Adsorption of Methylene Blue on Bituminous Coal: Adsorption Mechanism and Molecular Simulation

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ABSTRACT: Coal with its complex porous medium and abundant oxygen functional groups could be used as an adsorbent to adsorb organic compounds. Adsorption experiments and molecular dynamics simulations were carried out to study the behavior of methylene blue (MB) on the surface of Wiser bituminous coal. The influence of adsorption through factors, such as pulverized coal dosage, adsorption reaction time, initial concentration, and temperature effect, was investigated. The removal efficiency of MB reached 96.5% under optimum reactive conditions. The adsorption equilibrium was accorded with a Langmuir isotherm adsorption equation. The adsorption of MB onto coal was a spontaneous process because the adsorption free energy $\Delta G$ was negative. It was consistent with the conclusion of a negative interaction energy between bituminous coal and MB obtained by molecular dynamics simulation. Moreover, the density distribution along z-axis of each component molecule showed that MB molecules were adsorbed on the coal surface because of the polar interactions between the methyl groups of MB and the hydrophilic sites at the coal surface. Also, the diffusion degree of water molecule in liquid phase showed that as MB molecules formed hydrogen bonds with the water molecules, the activity of water molecules was restricted.

1. INTRODUCTION

Recently, China has become the world’s largest producer of soft goods with its enormous productivity. Dyeing wastewater plays a major role in industry wastewater outlet with the rapid development of chemical fiber and textile industry in China. Dye wastewater is generated from production processes of textile products. With the increasing complexity of production technology and unceasing expansion of industry, dye wastewater is becoming more and more difficult to treat. Dye wastewater has a complex composition, high pH, color depth, and poor biodegradability. It usually contains high concentrations of organic compounds, most of which are refractory, toxic, mutagenic, and carcinogenic. Methylene blue (MB) exists in water as cations and is widely used in dyeing processes.

Because of its strong affinity to solids, MB has been widely studied. There are many methods to treat dyeing wastewater, such as biological treatment, coagulation, electrochemical adsorption, and oxidation. Among these techniques, adsorption is characterized by use of less space, well decolorization effect, and high disposal efficiency, which can be applied to the disposal of textile dying wastewater. Modified ultrafine coal powder was much better than that of ultrafine coal powder, and the process was spontaneous and exothermic. The coking coal exhibited properties well-suited for the adsorption of organics, and the Freundlich isotherm provided reasonable models of the adsorption process. Moreover, the pH had an effect on the sorption of organic contaminants by coking coal in wastewater. The chemical oxygen consumption (COD) and phenol removal efficiencies increased with decreasing pH value, while the ammonia removal efficiency was decreased gradually. The process of coal adsorption–column flotation was developed for the treatment of oily wastewater, and it had a good effect.

With the rapid development of computer technology, computer molecular simulation has become a powerful tool to study the structure and behavior of molecules. Recently, quantum mechanics methods and molecular dynamics methods have been widely used to investigate interactions between water, organics, and minerals. For example, Rai et al. studied the crystal structure specificity of oleate molecules for different silicate minerals as well as its interactions with the same silicate minerals with different crystallographic planes. Wang et al. investigated the adsorption of dodecylamine (DDAH), oleate (NaOL), and their mixture on a muscovite surface in an aqueous solution. The results indicate that...
DDAH molecules are absorbed on the muscovite surface by electrostatic interactions and hydrogen bonding. In contrast, NaOL molecules are not independently adsorbed on the muscovite surface. Wang et al. also investigated the surface activity and self-aggregation behavior of the DDA/coal mixtures at the water/air interface using molecular dynamics simulation and surface tension measurement.22 Among the above-mentioned methods, MD simulations are also widely used to investigate the interactions on coal/surfactant (collector)/water surface. You et al. revealed the interaction of surfactant molecules with the water—coal interface using molecular dynamics calculations. The results showed that the adsorption was mainly controlled by polar interactions between the ethoxylate group of NPEO-10 and the hydrophilic sites on the coal surface.23 Lyu et al. studied the behavior of nonylphenol ethoxylate with 12 ethylene oxide groups (NPEO-12) on the model surface of Hatcher subbituminous coal using molecular dynamics simulations. The results showed that the adsorption capacity of C—O group for NPEO-12 was higher.24 Zhang et al. studied the density profiles of oxygen atoms and hydrogen atoms. Their result indicated that the coal’s surface properties affect the structural and dynamic characteristics of the interfacial water molecules.25 Zhang et al. studied the interactions between Wiser bituminous coal, different collectors, and water using molecular dynamics calculations. The results showed that the adsorption of nonylphenol on the coal surface via both π–π stacking and hydrogen bonds is most favorable, followed by that of nonylbenzene and dodecane. Nevertheless, few reports deal with the interactions of coal surfaces with organic pollutants in the dye wastewater. Herein, the effect of bituminous coal on the adsorption performance of MB was studied by adsorption experiments, and its adsorption thermodynamics were analyzed. In addition, we aimed to examine the adsorption of MB on the surface of Wiser coal using MD simulations. The details of MB—coal interactions were revealed by dynamical behavior of the coal/MB/water system. The findings of this investigation could possibly provide insights into the theoretical description of the interaction between MB and coal surface at a molecular level.

