Adsorption behavior of modified porous starch to methyl blue in aqueous solution

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Abstract. Porous starch was prepared by replacing ice crystals in frozen starch gel with ethanol using a solvent exchange method. It was then modified by phosphoric acid and urea via solid-state reaction to produce modified porous starch. The modified starch was used to adsorb methyl blue in aqueous solution. Five adsorption kinetics and five adsorption isotherm were used to fit the experimental data, and the fitting effect was evaluated using seven error analysis methods to get the best model.

1. Introduction
Dye pollutants are important sources of environmental contamination, and could cause serious hazardous impacts on humans, animals and plants. The research on removal of dyes is gaining more and more attention recently. As an organic dye, Methyl blue(MB) is a commonly used substance in dying industry. Numerous methods have been developed for the removing of MB from the wastewater effluents before it is discharged into water bodies[1]. Adsorption is the most favorable method because of the simplicity of design availability, ease of operation and comparatively low cost of application. Global interest in developing novel adsorbents has been made in recent years, modified starch is one of environment-friendly, cheap sources for adsorbent preparation.

In this work, modified porous starch was prepared as an adsorbent with high external surface area for the removal of MB from aqueous solution. Different adsorption kinetics and adsorption isotherm models were used to fit the experimental data, the best of which could well describe the adsorption process.

2. Experimental

2.1. Materials
Methyl blue, phosphoric acid, sodium hydroxide, hydrochloric acid, urea and ethanol of analytical reagent and potato starch of biochemical reagent were obtained from Guoyao Chemical Reagent Shanghai China. All reagents were used without further purification.

2.2. Preparation of porous starch
Porous starch was prepared by replacing ice crystals in frozen starch gel with ethanol using a solvent exchange method. The details were illustrated in the previous literature[2].
2.3. Preparation of modified porous starch
9.8 g phosphoric acid, 7.2 g urea, and 16.2 g milled porous starch powder were mixed vigorously for 5 min. The mixture was put in a drying oven to react at 140 °C for 3 h. The reactant was then grind into powder and purified with water and ethanol respectively. Modified porous starch was got after drying at 50 °C in vacuum oven.

2.4. Adsorption
Adsorption of MB with modified porous starch was carried out by the batch equilibrium technique with 0.2g of modified porous starch and MB solution with concentration range of 100 mg/L to 300 mg/L in a conical flask. In the experiments, separating flasks were prepared and shaken at 230 rpm for 0 to 120 min under the temperature over the range of 25 ℃ to 45 ℃. Then the supernatants were centrifuged at 2000 rpm for 10 min to be clear. UV-vis spectrophotometer was used to determine the concentration of MB after adsorption at 665 nm with a standard curve of

\[ y = 0.00472x - 0.05668 \]  

\[ (R=0.996) \]

Blank sample without adsorbate was used for the comparison under the same conditions.

The equilibrium adsorbed quantity of MB (\( Q_e \)) on modified porous starch is calculated in equation:

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

where \( C_0 \) and \( C_e \) are initial and equilibrium concentration of the MB solution expressed in mg/L, respectively; \( V \) is the volume of MB solution expressed in L; \( m \) is the mass of the modified porous starch expressed in g; \( Q_e \) is express in mg/g.

2.5. Adsorption models and error analysis equations
The most commonly used five kinds of adsorption kinetics(Lagergren first order, Lagergren second order-1, Lagergren second order-2, and Lagergren second order-3 and Lagergren second order-4, five kinds of adsorption isotherm(Langmuir-1, Langmuir-2, Freundlich-1, Freundlich and Dubinin-Radushkevich) and seven kinds of error analysis equations(ERRSQ, HYBRZD, MPSD, ARE, EABS, G-test and Chi-square test) were selected to fit the experimental data and evaluate the fitting effect, respectively. The expression could be found in the reference[3].

3. Results and Discussion

3.1. Error analysis of adsorption kinetics
The fitting results of five different adsorption kinetic models are analyzed by seven error function, and the data obtained are listed in Table 1. From Table 1, it can be seen that when Lagergren second order-1 adsorption kinetic model is used for fitting, five error analysis methods of the seven error analysis methods, such as HYBRZD, ERRSQ, MPSD, ARE and Chi-square test, get the minimum value. Only in the EABS and G-test, the Lagergren first order model is the best model, while the Lagergren second order-1 model is listed in the second place. Therefore, the Lagergren second order-1 model is the best adsorption kinetic model to fit the experimental data.

