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## Study on the Competitive Adsorption Performance of Direct Deep Blue and Methyl Orange on Expanded Graphite Adsorbent.

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### Research Article

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#### ABSTRACT

Expanded graphite (EG) adsorbent was prepared with chemical oxidation method using  $\text{H}_2\text{SO}_4$  as inserting reagent,  $\text{KMnO}_4$  as oxidizing agent and the intercalating product expanded at  $900^\circ\text{C}$ . The adsorption and competitive adsorption performance of methyl orange (MO) and direct deep blue (DDB) on the EG were assessed using a combination of the single and binary (MO and DDB) aqueous solution. Experimental results shown that: in single and binary aqueous solution, adsorption capacities of EG for these dyes increase with the increase of dye concentration, ionic strength and adsorbent specific surface area. In binary solution, the coexistence of DDB can obviously reduce MO adsorbance, and there are replacements of DDB for MO. It is worthwhile to note that there is a synergic effect of MO in the adsorption of DDB, the amount of DDB adsorbed on EG increases with the initial concentration of MO, and EG possess better adsorption performance for DDB than that for MO. The adsorption and competitive adsorption process of MO on EG follow the pseudo-second-order kinetic model, while the adsorption and competitive adsorption of DDB are affected by temperature. The kinetic data follow pseudo-first-order model at  $5^\circ\text{C}$  and  $20^\circ\text{C}$ , and pseudo-second-order model at  $45^\circ\text{C}$ , respectively.

#### INTRODUCTION

Dye wastewater produced by textile, paper and printing factories has become one of the major sources of pollution, and it has been proved that the wastewater is multi-component and with deep color, high COD, BOD and toxicity. Their disposal into receiving waters can cause damage to the environment. Specially, dyes may evidently affect the photosynthetic activity in aquatic life by reducing the penetration of light. Adsorption technique was believed to be an effective and low cost process to solve this question. The most attractive adsorbent is active carbon due to its high specific surface area [1, 2]. However, the expensive running cost is an apparent drawback in industry application.

Currently, much attention is paid to expanded graphite (EG). It is a kind of adsorbent with abundant 4 levels pores distributing from nanometer to micron [3], and those pores are expected to act quite differently in adsorption for various adsorbates [4]. In the adsorption of heavy oils, large open space among entangled worm-like particles, first-level and second-level pores were found very important, adsorbance of grade A heavy oil was determined as 83.0 g on 1.0 g of EG with a bulk density of  $0.006\text{ g/cm}^3$  [5]. Adsorption for oils with different viscosity represented a linear relationship between oil adsorbance and viscosity, EG expanded volume, respectively [6]. In comparison with oil, the adsorption capacity for dyes [7], phenyl molecules [8], polyethylene glycol [9, 10] were smaller due to their low viscosity. There were different adsorption mechanism of EG for oil and other pollutants. A linear relationship between adsorbance and EG specific surface area were proved. Furthermore, the adsorption capacity was mainly affected by adsorbates concentration in solution, temperature, pH and ionic strength.

Although much attention has paid to EG adsorption capacity for mono-component solution (aqueous solution containing a single adsorbate), pollutants rarely existed alone. Study for the multi-component solution

could reveal characteristics of competitive adsorption on the same site, distribution and adsorbance difference caused by the physical or chemical interaction between the coexisting adsorbates. For examples: In the adsorption of humic acid, fulvic acid, dodecyl benzene sodium sulfonate and phenol on DX - 906 macroporus resin [11], the results shown that competitive adsorption occurred when the differences between two adsorbates were small; When the differences were obvious, the small molecular organic substance would promote the absorption of the large one. In individual and competitive adsorption of phosphate and arsenate on goethite in artificial seawater (adding  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  to a 0.7 mol/L NaCl solution) [12], phosphate adsorbance increased slightly in the presence of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ; but a decrease in adsorbance was caused by the addition of  $\text{SO}_4^{2-}$  and low pH. In contrast, arsenate adsorption was not affected by the addition of  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ . In the adsorption of atrazine on powdered activated carbon [13], *p*-dichlorobenzene was found significantly reduce atrazine adsorbance, but it had no effect on atrazine adsorption kinetics. In contrast, the effect of poly (styrene sulfonate) (PSS, MW=1800) on atrazine adsorption capacity was very small. Furthermore, during simultaneous adsorption, PSS-1800 had no effect on atrazine surface diffusion. However, preloading powdered activated carbon with PSS-1800 would lower the atrazine surface diffusion coefficient by more than three orders of magnitude, and diffusion coefficient decreased with the increasing solid phase PSS-1800 concentration. In the adsorption of acid blue 25,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  on a physically activated bituminous carbon and a phosphoric activated carbon from wood [14], results showed a synergic effect of acid blue 25 in the adsorption of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ . The amount of metal ions adsorbed on both activated carbons increased with the initial concentration of acid blue 25.

