
A large amount of pharmaceuticals have been produced and applied in the treatment of human diseases. In the treatment of high blood pressure (hypertension), angina, arrhythmias and heart rhythm disturbances [1-3], β-blockers have been widely used for many years as a series of effective compounds. According to Ramil et al. [4], metoprolol was the most frequently used β-blocker, and can be detected in the environmental matrix and domestic black water frequently [2]. Like other pharmaceutically active compounds, β-blocker will be excreted through urine and faces as a mixture of metabolites, unchanged substances or conjugated with inactivating substances [5]. No matter in surface water, sewage treatment plants or blackwater, β-blockers and their metabolites can be detected in the concentration range from μg/L to mg/L [1,6]. Although no comprehensive study about the acute aquatic toxicity of β-blockers has been conducted, a significant cumulative effect on the metabolism of non-target organisms and the ecosystem can be achieved by them [7]. Nutrients like ammonia and phosphorus are still exist in sewage waste and black water. Recovering ammonia and phosphorus from wastewater in the form of struvite (MgNH4PO4·6H2O) was an ideal.
approach which had been applied in Japan, Netherlands, Italy and so on\cite{8-11}. Struvite was an excellent slow release fertilizer in agriculture industry because of its composition and physicochemical characteristics. Few researchers have studied the issues of micro-pollutants adsorption or coprecipitation in the process of struvite crystallization in source separated black water. Inestimable effects will be achieved on the soil and even the ecosystem when such struvite fertilizer used in agriculture. Therefore, the objectives of our work are: firstly, stimulating the main components of black wastewater to recover struvite and discussing the adsorption effects. Secondly, considering the coprecipitation mechanisms of metoprolol (MET) with struvite formation.

2. Materials and Methods

2.1. Materials

Inorganic salts in this experiment including MgCl$_2$·6H$_2$O, Na$_2$HPO$_4$·12H$_2$O, NH$_4$Cl, CaCl$_2$, KCl, KNO$_3$, Na$_2$SO$_4$, NaHCO$_3$, and ammonia hydroxide etc. All of them are guaranteed reagent and purchased from Sinopharm Chemical Reagent Co., Ltd. L-Ascorbic Acid ($\geq 99.99\%$), KH$_2$PO$_4$ ($\geq 99\%$) are bought from Acros Organic (USA). Potassium antimonyl tartrate sesquihydrate and ammonium molybdate are guaranteed reagent and bought from Energy Chemical (Shanghai, China). (±) metoprolol (+) tartrate salt (MET, CAS NO.56392-17-7) is bought from Sigma-Aldrich Inc. (USA) and dissolved in ultrapure water. Methanol and formic acid are UPLC/LC-MS and UPLC grades, both of them are bought from ANPEL Laboratory Technologies Inc. (Shanghai, China). The pH of metoprolol (MET) solution are adjusted to the required values with diluted 0.5mol/L NaOH or HCl.

2.2. Metoprolol Dsorption Experiment

2.2.1. Struvite Recovery from Synthetic Blackwater.

Inorganic salts are added into distilled water to simulate black wastewater matrix after treated by wastewater treatment plants. The initial phosphate concentration is set at $c_0=204$mg/L as the baseline of other ions. Stimulation of ionic concentrations in black water after treated by wastewater treatment plants are presented in Table.1. Magnesium ion concentration is a limiting factor, but excessive ammonium is highly beneficial to the precipitation of struvite \cite{12}. In order to get the maximum degree of phosphate recovery, the ratios of $C_{Mg^{2+}}: C_{NH_4^+}: C_{PO_4^{3-}}$ are adjusted as 0.8:1:1 to 2.0:1:1. The pH value of struvite precipitation is maintained in 8.0 according to previous literature \cite{13}. Meanwhile, struvite formation process will pass through two stages, including nucleation and crystal growth. Nearly 3 hours will be taken to complete struvite precipitation \cite{12,14}. Therefore the mixture will be shaken for 180 min on a rotary shaker at 120rpm under room temperature (298K). The concentrations of phosphate in different samples ($c_e$) are measured according to ascorbic acid colorimetric method \cite{15}. And the removal (%) is calculated by

$$\frac{c_0-c_e}{c_0} \times 100\%$$

After that, the precipitates will be filtered with 0.45μm cellulose acetate filter, washed with deionized water, and dried under 40℃ in oven for 48 hours.