2. RESULTS AND DISCUSSION

2.1. Adsorption Experiments. 2.1.1. Effect of Coal Consumption. The experimental process was as follows: 50 mL of MB solutions (50 mg/L) was placed in several conical flasks of 100 mL. Coal samples of different weights were respectively added to the conical flasks to determine the optimum dosage. The flasks were put into a thermostatic oscillator and stirred for 2.5 h at room temperature (about 25 °C).

The effect of pulverized coal consumption on the adsorption of MB is illustrated in Figure 1. It was evident that the adsorption capacities of MB by coal decreased with the increase of coal consumption. However, the removal efficiencies of MB increased. As to the removal efficiencies and adsorption capacity of MB by bituminous coal, the bituminous coal consumption is 2 g in this paper.

2.1.2. Effect of Oscillation Contact Time. The experimental process was as follows: 50 mL of MB solutions (50 mg/L) was placed in several conical flasks of 100 mL. Then, 2 g of the coal sample was respectively added to the conical flasks. The flasks were put into a thermostatic oscillator and stirred for different times at 288, 298, and 313 K.

The effect of temperature and time on the adsorption of MB on bituminous coal is illustrated in Figure 2. The adsorption capacity increased with increase of adsorption time. The adsorption capacity first increased rapidly and then slowed down and became constant after more than 6 h. Moreover, the adsorption capacity increased with the increase in temperature. The results showed that the adsorption of MB on bituminous coal is temperature sensitive. A higher temperature could increase the adsorption of MB on bituminous coal.

2.1.3. Effect of Initial Concentration. Experiment steps were as follows: MB solutions of different initial concentrations (50 mL) were placed in several conical flasks of 100 mL. Then, 2 g each of coal sample was added to the conical flasks. The flasks were put into a thermostatic oscillator and stirred for 12 h at 288, 298, and 313 K.

The effect of temperature and the initial concentration of MB on the adsorption of MB on coal is illustrated in Figure 3. Then, isotherm constants were obtained by using a linear regression analysis to the linear forms of the isotherm expression of the adsorption experiments. The isotherm constants and the correlation coefficients are shown in Table 1. The curves of Langmuir and Freundlich isotherm linear
regression are shown in Figure 4a,b, respectively. The Langmuir and Freundlich isotherm constants for MB adsorption on bituminous coal at different temperatures are listed in Table 1.

From Table 1, it can be found that the R² values of the Langmuir equation were all higher than 0.99, suggesting that the adsorption of MB on bituminous coal closely fits the Langmuir model. It indicated that the absorption was of monomolecular type. Then, the R_L values from the Langmuir model were all between 0 and 1, indicating a favorable sorption process. At the same time, the 1/n values from the Freundlich model were all less than 1, also indicating a favorable sorption process.

The adsorption free energy (ΔG°) can be expressed by the follow equation

$$\Delta G^0 = -RT \ln K_0$$

where R is the ideal gas constant, T is the absolute temperature, and K₀ is the distribution ratio. A straight line is obtained by the plot of \(\ln \left( \frac{Q}{Q_e} \right)\) as a dependent variable and \(Q_e\) as an independent variable. The intercept of the straight line is \(\ln K_0\). The adsorption free energy calculated are −9.003, −18.46, and −32.64 kJ/mol at 288, 298, and 313 K, respectively. The adsorption free energy is negative. The results indicated that the adsorption process was spontaneous.

