Preparation of NaOH Modified Spent Grain Adsorbent and Adsorptive Properties for Dyes

Yawei Wang [1]*, Yaxin Lv [1]*, Haiqi Shen [1], Shenyang Xu [1], Yu Guo [1], Zhijie Bao [1], and Yan Feng [1]**

School of Textile Science and Engineering, Tiangong University, 399 Binshui West Road, Xiqing District, Tianjin
Email: fengyan@tjpu.edu.com

Abstract. The spent grain which is the by-product of beer production contains cellulose, lignin and other substances. It can be used as an adsorbent material not only for waste utilization, but also to reduce environmental contamination. The structure and morphology of spent grain (SG) were discussed. The NaOH modified spent grain (ASG (alkaline spent grain)) was prepared. And the effects of the parameters such as NaOH concentration, temperature and time on the absorption performance of Methylene blue wastewater were analyzed. The results showed that, when the modifier concentration reached 5 g/L, the temperature and time was 60°C and 120 min respectively, the maximum decolorization could reach 95.87%. The decolorization rate of 55.82% of the original grain increased significantly. The adsorption process of themodified materials was chemical adsorption, and the adsorption behavior could be described by Freundlich and pseudo-second-order kinetics equation.

1. Introduction

With the rapid development of printing and dyeing industry, the discharge of dye wastewater has increased dramatically, which has resulted in serious environmental pollution. Dye wastewater is characterized by complex components, high chromaticity, more suspended substances, unstable water quality and more refractory substances. Wastewater often contains a large number of organic compounds with stable properties and certain absorption ability to external light, such as hydrocarbons, aromatic compounds, and polycyclic aromatic hydrocarbons. Further, several organic compounds found in wastewaters are non-biodegradable, thus reducing the transparency and self-purification ability of the water body, resulting in serious ecological and environmental problems. At present, several techniques have been tested for treating dye wastewaters including physical treatment, chemical treatment and biological treatment. Among them, physical and chemical treatment methods are more efficient, but the cost is also higher and easy to cause secondary pollution [1-3]. Biological treatment methods are environmentally friendly and cost-effective, but they are affected by treatment conditions and treatment environment. Adsorption is one of the physical methods to treat dye wastewater. It mainly purifies dye wastewater through porous and high specific surface area substances, such as activated carbon and resin. Among all the techniques, adsorption processes using solid media prove to be very efficient for the removal of dye from wastewaters. Adsorption processes offer several benefits in such as low capital, operational costs and widely used. Therefore, it is of great significance to develop new adsorbents with excellent adsorption function for dye wastewater.

Spent grains (SG), the major by-products in beer industry, most of them are discarded directly and a small amount is used in feed industry, resulting in waste of resources and environmental pollution. SG that basically consists of cellulose and lignin, is an attractive alternative for removing dye from

wastewater as it has a large specific surface area and biodegradability, with many functional groups such as carboxyl, hydroxyl and amino that are responsible for the binding of organics. Therefore, the adsorption of organics by SG has potential for industrial use. At present, the research on adsorbing materials of spent grain is focused on the chemical modification of SG by alkalization, acidification, esterification and mercaptoylation, which can be used for the adsorption of dye wastewater and heavy metal ion wastewater such as cadmium and lead. In this article, SG was chosen as a starting material for an adsorbent and NaOH as modifier [3-10]. The effects of process parameters and concentration of methylene blue solution on the adsorptive performance of alkaline spent grain (ASG) and its adsorption mechanism were studied. Finally, the application of SG in the treatment of dye wastewater was investigated.

2. Experimental

2.1. Materials
Spent grain was obtained from Junling brewery located in Tianjin, China. The waste was washed with deionized water to remove soil particles or dusts, then dried at 60 ℃ for 5h and ground to pass through a 28 mesh sieve in order to be used in further chemical modification. Sodium hydroxide (NaOH) and Methylene Blue (MB) were purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd., Tianjin, China and Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China, respectively.

