Modification of semi-coke powder and its adsorption mechanisms for Cr(VI) and methylene blue

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Abstract. In this paper, the semi-coke powder was modified by three kinds of physical or chemical methods and then modified semi-coke was used as adsorbent for removal of Cr\(^{6+}\) and methylene blue (MB) from aqueous solution. The effects of time, dosage and pH on removal rate were investigated using batch experiments. The process of Cr\(^{6+}\) and MB adsorption onto the modified semi-coke powder follows pseudo second-order kinetics. The analysis of SEM and BET showed the Specific surface area of modified semi-coke are 84.92 m\(^2\)/g, which is higher than that of raw semi-coke powder.

1. Introduction

With the development of global industrialization, more and more wastewater containing heavy metal ions or dying were discharged into water bodies, creating damage and harm to plants, animals, and humans for it is very difficult to biodegrade or prone to be accumulated in human bodies, leading to diseases and disorders [1]. Heavy metal ions in wastewater mainly come from various industries including mining operations, metal processing, leather tanning, water cooling, and pigment manufacturing, etc. Dying wastewater mainly produced by printing dyeing industry has complex water quality, high organic content, poor biodegradability, high alkalinity and strong biological toxicity. It also causes certain harm to humans and animals [2]. Various techniques were employed to treat heavy metal ions and dying contaminated wastewater, among these methods, adsorption is one of the commonly-used techniques. A number of adsorbents, such as coal fly ash[3], carbon nanotube sheets[4], bio-char[5], olive stone[6], zinc oxide nanoparticles[7], beech sawdust[8], banana peel[9], have been reported to be capable of adsorbing heavy metal ions or dying from aqueous solutions.

Semi-coke powder is one kind of solid waste, which is cheap and easy to get and has developed pore structure. Modification can improve pore structure and adsorption performance of semi-coke powder.

In this paper, the semi-coke powder was modified by three kinds of physical or chemical methods and then modified semi-coke was used as adsorbent for removal of Cr\(^{6+}\) and methylene blue (MB) from aqueous solution. The effects of time, dosage and pH on removal rate were investigated using batch experiments. SEM and surface area analysis were conducted.
2. Experimental

2.1. Materials and Instruments
Semi-coke powder was collected from a coke production plant in Shenmu, Shaanxi Province. Hydrochloric acid, sodium hydroxide, potassium dichromate, hydrogen peroxide (30%), nitric acid, potassium hydroxide, sulfuric acid, and methylene blue were used in this work and all chemical reagents were of analytical grade.

The main Instruments used including TU-1901 UV visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd. (SHA-B), constant temperature water bath oscillator of Changzhou Guohua Company), PHS-3C precision pH meter (Shanghai Leici Instrument Factory), Quanta 200 scanning electron microscope (Holland FEI), A3 (atomic absorption spectrophotometer Beijing Purkinje General Instrument Co., Ltd), AB104-N (Electronic Analytical Instrument Co Ltd), Fu-800 (Jintan Fuhua Electric Centrifuge Instrument Co. Ltd.), JW-BK122W surface area and pore size analyzer (Beijing JWGB Sci.& Tech. Co., Ltd).

2.2. Modification of semi-coke powder

2.2.1. Physical and plasma modification A certain amount of semi-coke powder was put into a microwave oven or the plasma reactor and irradiate 1 min under different power condition, then cooling to room temperature, the microwave modified semi-coke powder was obtained. The optimum modified conditions for the adsorption of Cr^{6+} and MB are plasma under 40W and microwave under 60W.

2.2.2. Chemical modification A certain amount of semi-coke powder was added into the same volume of different concentrations of HNO_3, KOH, H_2O_2 solution, shocked 120min in the constant temperature bath, then washed with deionized water to neutral and dried, after its natural cooling to room temperature, the chemical modified semi-coke powder was obtained. The optimum modified conditions for the adsorption of Cr^{6+} and MB are 25% H_2O_2 and 20%KOH solution.