**Table 1.** Stimulation of ionic concentrations in black wastewater after treated by wastewater treatment plants.

| Ionic species | HCO$_3^-$ | NH$_4^+$ | PO$_4^{3-}$ | Ca$^{2+}$ | K$^+$ | Na$^+$ | Cl$^-$ | SO$_4^{2-}$ | NO$_3^-$ |
|---------------|-----------|---------|-------------|-----------|------|-------|-------|----------|--------|
| Concentration (mg/L) | 1040.4 | 1414.0 | 204.0 | 39.0 | 424.0 | 604.0 | 695.0 | 157.0 | 26.0 |

After finding the optimum ratio of $C_{Mg^{2+}}: C_{NH_4^+}: C_{PO_4^{3-}}$, a large amount of struvite will be produced and stored in a sealed container for the subsequent experiments.

2.2.2. Struvite Characterization.

Surface morphologies and microstructure of struvite samples were examined by environmental scanning electron microscope with FEG (ESEM, Quanta FEG 250, FEI,
USA) and transmission electron microscopy (TEM, JEM-2800, 200kV, Japan). X-ray powder diffraction (XRD) patterns were recorded in the 2θ range of 10-80° at a scan speed of 10°/min by using a diffractometer (Ultima IV, Rigaku, Japan) with Cu Kα radiation (40mA,40kV). Nitrogen-adsorption-desorption isotherms were measured at the liquid nitrogen temperature 77K using ASAP 2460 (Micromeritics Inc., USA). The struvite samples were degassed at 50°C for 5h under vacuum prior to analysis. The specific surface area ($S_{BET}$) was determined from the linear part of the BET plot ($P/P_0 = 0.01 - 0.15$). The pore size (d) was calculated from the adsorption branch of isotherm by using Barrett-Joyner-Hallenda (BJH). The total pore volume ($V_{total}$) was determined from the adsorbed nitrogen amount at $P/P_0 = 0.99$.

2.2.3. Adsorption Processes. A series of batch experiments were performed to investigate the metoprolol adsorption performances of struvite adsorbents. Metoprolol solution with different concentrations were prepared by dissolving (+) metoprolol (-) tartrate salt (MET) in ultrapure water. Adsorption kinetic experiment was performed with metoprolol initial concentrations in 35, to 300 ppb. pH values of solution were adjusted to 8.0. The process was performed on a thermostat shaker under 120rpm, 298K. Samples were withdrawn from the flask at pre-determined time intervals from 15 to 180 min and filtered by 0.22μm syringe filters immediately before further analysis. The MET concentration was detected by ultra-performance liquid chromatography (UPLC, Waters, USA)/quadrupole-time-of-flight tandem mass spectrometry (MS/MS, Xevo TQ-S, USA.) with a 100mm (1.7μm particle size) UPLC BEH C18 column. The UPLC-MS/MS was operated in ESI positive mode with methanol (solvent A, 65%) and 0.2% formic acid (solvent B, 35%) at a flow rate of 0.3mL/min and an injection volume of 10μL. The adsorption capacities ($q_t$) were calculated by the following equation:

$$q_t = \frac{(C_0-C_t)V}{m}$$

(2)

where $C_0$ and $C_t$ were the MET concentrations in solution at initial and different time periods (μg MET/L), respectively; $V$ was the volume of solution (L) and $m$ was the mass of struvite adsorbent (g).

In order to analyse the kinetic mechanism of adsorption process, the experimental data were fitted in the pseudo first-order, pseudo second-order models which were calculated as (3) [16,17], (4) [16,17].