Accordingly, multi-component approach is obviously required in order to understand and predict the performance of the EG in the treatment of real wastewater, which normally contain complex admixtures of dyes and/or other pollutants. With direct deep blue (DDB) and methyl orange (MO) as model adsorbates, the aim of this work is to investigate adsorption and competitive adsorption characteristics of these dyes on EG. Influence of dye concentration, ionic strength of solution, temperature and adsorbent specific surface area on adsorption capacities in single aqueous solution and competitive adsorption capacities in binary aqueous solution were investigated and compared. The study can not only establish thermodynamic and kinetic models, give model parameter, but can also give some instruction for EG application as adsorbent in multi-component dyes wastewater treatment.

## MATERIALS AND METHODS

### Preparation of EG adsorbent

Certain volumes of sulfuric acid with a mass ration of 98% was diluted to 75% with de-ionized water in beaker, then added dry natural graphite and  $\text{KMnO}_4$  in turn according to the mass ratio graphite C :  $\text{H}_2\text{SO}_4$  (98%) :  $\text{KMnO}_4$  of 1.0: 0.15: 5.0. Mixed the ingredients using glass rod, and reaction lasted out 30 min at room temperature. The products were washed with de-ionized water and dipped in water for 2.0 h until pH of the water in bath reached to 6.0-7.0, then filtrated and dried at 60-80°C for about 6.0 h. The dried product was expanded at 900°C, and then the EG adsorbent gained. Expansion volume (EV) of the dried product was measured according to analysis method GB/T10698-1989 [15]. Various EG with different EV were prepared using raw material graphite with different size of 0.3 mm, 0.18 mm and 0.15 mm as listed in Table 1. The surface area, pore size distribution and pore cubage structure parameters were determined by BET according to the adsorption of nitrogen (listed in Table 1). In all the adsorption and competitive adsorption experiments, EG with an EV of 400 mL/g was used as adsorbent except for the special illustration.

Table 1: Structural parameter of the prepared EG adsorbents <sup>a</sup>

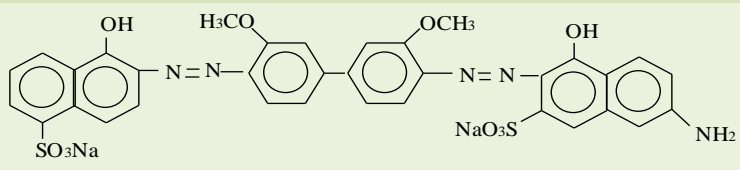
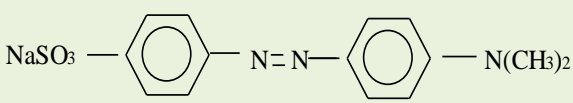
| Materials size (mm) | EV (mL/g) | Pore volume (cm <sup>3</sup> /g) | Surface area (m <sup>2</sup> /g) | Average pore Diameter 4V/A (nm) |
|---------------------|-----------|----------------------------------|----------------------------------|---------------------------------|
| 0.3                 | 400       | 0.1009                           | 34.35                            | 11.61                           |
| 0.18                | 150       | 0.0698                           | 23.84                            | 11.61                           |
| 0.15                | 35        | 0.06263                          | 21.30                            | 11.59                           |

<sup>a</sup> Instrument condition: adsorbate  $\text{N}_2$ ; aperture ranges 1.7000-300.0000 nm; equilibration interval 10 s; maximum relative pressure  $p/p_0 = 0.9858$

## Adsorbate

MO with azobenzene structure and DDB with naphthalene ring, biphenyl, azobenzene structures were used as model adsorbates. The chemical structure and molecular weight were shown in Table 2. Simulated wastewaters of DDB and MO in single and binary aqueous solution were prepared by dissolving these adsorbates in de-ionized water at various concentrations. In quantitative analysis, T6 New Century UV spectrophotometer (Puxi Tongyong Instrument Limited Company of Beijing) was used.

**Table 2: Structure of DDB and MO**

| Dye | Structure  | M     |
|-----|--|-------|
| DDB |  | 773.7 |
| MO  |  | 327.3 |