2.2.3. Physico-chemical modification For Cr^{6+} adsorption, the semi-coke powder was modified by plasma under 40W then treated 25% H_2O_2 solution. While for MB, the semi-coke powder was modified by microwave under 60W then treated by 20%KOH solution.

2.2.4. Adsorption experiment Batch experiment for removing Cr^{6+} or MB from aqueous solution was carried out using conical flasks in a temperature controlled shaker bath. Modified semi-coke powder was added into Cr^{6+} or MB solution. The mixture was shaken for a predetermined time. After that, the mixture was filtered and the filtrate was analyzed to calculate the concentrations of Cr^{6+} or MB. The pH value was adjusted by 0.1M HCl and 0.1M NaOH.

3. Results and discussion

3.1. Kinetics
The kinetic curves showing Cr^{6+} or MB adsorption onto modified semi-coke powder are shown in Fig.1. It can be seen from Figure 1, the physicochemical semi-coke powder adsorption capacity of Cr^{6+} and MB slightly higher than the other two. Before 120min, the removal rate of Cr^{6+} and methylene blue is obviously improved, but after 100min, the removal rate of increase rate, change the adsorption capacity of Cr^{6+} and methylene blue no longer increased, reached the adsorption equilibrium.

The Lagergren equation is commonly used to study the dynamic mathematical model of solid-liquid adsorption system: pseudo first-order kinetic equation [10] (1) and pseudo two-order kinetic equation [11] (2), to describe the dynamic process of modified semi-coke the adsorption of Cr^{6+}. The fitting results are shown in Table 1.
\[
\log_{10} \left( q_e - q_t \right) = \log_{10} q_e - \frac{k_1 t}{2303}
\]

(1)

\[
\frac{t}{q_t} = \left( \frac{1}{k_2 q_e^2} \right) + \left( \frac{1}{q_e} \right) t
\]

(2)

Where: \( q_e \) is the equilibrium adsorption capacity, mg/g; \( q_t \) is adsorption of \( t \) time, mg/g; \( k_1 \) is reaction rate constant of first order kinetic equation of min\(^{-1}\); \( k_2 \) reaction rate constant of two order kinetic equation, g·mg\(^{-1}\)·min\(^{-1}\).

Figure 1 and 2, the linear regression equation of two order reaction dynamics and data into Lagergren first-order reaction kinetics and second-order kinetics, the regression parameters are shown in Table 1 and Table 2, Table 2 and Table 1 show that three kinds of adsorption behavior of modified adsorbent of Cr\(^{6+}\) and MB simulated wastewater were more in line with the two level dynamic model according to the two order kinetics, the fitted adsorption capacity \( q_e \) and the saturated adsorption capacity is very close, but \( R^2 \) was more than 0.9, shows that the modified semi-coke is good for Cr\(^{6+}\) and methylene blue adsorption process accords with the two level dynamic model.

![Graph 1](image1.png)

**Figure 1.** Effect of time on the adsorption of Cr\(^{6+}\)

![Graph 2](image2.png)

**Figure 2.** Effect of time on the adsorption of MB

### Table 1. The adsorption kinetics curve fitting parameters of Cr\(^{6+}\) onto modified semi-coke powder.

| Modification-method        | First-order |            | Second-order |            |
|----------------------------|-------------|------------|--------------|------------|
|                            | \( q_e \) (mg/g) | \( k_1 \) (min\(^{-1}\)) | \( R^2 \)   | \( q_e \) (mg/g) | \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) | \( R^2 \) |
| Physical modification      | 3.729       | 0.012      | 0.723        | 3.572      | 0.419     | 0.989       |
| Chemical-modification      | 4.318       | 0.031      | 0.763        | 4.102      | 0.314     | 0.993       |
| Physicochemical-modification | 4.721      | 0.027      | 0.745        | 4.449      | 0.268     | 0.995       |