Pseudo first-order equation:

$$e^{-k_1t} = \ln(1 - \frac{q_t}{q_e})$$

(3)

Pseudo second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

(4)

where $q_t$ and $q_e$ were the amount of MET adsorbed over a given period of time t (mg MET/g) and at equilibrium (mg MET/g), respectively; $t$ was the adsorption time (min); $k_1$ (1/min), $k_2$ (g/mg/min) were the adsorption rate constants of the pseudo first-order adsorption, pseudo second-order adsorption, respectively.

Equilibrium experiment was conducted with different metoprolol concentrations and temperature respectively. The pH value of solution was adjusted to 8.0. Solutions were filtered through 0.22μm syringe filters after 1.5h immediately prior to further analysis. The MET concentration was detected by UPLC-MS/MS (Waters UPLC Xevo TQ-S, USA.).

The adsorption isotherms were fitted by Langmuir and Freundlich models which were described as (5) [17,18] and (6) [19].

Langmuir model: $q_e = \frac{q_mC_t}{1+\frac{1}{kC_e}}$  

(5)

Freundlich model: $q_e = \frac{1}{k_F C_e^{n_F}}$  

(6)

where $C_e$ (μg MET/L) was the concentration of MET solution at equilibrium; $q_e$ (mg MET/g) was the corresponding adsorption capacity; $q_m$ (mg MET/g) and $k_F$ (mg/g) were the constants in the
Langmuir and Freundlich isotherm models. $k_L$ (L/mg) was the constant in Langmuir isotherm model which related to the energy of adsorption. $n_F$ was the constant in Freundlich isotherm model which indicated the adsorption intensity.

2.2.4. Effects of Solution pH on Adsorption. Considering struvite was very sensitive to pH changes and mainly existed in alkaline condition. The interaction between struvite and metoprolol was only possible at pH levels between 8.0 and 10.5. This part experiment was performed with pH values from 8.0 to 10.5. After 1.5 hours, filtering the solution through 0.22 μm syringe filters immediately and analysed by UPLC-MS/MS.

2.3. Struvite Precipitation from Metoprolol Contaminated Blackwater

2.3.1. Effects of Solution pH on Co-precipitation. Adding 60ppb MET solution into black wastewater matrix based on Table 1. And pH values are from 8.0 to 11.0. After 3 hours, separating solution and solid compounds by filtering through 0.22μm syringe filters immediately. Testing the concentration of phosphate and MET. Meanwhile, the solid compounds were tested by XRD spectrogram.

2.3.2. Effects of MET Concentration and Contact Time on Co-precipitation. Adding 60ppb, 80ppb, and 100ppb MET solution into blackwater matrix under 298K, 120rpm. Adjusting pH value was 8.0. Sampling the solution in 20min intervals until 3 hours and testing MET concentration by UPLC/MS-MS after filtering through 0.22μm cellulose acetate membrane. The sediments were separated and tested by XRD spectrogram, which was compared with standard struvite.

3. Results and Discussion

3.1. Phosphate Removal and Struvite Characterization

Phosphate removal (%) from synthetic blackwater under different $C_{Mg}^{2+}:C_{NH_4^+}:C_{PO_4^{3-}}$ ratio were presented in Figure 1. When $C_{Mg}^{2+}:C_{NH_4^+}:C_{PO_4^{3-}}$ were 1.6:1:1, 1.8:1:1, and 2.0:1:1, phosphate removal (%) would reach to more than 95.5%, which was higher than other ratios. Meanwhile, no significant differences among these three results.

![Figure 1. Phosphate removal (%) under different $C_{Mg}^{2+}:C_{NH_4^+}:C_{PO_4^{3-}}$ ratio.](image)

"***"indicates P < 0.01 compared to 1.6, "**"indicates 0.01 < P < 0.05 compared to 1.6.