2.2. Preparation of ASG and Simulated MB Dye Solutions
Measure a certain concentration of NaOH, followed by blending with 0.5 g of spent grain prepared as above and stirring at room temperature for a certain time. Thereafter, quaternization of SG with NaOH was carried out at room temperature for a certain time. After the reaction, the unreacted NaOH was removed by washing with deionized water. Finally, the residues were dried at 60 ℃ to use.
A stock solution of MB dye was prepared (20 mg L^{-1}) by dissolving a required quantity of MB dye powder in deionized water.

2.3. Structural Characterization of SG, ASG
The surface and cross-sectional morphologies of SG and ASG were examined by field emission scanning electron microscopy (FESEM, TM-3030, Hitachi, Japan).
The surface functional groups of SG and ASG affecting the adsorption were identified by Fourier transforms infrared spectrometer (FTIR, Nicolet iS50, Thermo Fisher Scientific). The spectra were recorded from 4000 to 400 cm^{-1}.
The specific surface area of SG and ASG were determined by N2 adsorption method at 70 ℃ and the diameter of the tube was 6 mm (BET, ASiQM000000-6, Quantachrome).

2.4. Adsorption Experiments
Dried SG and ASG added to MB dye solutions, respectively. The test solutions were obtained by shaking, adsorbing and filtering. The clarified supernatants were collected from the flasks at predetermined time intervals. MB dye concentration in the solution before and after treatment was calculated from the calibration curve, which was prepared by measuring the absorbance of different concentrations of MB dye solutions at λ$_{max}$ 664 nm using a UV Spectrophotometer (UV-1800, Shanghai Metropolitan Instruments Co). Then, the decolorization rate and adsorption of MB dye by SG and ASG were calculated. The percent of dye removal was calculated by the following equation:

$$\% \text{ removal of MB dye} = \frac{c_0 - c}{c_0} \times 100\% \qquad (1)$$

Where C_0 and C are the initial and final MB dye concentration (mg L^{-1}) in the solution, respectively.
The amount of dye adsorbed at equilibrium onto BSG, q$_e$ (mg g^{-1}), was calculated as follows:

$$q_e = \frac{v(c_0 - c)}{m} \tag{2}$$

Where V is the dye solution volume (L) and m is the mass of adsorbent used (g).

2.5. Calibration Curve
The calibration curve was drawn in Figure 1 by measuring the absorbance of different known concentrations of MB dye solutions. The relationship between solution concentration C and absorbance A is: A=k·C. And a linear correlation was found between A and C. From Figure 1, it can be seen that the plots are linear, the fitting equation of the curve is Y=62.91057 X+0.07759, the correlation coefficient is $R^2 = 0.98226$, and the intercept is 0.07759.
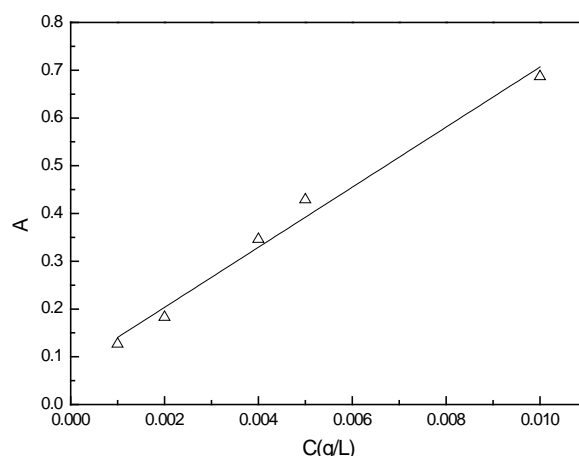

