Application of PVC-melamine-formaldehyde resin composite in drug adsorption

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Abstract. A new technique for the synthesis of melamine-urea-formaldehyde (MUF) resins was explored in conditions of normothermia. The MUF and common UF resin were analyzed by FTIR. The effects of activation time, pH on the adsorption performance (expressed by the adsorption capacity of Norfloxacin hydrochloride (NOR)) were investigated. The adsorption process of nonresident for Norfloxacin hydrochloride using batch technique was optimized by different parameters including pH, stirring time. The optimum stirring time was 180 min, the adsorption process was favored in acidic medium rather than alkaline one. The equilibrium data were fitted by the Freundlich and Langmuir isotherm models and the adsorption process fitted well with the linear Langmuir isotherm and pseudo-second order kinetics.

1. Introduction
Antibiotics, which are drugs developed to treat bacterial diseases, are widely used in the treatment of humans and animals. Norfloxacin Hydrochloride (NOR) is a third-generation fluoroquinolone antibiotic with high efficacy, low toxicity and good moral effect[1]. Due to the abuse of antibiotics, NOR as well as other fluoro-quinolone antibiotics has been frequently detected in nature waterbodies and sediments in the past few decades[2]. Among all of these, Antibiotic wastewater has an extremely complicated structure, which is harmful and difficult to be biodegrade and polluted. At the same time, direct discharge of antibiotic wastewater without treatment will produce serious environmental and biological influences. Therefore, to reduce environmental pressure and avoid aggravating water pollution, it is necessary to treat antibiotic wastewater[3]. At present, wastewater treatment methods generally employ physical adsorption, chemical adsorption, and biological treatment. Adsorbent types include organic adsorbents, inorganic adsorbents and composite materials. Polymer materials in composite materials are commonly used in wastewater treatment due to their unique structure and good adsorption effect. Most of the activated carbon adsorbs norfloxacin in wastewater. However, in practical applications, activated carbon is easily broken and difficult to recycle. Melamine formaldehyde resin is widely used in dyeing wastewater treatment due to its high nitrogen content and good thermal stability. Free-radically polymerized polyvinyl chloride has many molecular isomers, and its structural defects cause the molecular chain to be unstable, so it cannot be used alone and must be modified. By synthesizing MUF-PVC in this paper, PVC can exhibit different mechanical and physical properties.
2. Materials and methods

2.1. Rough treatment of PVC

4.0 g of sodium chloride, 5.0 g of PVC and 20.0 g of sodium hydroxide were mixed in a set of 100 mL flasks containing 100 mL of distilled water (100 mg/L). The flasks were shaken for 1 h at 35 °C. The impregnated precursor were filtered and dried, and then Obtaining rough PVC powder[4].

2.2. Preparation of melamine - urea - formaldehyde resin composite

1.26 of melamine, 3.0 g of urea and 20.0 g of sodium hydroxide were mixed in a set of 100 mL flasks containing 5mL of formaldehyde solution The flasks were shaken for 1 h at 70°C. The pH was adjusted by using triethanolamine as monitored by pH meter and the water bath is stirred at a constant temperature to obtain a preliminary prepolymer. and then, the samples were shaken in a temperature-controlled shaker at 2h After cooling, the prepared products were washed with deionized water until a neutral pH value was attained. The MUF-PVC were dried at 70 °Cand sieved into uniform granules for further use.

2.3. Characterization of MUF-PVC composite material

The optimum PVC - melamine - urea - formaldehyde (MUF-PVC) was characterized with scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and Fourier transform infrared spectroscopy (FTIR). Different quality of MUF-PVC was mixed in a set of 50 mL Erlenmeyer flasks containing different initial concentration drug of NOR solutions (100 mg/L). The flasks were shaken in a mechanical shaker for 1h. Then the samples were filtered and the residual CIP or NOR concentration was analyzed using a UV-Visible Spectrophotometer (UV-2012PV, China) at maximum wave-lengths of 400 nm and 200 nm for NOR, respectively. Each adsorption experiment was repeated three times and the average adsorption capacity at equili-brum, \( q_e \) (mg/g), \( R(\%) \) was calculated by Equation (1)(2)

\[
R(\%) = \frac{C_0 - C_e}{C_0} \cdot 100\%
\]

\[
q = \frac{(C_0 - C_e)V}{m}
\]

Where \( C_0 \) and \( C_e \) (mg/L) are the liquid-phase concentration of NOR at initial and at equilibrium, respectively. \( V \) (L) is the volume of the solution and \( m \) (g) is the mass of Material[5].