XRD and SEM images were also used to analyse the synthetic struvite samples. Figure 2 was the comparison of synthetic struvite samples with standard substance by XRD spectrogram. There were no significant differences among synthetic and standard struvite. The SEM images of synthetic struvite samples were presented in Figure 3. In Figure3 (a) and (b), a large amount of transparent rod-like crystals were observed which can be considered as struvite. But in Figure3 (c), circular coacervates impurities were appeared.
Figure 2. XRD graph of synthetic and standard struvite.

Figure 3. SEM images under different $C_{Mg^{2+}}:C_{NH_4^+}:C_{PO_4^{3-}}$ conditions
(a) $C_{Mg^{2+}}:C_{NH_4^+}:C_{PO_4^{3-}}=1.6:1:1$, (b) $C_{Mg^{2+}}:C_{NH_4^+}:C_{PO_4^{3-}}=1.8:1:1$, (c) $C_{Mg^{2+}}:C_{NH_4^+}:C_{PO_4^{3-}}=2.0:1:1$.

In spite of phosphate removal (%), the specific surface area of generated struvite samples would be considered at the same time. Table 2 was the BET surface area of different struvite samples.

Table 2. BET surface area of struvite produced from different $C_{Mg^{2+}}:C_{NH_4^+}:C_{PO_4^{3-}}$ ratio.

| $C_{Mg^{2+}}:C_{NH_4^+}:C_{PO_4^{3-}}$ | BET surface area (m$^2$/g) |
|---------------------------------------|-----------------------------|
| 1.6:1:1                               | 97.4460                     |
| 1.8:1:1                               | 83.3276                     |
| 2.0:1:1                               | 70.5147                     |

The surface area of struvite sample produced under the $C_{Mg^{2+}}:C_{NH_4^+}:C_{PO_4^{3-}}$ ratio was 1.6:1:1 can reach to 97.4460m$^2$/g, which was much larger than any other ratios. N$_2$ adsorption-desorption curve and pore size distribution for struvite powder were shown in Figure 4.

Figure 4. Nitrogen adsorption-desorption curves (a) and pore size distribution (b) for struvite powder. Therefore, 1.6:1:1 of $C_{Mg^{2+}}:C_{NH_4^+}:C_{PO_4^{3-}}$ ratio was chosen as the best one to generate struvite, which used in the next adsorption experiments. Its TEM images was shown in Figure 5.
3.2. Metoprolol Adsorption Experiment

3.2.1. Metoprolol Adsorption Kinetics. The adsorption quantity by adding struvite in the solution with different MET concentrations, e.g. 35ppb, 60ppb, 80ppb, 100ppb, 200ppb, and 300ppb respectively, was shown in Figure 6 (a). The adsorption kinetics graphs were shown in Figure 6 (b) and Figure 6 (c), and the correlation coefficients and parameters of adsorption kinetics were presented in Table. 3. As seen from Figure 6 (a), when the MET concentrations maintained in relative low levels, e.g. 35ppb, 60ppb, and 80ppb, and the solution pH was 8.0, chemisorption was predomination. Meanwhile, the adsorption efficiency improved with the MET concentration increased. In these concentrations, the whole adsorption processes can be divided into three stages, rapid adsorption stage (0-15min), fluctuation stage (15-120min), and steady stage (120-180min). The maximum adsorption quantity was 0.05029mg/g in 80ppb MET concentration.

While, physical adsorption, e.g. Van der Waals’ force, preponderated when the concentrations of MET reached to relative high levels, like 100ppb, 200ppb, and 300ppb under pH 8.0. It was highly notable that MET concentrations can affect Van der Waals’ force. The adsorption efficiency maintained in low level when the concentration of MET was in high level. Overall, the physical adsorption efficiency was decreased when the MET concentration increased. High concentrations of MET will resign adsorption between MET and struvite.

Under practical conditions, the average concentration of MET in source separated black wastewater was 45ppb, and the maximum was 68ppb [6]. Thus, MET adsorption in struvite will not affect its quality theoretically. The environmental risks generated from MET adsorbed in struvite can be ignored.