Figure 1. MB Calibration Curve

3. Results and Discussion

3.1. Characterization of SG, ASG

3.1.1. SEM of SG, ASG
Figure 2 shows the SEM micrographs of SG, ASG ((a) and (b) SEM micrographs of SG, (c) and (d) SEM micrographs of ASG). There is some ridges and gullies on the surface of the SG sample, and most of the surface is rough and porous. Compared with SG, great changes are observed on the surface of the modified SG. The number of ridges and gullies on the surface of ASG increased greatly, which further increased the specific surface area, facilitated the exposure of surface functional groups, provided sufficient adsorption space for ASG as adsorbent material, and promoted its adsorption of dye.
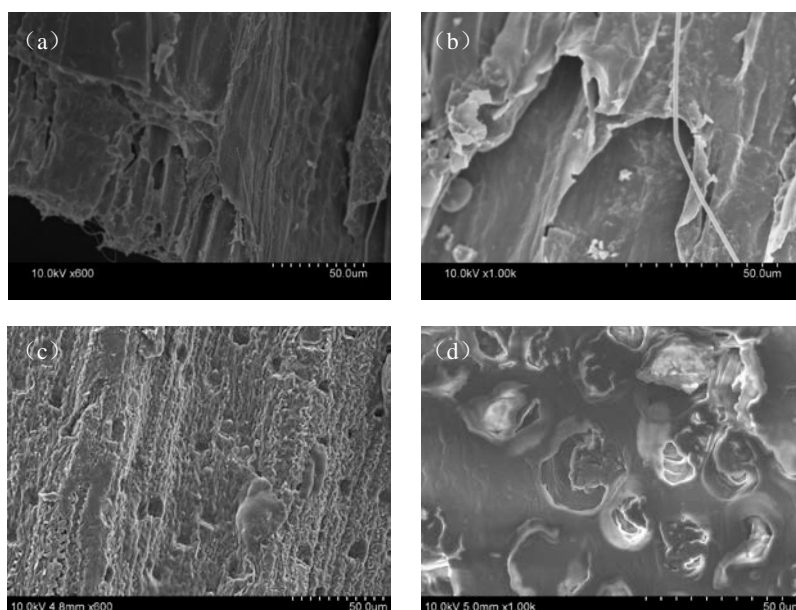
Figure 2. SEM Images of Spent Grain (a, c. 600 Times Larger, b, d. 1000 Times Larger，a, b. SG, c, d. ASG)

3.1.2. Infrared spectra of SG, ASG

The spent grains are predominantly composed of cellulose and lignin. The lignocellulosic polymers lignin and cellulose comprise over 45% of SG's dry weight, while proteins account for another 21%.The infrared spectra of SG and ASG are shown in Figure 3, respectively. The broad peaks at 3000-3700 cm^{-1} are attributed to the hydroxyl groups which formed hydrogen bonds between carbohydrate molecules in spent grain; the absorption peaks at 2920 cm^{-1} and 2850 cm^{-1} are caused by asymmetric-CH_2; the absorption peaks at 1650 cm^{-1} are attributed to carbonyl C=O; the absorption peaks at 1030 cm^{-1} are mainly caused by C-O bonds; and the absorption peaks at 529 cm^{-1} and 443 cm^{-1} are mainly caused by C-Cl bonds. Therefore, spent grain contains hydroxyl, carboxyl and other active functional groups, which can participate in active adsorption.

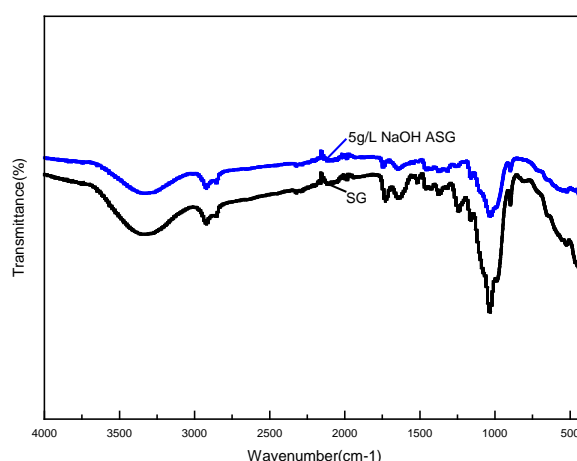**Figure 3.** FTIR of Spent Grain

3.1.3. BET of SG, ASG

The results of specific surface area, pore volume and pore sizes of spent grains are shown in Table 1. It can be seen that the grain grains have smaller pore size and higher specific surface area. They are

porous biomaterials and can be used to prepare adsorption materials.

