Adsorption equilibrium and kinetics of methylene blue on rice husk ash straw Composites

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Abstract. In this paper, corn straw in Jilin area was used as the base material, and the corn straw was modified by the alkaline solution system formed by urea trisodium phosphate sodium tetraborate, then the residue of rice husk burning in power plant was added. The rice husk ash / straw composite material was made by spin coating evaporation process, and the adsorption performance of methylene blue in wastewater was explored, and the linear regression analysis was carried out by Origin software The kinetic equation was obtained by regression fitting. The experimental results showed that: when the ratio of rice husk ash and straw was 1:2, the adsorption performance of methylene blue in wastewater was the highest, the adsorption rate was 96.3%, and the maximum adsorption capacity was 578.0mg/g; at the same time, it was found that the kinetic model was in line with the pseudo second order adsorption kinetic model, indicating that the adsorption process of methylene blue in wastewater by rice husk ash / straw composite was mainly chemical reaction.

1. Introduction
Rice husk ash is the product of rice husk incineration power generation. Rice husk ash contains a lot of silica and carbon, of which silica is about 72% and carbon is about 9% [1]. However, the domestic treatment and utilization of rice husk ash are not mature, and most of them are sold as plant ash. The placement and storage of rice husk ash has a certain impact on the environment. Because of its light weight and small fineness, it is easy to migrate with wind and water. The price of rice husk ash is extremely low and it has not exerted its economic value [2]. Therefore, it is necessary to explore a more economical and effective way to utilize it as a resource. Because of its high specific surface area and high porosity, rice husk ash has great potential to be used as an effective adsorbent [3-4]. At present, rice husk ash is commonly used in the field of building materials to enhance the mechanical properties of concrete [5-6], replace clay to enhance the compressive strength of block [7], and apply to the adsorption of gas [8].

2. Experiment
2.1. Raw materials and equipment
Rice husk ash, from Huanneng Jilin Power Generation Co., Ltd.; corn straw, from Jilin region; sodium tetraborate, Beijing chemical plant; trisodium phosphate, Tianjin Huadong chemical plant; urea,
Xilong Science Co., Ltd.; Sodium hydroxide, East China Chemical Plant in Tianjin; PH test paper, oak Bioengineering (Yangzhou) Co., Ltd.; Ve-a laboratory water purifier, Shenzhen Hongsen Environmental Protection Technology Co., Ltd; Qm-3sp4 planetary mill, LAB Leibu Technology Co., Ltd; HJ-3 digital constant temperature magnetic stirrer, Gongyi Yuhua Instrument Co., Ltd.; 1000g swing crusher, Guangzhou leimai mechanical equipment Co., Ltd.; wd-9 Model 415B ultrasonic cleaner, Beijing Liuyi Instrument Factory; TGL-16M high speed freezing centrifuge, Hunan Xiangyi Laboratory Instrument Development Co., Ltd.; xgl-65 electric blast drying oven, Tianjin taist Instrument Co., Ltd.; uv-2600 visible spectrophotometer, Shimadzu enterprise management (China) Co., Ltd.

2.2. The straw was modified
In this experiment, the alkali solution system formed by urea trisodium phosphate borax was used to modify the straw. The specific process is as follows: the straw material was separated from the outer skin and the inner core of the straw, the straw material used in the experiment was the outer skin of the straw, and the corn straw was crushed by a 1000g swing crusher. The corn straw fiber with the particle size of 0.5-2.0mm was selected and put into the 80 ℃ drying oven for drying. After drying for 4h, the moisture content of straw was less than 10%; then the alkali solution formed by urea trisodium phosphate sodium tetraborate was added for soaking treatment, and after soaking for 4h, the straw was washed until the pH was neutral, and finally the modified straw material was obtained.

2.3. Preparation of rice husk ash / straw Composites
The rice husk ash used in the experiment has high activity when calcined at high temperature. Calcined rice husk ash was placed in planetary ball mill, and then milled for 30min at the speed of 300r / min to make the particle fineness more uniform; the milled rice husk ash, corn straw modified by alkali solution and distilled water were put into the container according to a certain proportion to stir evenly, and then put into the ultrasonic cleaner for uniform dispersion, and then put into the temperature of 90 ℃ and rotating speed for 30min,300 R / min magnetic stirrer was used to stir until the sticky rice husk ash / straw composite was formed.