As is show in the Figure 1 the obvious band at 3357 cm\(^{-1}\) was attributed to the stretch vibration of O-H and-NH\(_3\). The peak at 1339 cm\(^{-1}\) and 812 cm\(^{-1}\) could be attributed to the stretch vibration of C=N and Triazine ring. And MUF-PVC and MUF produce the same characteristic peak, which mask the vibration peak of PVC at 1255cm\(^{-1}\),688cm\(^{-1}\),615cm\(^{-1}\). demonstrating the interaction of the piperazinyl group of MUF with PVC. Figure 2 and 3 show the surface morphology of the PVC and MUF-PVC[6]. A distinct and well-developed Clusters of material was observed on the surface of the MUF-PVC. Because there is a large amount of voids between the particles and the particles, the presence of cluster-like substances increases the space and presents a huge advantage of adsorption[7].

3. Results and discussion

3.1. Effect of pH

Due to the adsorption capacity is affected by the pH value and time. The effect of initial MUF-PVC concentration, temperature, PH and time on the adsorption capacity was performed. As showed in Figure 4, the influence of pH variation from 1 to 8 on the removal of NOR solutions is observed. when the PH=6, The adsorption of NOR solution was found to correspond to the maximum %-adsorptions in
the range 95.4-96%, while in the acidic pH range >2-6 and moderately acidic or nearly neutral medium range pH 6-10, the values were slightly decrease.

![Figure 1. FT-IR spectrum of PVC, MUF and MUF-PVC composites.](image)

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![Figure 2. SEM image of PVC material (left), SEM image of roughened PVC material (right).](image)

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![Figure 3. SEM image of MUF-PVC.](image)

**Figure 3.** SEM image of MUF-PVC.

The pH value mainly affects the surface charge characteristics of MUF-PVC and the existence form of norfloxacin. Norfloxacin exists in three forms at different pH values: cation, anion and zwitterion. When the pH < 5.58 (zero charge of the MUF-PVC composite), the surface of the MUF-PVC is positively charged and generates electrostatic repulsion with the norfloxacin of the cation. At this time, the adsorption may depend on the $\pi - \pi$ interaction. When the pH > 7, the surface of MUF-PVC is negatively charged, and the norfloxacin molecule exists as an anion, which causes electrostatic repulsion and reduces the removal rate. Norfloxacin in the zwitterionic region, the removal rate of NOR by MUF-PVC is higher, because the norfloxacin molecule shows strong hydrophobicity in the amphoteric region[8]. Therefore, there may be hydrophobic interaction and $\pi - \pi$ interaction between MUF-PVC and NOR.
3.2. The effect of time
The time effect on adsorption reaction of 25 mL, and NOR at pH 6, 0.02 g MUF-PVC, and 10 min stirring time were made at interval time 30, 60, 90, 120, 150 and 180 min. As shown in Figure 5, the adsorption rate gradually increases with the increase of time. Thus, we can conclude that the removal of NOR is affected by the time. When the adsorbent time is low, the contact area between MUF-PVC and the NOR molecules in the solution is small, which reduces the removal effect; when the adsorption time is increased, the effective adsorption sites on the surface of the MUF-PVC increase, and the surface area of the adsorbent also follows. Increase to increase the adsorption effect. The adsorption of 25mg/L\(^{-1}\) NOR solution was found to correspond to the maximum %-adsorptions in the range 90-100% at 180 min.

3.3. Adsorption thermodynamics
To propose the adsorption mechanism and measure the correlation between the amount of MUF-PVC on the NOR in aqueous solution, the adsorption equilibrium data were fitted with Langmuir and Freundlich isothermal equation.

**Langmuir equation:**

\[
\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m}
\]

\[
R_L = \frac{1}{1 + bc_0}
\]

**Freundlich equation:**

\[
\ln q_e = \ln K_f + \frac{\ln c_e}{n}
\]

Where \(C_e\) is the equilibrium NOR concentration (mg/L), \(q_e\) is the amount of NOR adsorbed at equilibrium, \(q_m\) is the maximum adsorption capacity of MUF-PVC (mg/g), \(C_0\) is the initial concentration of NOR (mg/L), \(b\) is the Langmuir coefficient, and \(q_e\) is the maximum of NOR adsorbed at equilibrium.
Figure 6. Langmuir, freundlich, model fitting curves.