Table 1. Structural Characterization Parameters of SG

Surface area (m^2/g)	Pore volume (mL/g)	Pore size (nm)
67.231	0.123	1.751

3.2. Effect of Technological Parameters on MB Dye Adsorption
The modification technology includes NaOH solution concentration, modification temperature and time, which have important influence on the adsorption performance of SG.

3.2.1. Effect of Modification Temperature and Time on MB Dye Adsorption
The modification temperature is a key parameter affecting the adsorption performance of ASG. Figure 4 and Figure 5 show the effects of modification temperature and time on the adsorption properties of SG and ASG. It can be seen from Fig. 4 that with the increase of temperature, the decolorization rate and adsorption of the SG and ASG on the MB solution increase, and the equilibrium was attained, after which it remained constant. The optimum modification temperatures are 50℃ and 60℃, respectively. This is due to the activation of partially inactivated adsorption sites with the increase of temperature, which generates more adsorption sites and increases its adsorption effect on MB. This effect is stronger for ASG. As the temperature continues to rise, the adsorption sites of the two tend to be saturated, and the number does not continue to increase. As a result, the curves tend to be stable.

Another important parameter in the adsorption process is modification time because it gives an idea of the equilibrium time for the adsorption process. It can be clearly observed from Figure 5 that the decolorization rate and adsorption increase with an increase in contact time and the equilibrium is attained during the time interval of 120 min for ASG, after which it remained constant. For SG, the decolorization rate and adsorption only slightly fluctuated with time, and the maximum is attained during the time interval of 90 min. With the increase of modification time, the effect of NaOH on spent grain is obvious, and the surface activity of spent grain is continuously improved. But when modification time reaches a certain value, the activity of spent grain tends to be stable, so its adsorption effect is no longer obvious change.
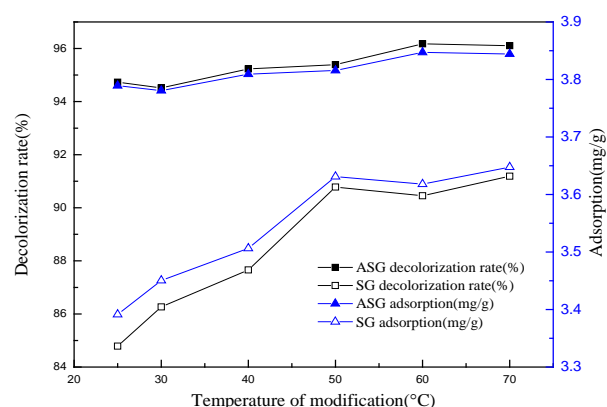

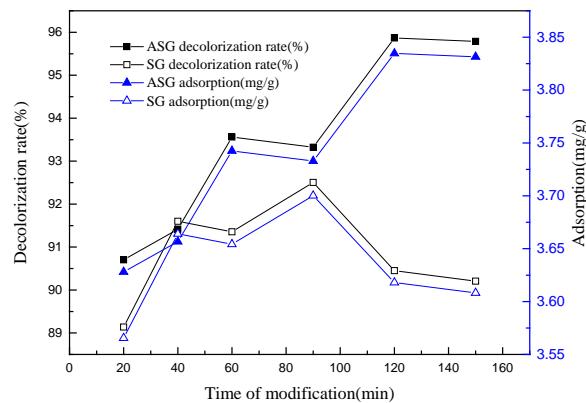**Figure 4.** Effect of Modified Temperature on Adsorption Effect