2.4. Drawing of methylene blue standard curve
Prepare six volumetric flasks with a volume of 100ml, stick labels No. 1-6 on the surface, respectively transfer 1ml, 2ml, 4ml, 6ml, 8ml, 10ml from 100mg/L methylene blue standard solution into the prepared volumetric flasks, add water to dilute until the scale line is tangent to the lowest concave liquid level of the volumetric flasks, and finally 1mg/L, 2mg/L, 4mg/L, 6mg/L, 8mg/L, 10mg/L methylene blue solution can be obtained. Liquid. Use uv-2600 visible spectrophotometer to measure the absorbance a of methylene blue in the label volumetric flask. The standard curve of methylene blue can be obtained by using concentration C as abscissa and absorbance Ai as ordinate, and then fitting the above six points with linear regression[9].

2.5. Adsorption of methylene blue on rice husk ash / straw composites
At room temperature, 5g rice husk ash / straw composite was added to the methylene blue solution with the concentration of 30mg/L, and the mixed solution was placed on the magnetic stirrer to stir and adsorb until the adsorption reached equilibrium. The absorbance of the solution was measured by uv-2600 visible spectrophotometer at 665nm. The concentration could be calculated according to the standard curve, and then the adsorption rate of methylene blue on rice husk ash / straw composite was calculated.

The formula for calculating the adsorption rate η and adsorption capacity Wt of rice husk ash / straw composite for methylene blue is as follows:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\%$$  \hspace{1cm} (1)
In the formula: \( C_0 \) is the initial concentration of methylene blue, mg/L; \( C_e \) is the equilibrium concentration of methylene blue, mg/L.

\[
W_t = \frac{CV - CV}{m}
\]  

(2)

In the formula: \( W_t \) is adsorption capacity of rice husk ash / straw composite material at time \( t \), mg; \( C \) is the initial concentration of methylene blue, mg/L; \( C_t \) is concentration of methylene blue at time \( t \), mg/L; \( V \) is volume of methylene blue, L; \( m \) is rice husk ash / straw composite material quality, mg.

3. Results and discussion

3.1. Drawing of methylene blue standard curve
The linear regression equation of methylene blue standard curve was as follows:

\[
A = 0.0488 + 0.15046C
\]  

(3)

\( A \) is the absorbance of methylene blue, Abs; \( C \) is the concentration of methylene blue, mg/L; Fitting coefficient of fitting equation \( R^2 = 0.9989 \).

Fig. 1. Methylene blue standard curve

3.2. Effect of different contents of rice husk ash on adsorption rate
Figure 2 shows the influence curve of different contents of rice husk ash on the adsorption rate, and table 1 shows the adsorption results of different contents of rice husk ash on methylene blue. It can be seen from Figure 2 that with the increase of the content of rice husk ash, the adsorption performance of modified straw material shows an increasing trend. When the content of rice husk ash is 5g, the adsorption rate of methylene blue is the highest, reaching 96.3%. Compared with the blank control, it increased by 15%. Then, with the increase of the amount of rice husk ash, it is inversely proportional to its adsorption rate, indicating that the adsorption of methylene blue in water by rice husk ash straw composite has reached saturation. It can be seen from table 1 that the adsorption capacity of methylene blue by rice husk ash straw composite can be divided into two stages with the content of rice husk ash of 5g as the middle point. The first stage is with the increase of rice husk ash, the adsorption capacity of methylene blue is fast. The second stage is that the addition amount of rice husk ash is inversely proportional to the adsorption amount of methylene blue, which indicates that the adsorption of methylene blue by rice husk ash has reached equilibrium. Figure 3 is to explore the effect of adsorption time of rice husk ash straw composite on its adsorption capacity when the ratio of rice husk ash and corn straw is 1:2. It can be seen from the figure that with the extension of adsorption time of
rice husk ash straw composite on methylene blue in wastewater, the adsorption capacity is gradually increasing.