From Table.3, the correlation coefficients of pseudo first-order were not good enough. But the pseudo second-order correlation coefficients were better when MET concentration was lower than 100ppb. These suggested that there were chemical forces by sharing or exchanging electrons at the solid/solution interface [16,21].

![Figure 6. MET adsorption quantity graph (a), pseudo first-order model (b), and pseudo second-order model (c).](image-url)
### Table 3. Pseudo first-order model and pseudo second-order model parameters under different MET concentrations.

| Pseudo model      | MET concentration | 35ppb  | 60ppb  | 80ppb  | 100ppb | 200ppb | 300ppb |
|-------------------|-------------------|--------|--------|--------|--------|--------|--------|
| Pseudo first-order model | \( R^2 \)         | -      | -      | -      | 0.1312 | 0.60711| 0.06188|
| Pseudo second-order model | \( q_e \) (mgMET/g) | 0.0192 | 0.031213 | 0.049843 | 0.024402 | 0.305119 | 0.002422 |
|                    | \( k_2 \) (g/mg/min) | 5.95843 | -3.0675 | -3.64009 | -14.919 | 0.056011 | -9.85424 |

#### 3.2.2. Metoprolol Adsorption Isotherms.

MET removal rate graphs under 20 °C, 35 °C, 40 °C, and 60 °C were shown in Figure 7 (a), Langmuir and Freundlich isotherms were shown in Figure 7 (b) and (c), respectively. From Figure 7 (a), under 20 °C condition, MET removal rate was the highest among the other temperatures no matter in any concentration level. The highest removal rate reached to over 70% when MET concentration was 50ppb, and in other temperatures, the removal rate of MET were lower than 35%. A conclusion can be drawn from Figure 7(b), (c) and Table 4, neither Langmuir isotherm nor Freundlich isotherm fitted for MET adsorption. So the adsorption between MET and struvite was not monolayer, homogenous or multilayer, heterogeneous adsorption [2,17,22,23].

![Figure 7](image)

**Figure 7.** MET removal rate under 20 °C, 35 °C, 40 °C, and 60 °C (a), Langmuir isotherm (b), and Freundlich isotherm (c).

### Table 4. Correlation coefficients of Langmuir and Freundlich isotherms under 20 °C, 35 °C, 40 °C, and 60 °C.

| Temperature (°C) | Langmuir isotherm | Freundlich isotherm |
|------------------|-------------------|---------------------|
| R²               | 20                | 35                  | 40                  | 60                  |
|                  | 0.7083            | 0.71651             | -                   | -                   |
|                  | 0.90292           | 0.90057             |                     |                     |

#### 3.3. The Effect of pH

Solution pH was another important factor which may affect the adsorption between struvite and MET. Both MET residual rate and removal rate under pH 8.0 to 10.5 were shown in Figure 8. In the pH ranges from 8.0 to 9.5, the removal rate of MET was decreasing gradually. While the removal rate was increasing sharply after pH 9.5.
Figure 8. MET residual and removal rate under pH 8.0-10.5.

It has been known that struvite crystal consists of PO$_4^{3-}$ and NH$_4^+$ tetrahedral and Mg[H$_2$O]$_6^{2+}$ octahedral, and the rectangular ac or bc crystallite facets (a, b, c, are the three-dimension coordinate axes) are rich in Mg[H$_2$O]$_6^{2+}$ or positive charge as compared to ab crystal facets [18,24]. Considering that $pK_a$ of MET was 9.68 [25], it would protonate when the pH range was 8.0 to 9.5 and deprotonate at pH 10.0 and 10.5. Therefore struvite crystallite facets in Mg[H$_2$O]$_6^{2+}$ were prone to reject MET at pH 8.0, 8.5, and 9.0, and the adsorption of MET would occur when pH values were 10.0 and 10.5.

3.4. Effects of pH on Co-precipitation

Under different pH values, phosphate removal rate and MET residual rate in solution were shown in Figure 9(a), and the XRD spectrograms under different pH conditions after 3 hours were compared with standard struvite samples presented in Figure 9(b).