Figure 5. Effect of Modification Time on Adsorption Effect

3.2.2. Effect of NaOH Solution Concentration on MB Dye Adsorption

When modification temperature is 60℃ and time is 120 min, the effect of NaOH solution concentration on the adsorption performance of ASG is shown in Figure 6. In the initial stage, with the increase of NaOH solution concentration, the decolorization rate and adsorption of ASG to MB dye increased. When the concentration reached 5 g/L, the decolorization rate and adsorption of ASG to MB dye reached the maximum. When the concentration of NaOH solution continued to increase, the decolorization rate and adsorption decreased, and when the concentration reached 8 g/L, the decolorization rate and adsorption of ASG to MB dye were lower than SG. The reason is that when the concentration of modifier is low, the alkalinity of the solution increases with the increase of the concentration of modifier, which is conducive to hydrogen bonding, improving the surface activity of wort and improving its adsorption effect. But when the concentration of NaOH solution is too high, the surface structure of spent grain will be destroyed and the adsorption effect will be affected. Therefore, the optimum concentration of NaOH solution was taken as 5 g/L.
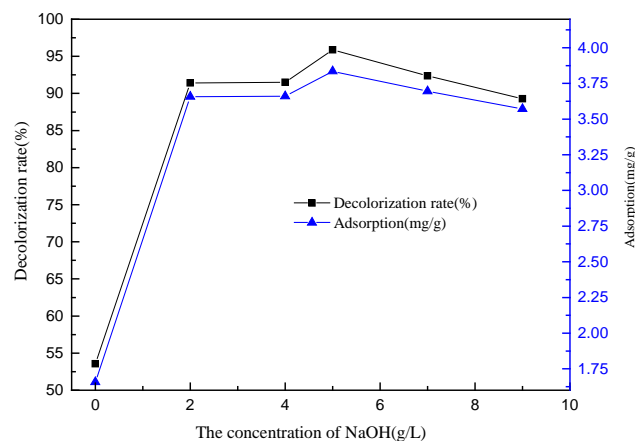

Figure 6. Effect of NaOH Concentration on Adsorption Effect

3.3. Effect of Adsorbent Dose on MB Dye Adsorption

The effect of adsorbent dose on the decolorization rate was investigated under the optimal modification temperature and time conditions and the results are presented in Figure 7. The experimental results show that the decolorization rate of SG and ASG to MB increases with increase in adsorbent dose loading, up to 0.5 g/L and 1.5 g/L respectively. However, the adsorption of SG and ASG to MB decreased above the adsorbent dosage value. This is because when the amount of spent grain reaches a certain value, the reaction between them and MB reaches equilibrium. When the spent grain is added, the adsorption amount per unit mass of spent grains is reduced, that is, the adsorption
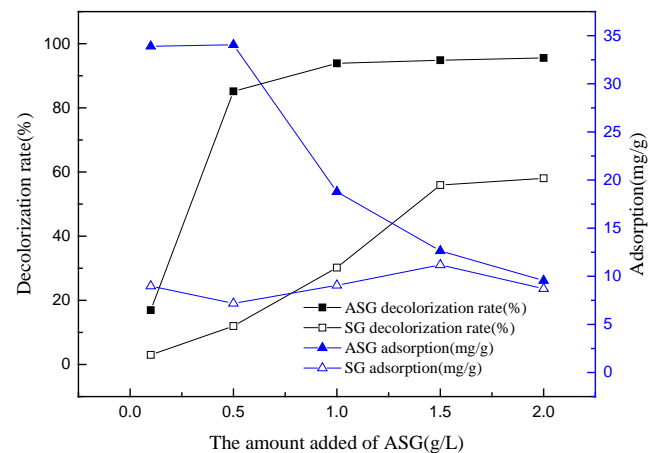
amount is decreased.