![Graph](image-url)

**Fig. 2. Effect of different contents of rice husk ash on adsorption rate**

![Graph](image-url)

**Fig. 3. Effect of adsorption time on adsorption capacity**

| Different contents of rice husk ash (g) | 1    | 2    | 5    | 10   | 20   |
|----------------------------------------|------|------|------|------|------|
| Equilibrium absorbance (A)             | 1.730| 0.786| 0.215| 0.460| 0.537|
| Equilibrium concentration (mg/L)       | 11.174| 4.899| 1.104| 2.866| 3.245|
| Equilibrium adsorption capacity (mg/g) | 376.6| 502.0| 578.0| 543.0| 535.1|

3.3. Study on the kinetics of methylene blue in rice husk ash / straw Composites

In order to study the adsorption kinetics of methylene blue in water by rice husk ash / straw composite, the quasi first order kinetics model and quasi second order kinetics model were used to study the adsorption kinetics mechanism of rice husk ash / straw composite.

The quasi first order kinetic equation is as follows:
The quasi second order kinetic equation is as follows:

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]  

(4)

where \(q_e\) is the adsorption capacity at equilibrium, mg/g; \(q_t\) is the adsorption capacity at time \(t\), mg/g; \(k_1\) is the first order adsorption rate constant.

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

(5)

\(q_e\) is the adsorption capacity at equilibrium, mg/g; \(q_t\) is the adsorption capacity at time \(t\), mg/g; \(k_1 / k_2\) is the first order adsorption rate constant.

Fig. 4. Adsorption kinetics of methylene blue at 298.15K

The different adsorption kinetic curves are shown in Fig. 4. Fig. 4 (a) shows the quasi first order kinetic curve of methylene blue adsorption of rice husk ash straw composite at 298.15K, and Fig. 4 (b) shows the quasi second order kinetic curve of methylene blue adsorption of rice husk ash straw composite at 298.15K. The regression correlation coefficient \(R^2\) of quasi first order kinetic curve was 0.7686, and that of quasi second order kinetic curve was 0.9999.

Therefore, in the temperature range studied, the adsorption of methylene blue by rice husk ash straw composite is more in line with the pseudo second order kinetics (\(R^2 > 0.99\)), indicating that the adsorption of methylene blue by rice husk ash straw composite belongs to chemical adsorption[10].
3.4. SEM analysis
Figure 5 is a scanning electron microscope picture of rice husk ash/straw composite material. Figure c is a scanning electron microscope picture of corn stalks treated with NaOH solution, figure d shows the corn stover after soaking in the alkali solution formed by urea-trisodium phosphate-sodium tetraborate. In the figure c, it can be seen that the organic matter and other impurities on the surface of the corn stalk treated with the NaOH solution have almost disappeared, and the “gully” formed on the surface of the corn stalk is more clear. In the figure d, the surface of the corn stalks treated with urea-trisodium phosphate-sodium tetraborate is flatter, and some of them have micropores, which increases the surface area of the stalks and enhances its adsorption capacity. From the two figures, it can be seen that the alkaline solution greatly increases the specific surface area of the corn stalk and eliminates the residual organic impurities in the corn stalk skin.

![Figure 5: Scanning electron micrograph of rice husk ash/straw composite material](image)

(c) Corn straw after NaOH solution treatment

![Figure 5: Scanning electron micrograph of rice husk ash/straw composite material](image)

(d) Corn stover treated with urea-trisodium phosphate-sodium tetraborate

4. Conclusion
(1) The alkali solution system of urea trisodium phosphate borax was used to modify corn straw, because the alkali solution can eliminate the sugar, esters and some inorganic components in corn straw. Measuring the absorbance of methylene blue at different concentrations with UV-2600 visible light spectrophotometer, then use Origin software to perform linear regression fitting on the absorbance of methylene blue at different concentrations. Finally draw the methylene blue standard curve, the fitting coefficient in the fitting equation is $R^2=0.9989$.

(2) The adsorption performance of rice husk ash straw composite prepared by spin coating evaporation process for methylene blue was investigated. The results showed that when the ratio of rice husk ash to straw was 1:2, the composite had the best adsorption performance, with the highest
adsorption rate and capacity of 96.3% and 578 mg/g, respectively, compared with the blank control, it increased by 15%; from the curve of adsorption rate of different content of rice husk ash, it can be seen that the adsorption rate of rice husk ash straw composite for methylene blue in wastewater increases with the increase of rice husk ash content, and the adsorption rate curve slightly tends to decline when the content of rice husk ash is 5g, indicating that the adsorption of methylene blue by rice husk ash has reached equilibrium. The results showed that the pseudo second order kinetic model could better reflect the adsorption of methylene blue by rice husk ash straw composite, and the adsorption process was mainly chemical reaction.

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