Figure 9. under pH value was 8.0, 9.0, 10.0, and 11.0, PO$_4^{3-}$ removal rate and MET residual rate (a), and XRD graphs of struvite samples compared with standard struvite (b).

In Figure 9(a), phosphate removal rate was in the range of 95% to 100%. Comparing the sediments with standard struvite, there were no differences between their XRD graphs (Figure 9(b)). We can conclude from Figure 9(a) and (b) that the existence of MET will not obstruct the formation of struvite. On the other hand, adding MET into the black wastewater matrix at the pH value was 8.0, 9.0, and 10.0 will increase the residual of MET in solution significantly and this conclusion can be demonstrated by comparing Figure 9(a) with Figure 8. In addition, the residual rate of MET under different pH value was in the range of more than 65% to nearly 100%, most of MET will be maintained in the solution rather than getting into the crystal of struvite. Although when pH was 9.0, residual rate of MET was only 66%, the phosphate removal rate was close to 100% and XRD graph was very similar to standard struvite. A conclusion still can be drawn that phosphate recovery from blackwater will not be affected by the existence of MET obviously. This conclusion was similar to the research taken by Abel-Denee, Abbott and Eskicioglu [26] who studied the disturbance of struvite formation when triclosan and triclocarban existed.
3.5. Effects of MET Concentration and Contact Time on Co-precipitation

MET residual rate under the concentrations of MET were 60ppb, 80ppb, and 100ppb from 20min to 180min at 8.0 pH value was shown in Figure 10. XRD spectrograms of sediments after 3 hours’ reaction and compared with standard struvite was shown in Figure 11.

![Figure 10](image)

**Figure 10.** MET residual rate under time intervals

![Figure 11](image)

**Figure 11.** XRD graphs of sediments.

From Figure 10, there was no significant increase or decrease trend of MET residual rate in solution when MET added into black wastewater matrix. But a conclusion can be drawn that no matter in low or high MET concentration conditions, the final residual rate was higher than the initial state. The residual rate of MET in any time intervals were higher than 96.5%. Figure 11 indicated that the sediments of reaction were struvite.

Thus, we can conclude that, MET molecule shuttled back and forth in the interface of solid-liquid during the process of struvite crystal, and the vast majority of MET will stay in the solution in the end. This phenomenon may be explained by the two steps of struvite formation, which called nucleation and crystal growth [12,14], both of them would complete no more than 45min [18]. So after 60min, MET molecule will get in touch with struvite in the interface of solid-liquid and be rejected by struvite, which was consistent with 3.3.

4. Conclusion

This study gave information about the adsorption and co-precipitation of MET in the formation of struvite from synthetic black wastewater. In adsorption experiment, the whole process can be divided into three stages: rapid adsorption, fluctuation stage, and steady stage. The maximum adsorption quantity was 0.05029mg/g (20℃, pH was 8.0). Chemical adsorption predominated in the low concentration condition, but physical adsorption preponderated in high concentration of MET and decreased with MET concentration increased. Pseudo second-order kinetics fitted for MET adsorption when the concentration was lower than 100ppb. Neither Langmuir nor Freundlich adsorption isotherms fitted for the adsorption experiments.

The pH value was another significant factor which will affect the adsorption efficiency. Mg[H₂O]₆²⁺ in the surface of struvite crystal will adsorb deprotonated MET molecule when pH > pKₐ, and reject protonated MET molecule when pH < pKₐ.

The existence of MET in blackwater matrix would not obstruct the formation of struvite in alkaline codition generally. But MET molecule will shuttle back and forth in the interface of solid-liquid during the formation of struvite and the vast majority of MET will stay in the solution finally.

No matter in the adsorption or co-precipitation experiments, the existence of MET would not affect the struvite recovery from black wastewater. A very majority of MET will be maintained in the solution. The adsorption quantity of MET in the surface of struvite was very few which will not generate serious influences when using struvite as the fertilizer in the agriculture area.
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