Figure 7. Effects of Adsorbent Dose on MB Dye Adsorption

3.4. Effect of Initial Concentration on MB Dye Adsorption

The effect of initial concentration of MB dye solution by SG and ASG on adsorption efficiency was investigated and the experimental results are shown in Figure 8. With the increase of the initial concentration of MB dye solution, the adsorption of SG and ASG increased, while the decolorization rate of ASG increased first and then decreased, while the decolorization rate of SG to MB dye solution remained stable and slightly decreased. This is because when the concentration of MB solution is within a certain range, the active groups on the surface of ASG can fully interact with MB molecule and have a good adsorption effect. However, when the MB dye solution is too high, the adsorption of MB dye on spent grain reaches saturation, and its adsorption changes slightly, while the decolorization rate decreases.
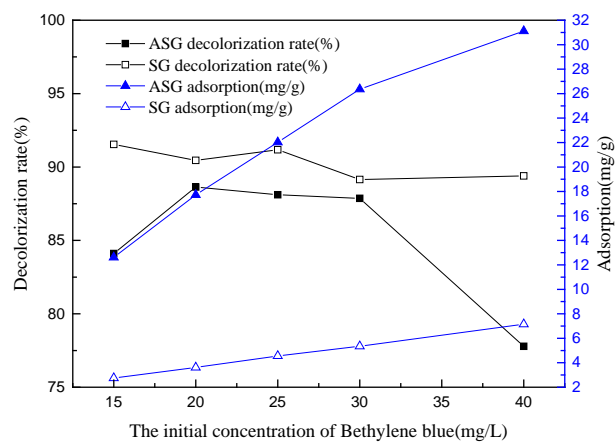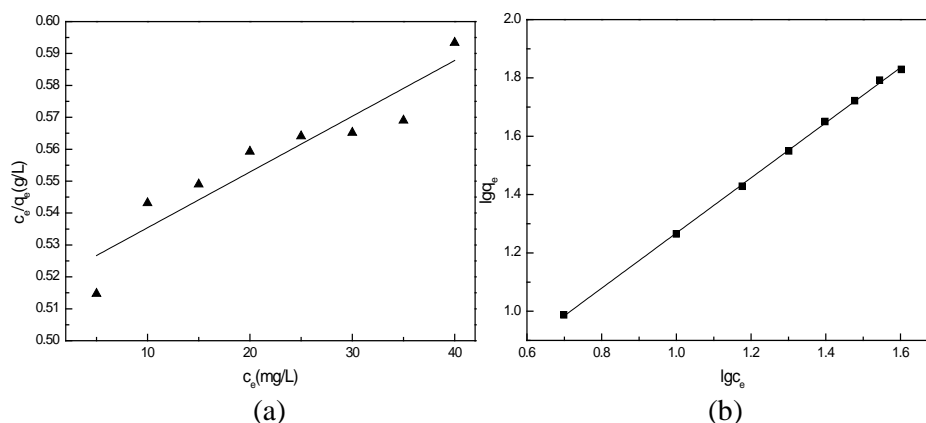

Figure 8. Effects of Initial Concentration on MB Dye Adsorption

3.5. Adsorption Mechanism

The Langmuir and Freundlich adsorption isotherm equations were used to fit the data of ASG adsorbed with MB dye solution. The fitting curve is shown in Figure 9. The relevant adsorption constants (q_{max}、 b、 K_f、 n) and correlation coefficients (R^2) is shown in Table 2.

Table 2. ASG Adsorption Isotherm Model Parameters

Langmuir			Freundlich		
q_{max} (mg/g)	B (L/mg)	R^2	K_f (mg/g)	n	R^2
571.428	0.338	0.861	2.101	1.057	0.999

Figure 9. ASG Langmuir (a) and Freundlich (b) Adsorption Isotherm Model

It can be seen from the correlation coefficient of the fitted curve in Table 2 that the adsorption isotherm of ASG to MB dye solution has a better fit to the Freundlich equation, R^2>0.99. The K value can indirectly reflect the adsorption surface area of the adsorbent, reflecting the total capacity of the adsorbent activity or decolorization, and n is the adsorption characteristic of the adsorbent itself, representing the coefficient of adsorption strength. When 1<n<10, it is favorable for the adsorption reaction happened. The value of n in the table is 1.057, and the reaction of ASG to adsorb methylene blue solution is more likely to occur.

The adsorption kinetics of adsorption of MB dye by ASG was studied by using different kinetic equations. The fitting curve is shown in Figure 10. The relevant kinetic model parameters and correlation coefficient (R^2) are shown in Table 3.