Table 1. Error analysis of five adsorption kinetic models.

| Error function | Lagergren first order | Lagergren second order-1 | Lagergren second order-2 | Lagergren second order-3 | Lagergren second order-4 |
|----------------|-----------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| ERRSQ          | 122.9964              | 0.0000405                | 0.0000788                | 0.0001118                | 0.0000474                |
| HYBRZD         | 6248.4568             | 0.0018383                | 0.0023616                | 0.0042603                | 0.0021963                |
| MPSD           | 2.9187820             | 0.0000012                | 0.0000035                | 0.0000042                | 0.0000013                |
| ARE            | 124.9338              | 0.0698000                | 0.0695000                | 0.0909900                | 0.0769000                |
| EABS           | 2.9590780             | 0.0018226                | 0.0023385                | 0.0027265                | 0.0019501                |
| G-test         | 535.59900             | 0.0322203                | 0.0679394                | 0.0360099                | -0.0048763               |
| Chi-square test| 8888.9585             | 0.0000405                | 0.0000789                | 0.000161                 | 0.0000474                |
3.2. Error analysis of adsorption isotherm

The fitting results of five different adsorption isotherm models are analyzed by seven error function, and the data obtained are listed in Table 2. From Table 2, it can be seen that when Langmuir-2 adsorption isotherm model is used for fitting, six error analysis methods of the seven error analysis methods, such as ERRSQ, MPSD, ARE, EABS, G-test and Chi-square test, get the minimum value. Only in the HYBRZD, the Freundlich-1 model is the best model. Therefore, the Langmuir-2 model is the best adsorption isotherm model to fit the experimental data.

| Error function | Langmuir-1 | Langmuir-2 | Dubinin-Radushkevich | Freundlich-1 | Freundlich |
|----------------|------------|------------|----------------------|---------------|------------|
| HYBRZD         | 175.6337913| 175.6337913| 7.384249616          | 6.64810171    | 140.6322765|
| ERRSQ          | 6315.988945| 65.5675343 | 188.5017872          | 182.7672723   | 5182.285545 |
| MPSD           | 5.987543958| 0.105595652| 0.545182915          | 0.342189222   | 4.536404033 |
| EABS           | 175.7168100| 18.3679600  | 27.2751000           | 30.7250000    | 157.0840200 |
| ARE            | 5.99376212 | 0.736973083 | 1.31734399           | 1.28202599    | 5.204881592 |
| G-test         | 1452.865306| 5.541488241 | 17.23867398          | 27.91188695   | 402.3451596 |
| Chi-square test| 893101.0824| 2.560903542 | 14.4192626          | 7.764522335   | 1465.042816  |

3.3. Fitting result

The experimental data from adsorption process of modified porous starch to MB in aqueous solution was fitted, and the fitting result is shown in Figure 1 and Figure 2, when fitting by the best adsorption kinetic model and the best adsorption isotherm model, respectively.

![Figure 1. Fitting result of Lagergren second order-1 adsorption kinetic model.](image1)

![Figure 2. Fitting result of Langmuir-2 adsorption isotherm model.](image2)

4. Conclusions

Modified porous starch was prepared by reacting porous starch with phosphoric acid and urea via solid-state reaction, and used as an adsorbent to adsorb methyl blue in aqueous solution. Five adsorption kinetic models, like Lagergren first order, Lagergren second order-1, Lagergren second order-2, Lagergren second order-3 and Lagergren second order-4, and five adsorption isotherm models, like Langmuir-1, Langmuir-2, Freundlich-1, Freundlich and Dubinin-Radushkevich, were used to fit the adsorption process. Seven kinds of error analysis functions, like ERRSQ, HYBRZD, MPSD, ARE, EABS, G-test and Chi-square test, were selected to evaluate the fitting effect. The results show that
Laguerre second order-1 and Langmuir-2 are the best model, which could be used to well describe the adsorption behavior of modified porous starch to methyl blue in aqueous solution.

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