The fitting results were shown in Table 1. As can be seen in Figure 6, the higher $R^2$ showed that the adsorption data can be fit better by Langmuir model than by Freundlich model. The results suggested the adsorption performance of MUF-PVC on NOR was on a heterogeneous surface with sites of varied affinities[9]. Values of $1/n$ were less than 1, which presents a high degree of heterogeneity and a favorable process of adsorption for MUF-PVC onto NOR.

### Table 1. Adsorption thermodynamic parameters at different temperatures.

| Adsorption model     | parameter          | temperature   |
|----------------------|--------------------|---------------|
|                      |                    | 293 K | 303 K | 313 K |
| Langmuir             | $q_m (mg \cdot g^{-1})$ | 12.53 | 12.96 | 13.72 |
|                      | $b (L \cdot mg^{-1})$ | 0.7222 | 0.7222 | 1.361 |
| Freundlich           | $R_L$              | 0.2571 | 0.2571 | 0.1552 |
|                      | $R^2$              | 0.9954 | 0.9991 | 0.9997 |
| Adsorption isotherm  | $K_f (mg \cdot g^{-1})$ | 5.978 | 5.978 | 7.191 |
|                      | $1/n$              | 0.2378 | 0.2378 | 0.2150 |
|                      | $R^2$              | 0.9421 | 0.8531 | 0.8098 |

3.4. Adsorption kinetics
The experimental data of MUF-PVC adsorption on the NOR were fitted by pseudo-first-order model, pseudo-second-order model and intraparticle diffusion model. Figure 7 shows the experimental values of kinetics for MUF-PVC on the NOR[10].
Table 2. Adsorption thermodynamic parameters of ciprofloxacin hydrochloride on MUF-PVC.

| $C_0$ (mg L$^{-1}$) | $q_e$ (mg g$^{-1}$) | Pseudo first-order kinetic model | Pseudo-second-order kinetic model |
|---------------------|--------------------|----------------------------------|----------------------------------|
|                     |                    | $k_1$ ($h^{-1}$) | $q_{e,cal}$ (mg g$^{-1}$) | $R^2$ | $k_2$ (h·g mg$^{-1}$) | $q_{e,cal}$ (mg g$^{-1}$) | $R^2$ |
| 10.0                | 5.8                | 0.0580             | 1.253                          | 0.7861 | 0.6160             | 6.201                          | 0.9995 |
| 12.0                | 7.5                | 0.5011             | 1.690                          | 0.9718 | 0.7514             | 7.586                          | 0.9996 |
| 14.0                | 9.1                | 0.5786             | 1.758                          | 0.9583 | 0.7692             | 9.230                          | 0.9995 |

As shown in Table 2, it can be seen that the pseudo-second-order kinetic model parameters $R^2$ (0.9995, 0.9996, and 0.9995) are closer to 1. The results suggested the adsorption performance of MUF-PVC on NOR was on a heterogeneous surface with sites of varied affinities. This shows that the pseudo-second-order kinetic model is more consistent with the adsorption process[11]-[12].

As is show in the Figure 8, represented the diffusion of NOR molecules from solution to the external surface of SPAC. The plots did not pass through the origin, indicating the intra-particle diffusion was not the unique rate-controlling step.
4. Conclusion
Solvothermal was successfully applied to explore the effects of concentration of MUF-PVC, activation temperature and activation time on the adsorption capacity of NOR. The optimum preparation conditions of MUF-PVC were obtained using pH=6 and 180 min activation time.

(1) Adsorption thermodynamics studies show that the adsorption process of NOR by MUF-PVC conforms to the Langmuir adsorption model.

(2) Adsorption kinetics shows that the adsorption process of NOR by MUF-PVC complies with the pseudo-second-order kinetic equation, and the adsorption process is controlled by both liquid film diffusion and intra-particle diffusion.

(3) The adsorption mechanism showed that there were hydrophobic action and $\pi-\pi$ action on MUF-PVC surface.

(4) Obviously developed material clusters were observed on the MUF-PVC surface. Due to the large number of voids between the particles, the presence of clusters of matter increases the space and shows a huge adsorption advantage.

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