Table 3. ASG Adsorption Kinetics Model Parameters

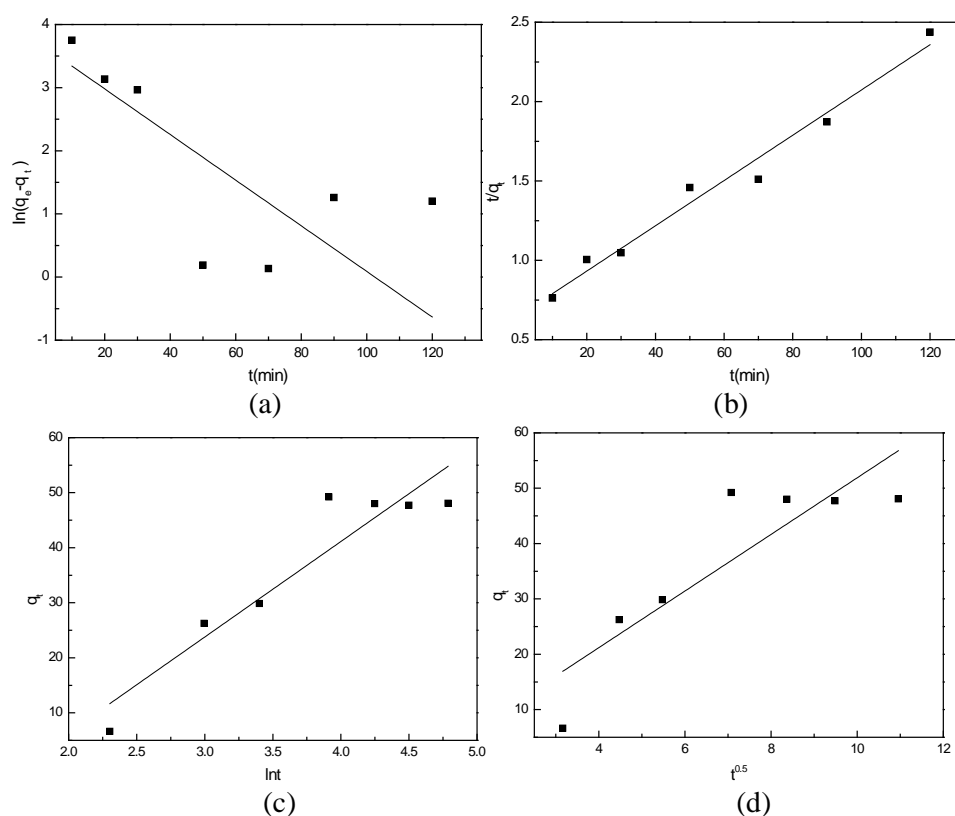| Serial number	Model name	Model parameter		R^2
a	pseudo-first-order kinetic equation	K_{ad} : 0.036	q_e : 40.629	0.836
b	pseudo-second-order kinetic equation	K_2 : 15.625	q_e : 70.126	0.973
c	Intraparticle diffusion equation	K_I : 17.357	A : -28.298	0.864
d	Elovich equation	K_p : 5.114	C : 0.743	0.726

Figure 10. Adsorption Kinetics Curve of ASG

It can be seen from Figure 10 and Table 3 that the pseudo-second-order kinetic equation can better describe the adsorption test kinetics of ASG. The correlation coefficient is 0.973. The pseudo-second-order kinetic equation can be considered as chemical adsorption.

4. Conclusion

(1)Using NaOH as modifier, the modified spent grain adsorption material was prepared. The maximum decolorization rate of MB dye solution (95.87%) was attained under the conditions of 5g/L modified concentration, 60℃ modified temperature and 120 min modified time. The ASG showed better adsorption performance to MB solution.

(2)The adsorbent dose and the initial concentration of dye solution affected the adsorption performance of ASG to MB. When the adsorbent dose was 0.5 g/L and the concentration of MB dye solution was 30 mg/L, the decolorization rate and adsorption were higher.

(3)The Freundlich equation can better fit the adsorption behavior of ASG with R^2>0.99. The kinetic adsorption process can be characterized by pseudo-second-order kinetic equation with a correlation coefficient of 0.973.

5. References

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