### 2.2. MD Simulations

#### 2.2.1. Adsorption of MB on Bituminous Coal Surface

The adsorption of MB and water molecules on the bituminous coal surface was calculated by MD simulations. The final equilibrium adsorption configuration is shown in Figure 5. It was evident that MB was closer to the coal surface by comparing the configuration before and after adsorption. It can be concluded that MB was adsorbed on the coal surface. To study the adsorption of MB on the bituminous coal surface further, the mass Z-dependent density profiles for MB were calculated with the simulation results. The Z-axis is normal to the coal surface. The Z-dependent density distributions are shown in Figure 6. From Figure 6, it can be found that the density distribution of coal is basically uninfluenced by the surrounding environment. In addition, MB molecules can be detected at the coal–water interface. In the bituminous coal/MB/water system, the density of MB molecules peaked at 57.49 Å and the density of water molecules peaked at 82.49 Å. MB was closer to the coal surface. In addition, at the same distance from the coal surface, the molecular density of water without MB is slightly higher than that of water with MB. The result demonstrated that MB molecules were adsorbed on the coal surface. Coal comprises hydrophilic sites distributed on a hydrophobic surface. MB adsorption was probably driven by the polar interactions between the methyl groups of MB and the hydrophilic sites at the coal surface.

#### 2.2.2. Interaction Energies

The interaction energy can be used to measure the intensity of interaction between MB and...
the coal surface. The interaction energy between MB and the coal surface can be expressed by the following formula

$$E_{\text{MB-coal}} = (E_{\text{total}} - E_{\text{MB}} - E_{\text{coal+water}} - E_{\text{coal}} - E_{\text{water+MB}} + E_{\text{water}} + E_{\text{coal+MB}})/2$$  \hspace{1cm} (2)

where $E_{\text{total}}$ is the total energy of the system and $E_{\text{coal}}, E_{\text{MB}},$ and $E_{\text{water}}$ are the energy of the coal surface, MB, and water, respectively. $E_{\text{coal+water}}, E_{\text{water+MB}},$ and $E_{\text{coal+MB}}$ are the total energy of the coal surface and water, the total energy of the water and MB, and the total energy of the coal surface and MB, respectively. The interaction energy between the coal surface and MB is $-122.28 \text{ kJ/mol}$ by simulation calculation. The negative value indicates that the adsorption process between the coal surface and MB is spontaneous. The simulation results are consistent with the adsorption isothermal experiment results, which proves the accuracy and feasibility of the simulation calculation.

2.2.3. Mobility of Water Molecules. After the addition of MB on the coal surface, its surface properties changed, which influences the behavior of water. The mobility of water molecules on the coal surface could be evaluated by calculating their mean square displacement (MSD) and diffusion coefficient ($D$).

MSD can be used to describe the deviate degree of particle position and initial position at some point. It can be expressed as follows

$$\text{MSD} = \frac{1}{N} \left( \sum_{i=1}^{N} |r_i(t) - r_i(0)|^2 \right)$$ \hspace{1cm} (3)

where $N$ is the number of atoms, $r_i(0)$ is the particle initial position, and $r_i(t)$ is the position vector at time $t$.

Diffusion coefficient can be used to reflect the intensity of water molecule’s mobility. The expression is as follows

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} \langle |r_i(t) - r_i(0)|^2 \rangle$$ \hspace{1cm} (4)

The expression of diffusion coefficient by combining expression (3) and (4) is as follows

$$D = \lim_{t \to \infty} \frac{\text{MSD}}{6t} = \frac{1}{6}K_{\text{MSD}}$$ \hspace{1cm} (5)

From formula 5, it is seen that the diffusion coefficient can be obtained by measuring the slope of the mean square displacements. The MSD curve of water molecules in coal/MB/water system is shown in Figure 7. At the same time, the diffusion coefficients of water molecules are obtained by fitting the curves in the graph, as shown in Table 2.

It can be seen that the diffusion coefficient of water molecule in the coal/water system is larger than that in the bituminous coal/MB/water system. It was evident that the mobility of water molecules is reduced after the adsorption of MB on the coal surface. Because MB formed hydrogen bonds with the water molecules, as shown in Figure 8, the activity of water molecules was restricted.
3. CONCLUSIONS

Both experiments and MD simulation methods were carried out to investigate the adsorption behavior of methylene blue (MB) on bituminous coal. The obtained experimental data indicated that the adsorption could be a typical monolayer adsorption, best described by a Langmuir isotherm adsorption equation. The adsorption was spontaneous.

MD simulations were used to examine the interaction of MB with the model surface of Wiser bituminous coal in the aqueous phase. The Z-dependent density distributions showed that MB molecules were adsorbed on the coal surface. Coal comprises hydrophilic sites distributed on a hydrophobic surface. MB adsorption was probably driven by the polar interactions between the methyl groups of MB and the hydrophilic sites at the coal surface. In addition, the calculated MSD and diffusion coefficients of water molecules demonstrated that their mobility reduced after the adsorption of MB on coal surface. It also showed that MB molecules attracted the water molecules because of hydrogen bond. The adsorption free energy $\Delta G^0$ was negative, in agreement with the spontaneous adsorption simulations observed.