### Table 2. The adsorption kinetics curve fitting parameters of MB onto modified semi-coke powder.

| Modification-method        | First-order |            | Second-order |            |
|----------------------------|-------------|------------|--------------|------------|
|                            | \( q_e \) (mg/g) | \( k_1 \) (min\(^{-1}\)) | \( R^2 \)   | \( q_e \) (mg/g) | \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) | \( R^2 \) |
| Physical-modification      | 3.817       | 0.018      | 0.731        | 3.769      | 0.374     | 0.988       |
| Chemical-modification      | 4.287       | 0.022      | 0.730        | 4.215      | 0.301     | 0.996       |
| Physicochemical-modification | 4.441       | 0.041      | 0.778        | 4.507      | 0.262     | 0.997       |
3.2. Effect of dosage
Under different dosage conditions, the adsorption capacities of Cr(Ⅵ) and methylene onto modified semi-coke powder results as shown in Figure 3 and 4. As can be seen from the Figure 3 and 4, the adsorption capacity decreases with the increase of modified semi-coke powder the dosage when the dosage less than 0.6g. The adsorption capacity decrease becoming slowly as the dosage more than 0.6g.

![Figure 3. Effect of dosage on adsorption of Cr(Ⅵ)](image1)

![Figure 4. Effect of dosage on adsorption of MB](image2)

3.3. Effect of pH
Under different pH values, adsorption capacities of Cr(Ⅵ) and methylene blue onto modified semi-coke powder are shown in Figure 5 and 6. It can be seen from Figure 5 and 6, in pH=3.0~5.0, the modified semi-coke powder adsorption capacity of Cr(Ⅵ) and MB with the increase of pH gradually increased, in acidic conditions, the modified semi-coke powder Cr(Ⅵ) and MB adsorption effect was obviously better than that in strong acid condition, when pH=5.0~6.0, the adsorption capacity reaches the maximum.

![Figure 5. Effect of pH on adsorption of Cr(Ⅵ)](image3)

![Figure 6. Effect of pH on adsorption of MB](image4)

3.4. Specific surface area and SEM analysis
The pore structure before and after the modification of semi-coke powder is shown Table 3. It can be seen from Table 3, the specific surface area of semi-coke powder is 13.21395m²/g, the average pore size is 2.1927nm; while the specific surface area of the physicochemical modified semi-coke powder is 84.91673m²/g, the average pore size of physicochemical modified semi-coke powder is 3.8159nm. The specific surface area and average pore size increased after modification, that is very beneficial for adsorption.
### Table 3. Modified semi coke at the end of the pore structure parameters

| Sample                | Specific surface area (m²/g) | Total volume (cm³/g) | Average pore diameter (nm) |
|-----------------------|------------------------------|----------------------|----------------------------|
| Semi-coke             | 13.21395                     | 0.006187             | 2.1927                     |
| Modified semi-coke    | 84.91673                     | 0.034198             | 3.8159                     |

Figure 7 is the scanning electron microscope of semi-coke powder before and after modified. It can be seen, there are more pores in modified semi-coke powder and the diameter of pores in modified semi-coke powder is more higher than that in raw semi-coke powder.

![Figure 7. The SEM of semi-coke powder before and after modified by physicochemical methods](image)

4. Conclusions

In this paper, the semi-coke powder was modified by three kinds of physical or chemical methods and then modified semi-coke was used as adsorbent for removal of Cr⁶⁺ and methylene blue (MB) from aqueous solution. The process of Cr⁶⁺ and MB adsorption onto the modified semi-coke powder follows pseudo second-order kinetics. The analysis of SEM and BET showed the Specific surface area of modified semi-coke are 84.92 m²/g, which is much higher than that of raw semi-coke. There are more pores in modified semi-coke powder and the diameter of pores in modified semi-coke powder is higher than that in raw semi-coke powder.

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