4. EXPERIMENTAL SECTION

4.1. Materials Synthesis. A bituminous coal sample was provided by Linhuan Coking Co., Ltd located in Linhuan, Anhui province, China. The coal sample was first hammer-crushed and then ground in an agate mill. The ground material was sieved to obtain $\sim 74 \mu m$ size particles for adsorption experiment. MB with purity greater than 99.5% was purchased from Sinopharm Chemical Reagent Co., Ltd. and used as the adsorbate in this paper.

4.2. Batch Adsorption Test. The adsorption capacities of MB on bituminous coal were investigated in batch adsorption experiments. The adsorption capacity of coal was measured indirectly with a UV–vis spectroscopy at 665 nm, which was the maximum wavelength for MB in the paper. Then, 50 mL of MB solutions was placed in several conical flasks of 100 mL. The coal samples of different weights were respectively added to the adsorbate solutions of different concentrations. The flasks were put into a thermostatic oscillator and stirred for different times at a constant temperature. After that, the aqueous phase was filtered using a syringe filter and the residual concentration in solution was analyzed. All the adsorption experiments were conducted in three parallel groups. The residual concentration was then converted to concentration using calibration curves for MB. The adsorption capacity of coal was calculated using the expression

$$Q_t = \frac{(C_0 - C_t)V}{W}$$

(6)

The removal efficiency of MB was calculated using the expression

$$\gamma = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

(7)

where $Q_t$ (mg/g) is the MB adsorption of per gram adsorbent, $C_0$ (mg/L) is the initial MB concentration, $C_t$ (mg/L) is the...
Figure 9. (a) Molecular model of Wiser bituminous coal. (b) Optimized bituminous coal molecule. (c) Optimized MB molecule. (d) Optimized water molecule. O: red, C: gray, H: white, N: blue, S: yellow, and Cl: cyan.

Figure 10. (a) Structure of 20 optimized bituminous coal surface models. (b) Initial structure snapshot of MB near the bituminous coal.
4.3. MD Simulations. MD simulations were conducted using Materials Studio 8.0 package. The COMPASS forcefield was applied for all simulations.25,26 Because the physical and chemical structures of coal are very complex, the bituminous coal surface was built using previously proposed molecular structure of Wiser coal, as shown in Figure 9a.28,29 The coal structure model proposed by Wiser in the United States in 1970s is considered to be a more comprehensive and reasonable model. It presents the most modern concepts of the macromolecular structure of coal and can reasonably explain the liquefaction and other chemical reaction properties of coal. Then, the Wiser, MB, and molecular structures of water were evaluated. To obtain a relatively stable three-dimensional molecular space model, the structures of all molecules were optimized. The optimized molecular models are shown in Figure 9b—d. Then, 20 optimized Wiser molecules were randomly packed in a cubic simulation cell 43 × 43 × 43 Å3 with three-dimensional periodic boundary conditions. Anneal algorithm calculation for Wiser coal cell was carried out to achieve structure relaxation of the coal surface model. Structure relaxation carried out from 1098 to 298 K was followed by optimization and equilibration for 100 ps at 298 K. A van der Waals interaction cutoff of 15.5 Å was employed, and the Ewald summation method with an accuracy of 10−5 kcal/mol was used to account for the long-range electrostatic interaction. Figure 10a shows the structure. Then, the Z-axis was extended such that slabs in neighboring cells will not interact with each other. Moreover, the cell containing 10 MB molecules and 3000 water molecules were constructed and optimized according to the above methods, respectively. Finally, a new rectangular simulation cell 43 × 43 × 250 Å3 (X × Y × Z) containing the above three optimized cells was obtained by a building layer. The coal cell, MB cell, and water cell are the bottom, middle, and top layer, respectively. The system is shown in Figure 10b.

MD simulations were run at NVT ensemble at 298 K employing a Nose thermostat, with the time step equaling 1.0 fs.20 Also, the van der Waals interaction cutoff of 15.5 Å was employed, and the Ewald summation method with an accuracy of 10−5 kcal/mol was used to account for the long-range electrostatic interaction. A simulation was performed for 1 ns. The final results were calculated based on the production of 1000 ps simulation after the equilibration period. During the simulation, the coal surface was frozen to save computational time.

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Notes

The authors declare no competing financial interest.

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