## Adsorption experiments

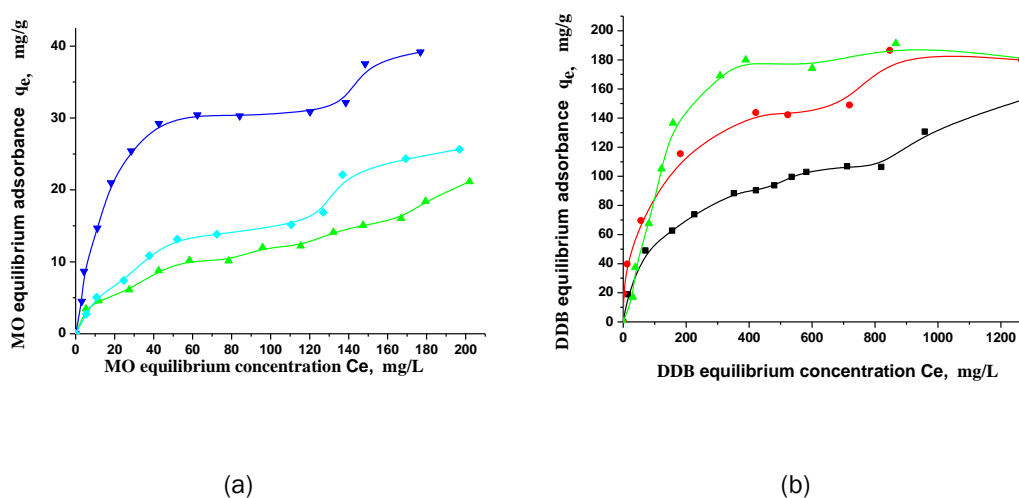
The adsorption experiments of EG for DDB and MO were carried out using single (MO or DDB) aqueous solution and binary (MO and DDB) aqueous solution, at different concentration, temperature and ionic strength, respectively. Absorbance and concentration changes of DDB and MO solution were recorded and calculated according to quantitative equation. The methodology of the experiment and equipments are analogous to those we reported in literature [9].

## RESULTS AND DISCUSSION

### Adsorption and competitive adsorption isotherm

Balance adsorbance corresponding to MO and DDB different initial concentration in single aqueous solution and binary aqueous solution were determined at 20 °C, and the results were shown in Figure 1.

**Figure 1: Absorption and competitive adsorption isotherms of DDB and MO on EG at 20 °C**



- (a) Concentration of DDB (▼) 0 mg/L; (◆) 250 mg/L; (▲) 800 mg/L  
(b) Concentration of MO (■) 0 mg/L; (●) 40 mg/L; (▲) 140 mg/L

In the tested concentration range, the equilibrium adsorbance of MO and DDB are all increase with the increase of dyes initial concentration no matter in MO or DDB single aqueous solution or MO-DDB binary aqueous solution. But the coexistence of DDB can obviously affect MO adsorbance on EG, and it decreases with the increase

of DDB initial concentration, that should be caused by the competitive adsorption for the same adsorbing sites on EG and replacement of DDB for MO. Specially, the coexistence of MO can increase adsorption capacity of EG for DDB, and it increases with the increase of MO initial concentration. The possible reasons are discussed. First, on the surface of EG, the main elements are carbon and oxygen [16], and they exist in the forms of -C-C, C=O, -C-O-, -O-O function groups, which can cause stronger affinity between DDB and EG. On the other hand, adsorption rate of MO is higher than DDB for its smaller molecular weight (at room temperature, the adsorption balance times of DDB and MO are about 33.0 h and 25.0 h, respectively). MO molecules can adsorb in advance, and then these adsorbed sites can become active sites for the adsorption of DDB. Subsequently, the replacement of DDB for MO was the result of DDB stronger adsorption affinity and leading to enhanced adsorbance. Similar results were proved in the competitive adsorption of four common organic compounds (humic acid, fulvic acid, dodecyl benzene sodium sulfonate and phenol) on DX-906 macro-porous adsorbent resin [14]. They deduced that the adsorption of small molecules such as dodecyl benzene sodium sulfonate and phenol could reduce the repulsion between resin framework and humic acid or fulvic acid, which could bring more new adsorbing sites or be more propitious to the adsorption of large molecule. At the same time, a synergic effect was suggested of acid blue 25 in the adsorption of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  on activated carbons [14]. Acid blue 25 was deduced acted as an ionic exchanger in aqueous solution thus becoming an active site for the adsorption of heavy metals.

Further experiments were carried out to testify the coexistence of MO being propitious to the adsorption of DDB. DDB single aqueous solution of 250 mg/L and 800 mg/L were prepared, respectively. EG was added to keep the mass of EG to solution volume 2.0 g/L, and the equilibrium adsorbance of DDB was firstly determined at 20 °C. Subsequently, MO was added to the DDB equilibrium solutions to maintain MO initial concentration of 40 mg/L and 100 mg/L, respectively. The final equilibrium adsorbances of DDB on EG preloading DDB were determined again. As shown in Table 3, the addition of MO to preloading EG with DDB can further enhance DDB adsorbance, and it increases with the increase of MO initial concentration. Accordingly, the addition of MO can bring active sites for the adsorption of DDB and cause the increase of adsorbance.

**Table 3: Influence of MO on DDB adsorbance in MO-DDB binary solution <sup>b</sup>**

| DDB initial concentration (mg/L)  |                                   | 250  | 800   |
|-----------------------------------|-----------------------------------|------|-------|
| DDB equilibrium adsorbance (mg/g) | MO initial concentration 0 mg/L   | 63.9 | 159.8 |
|                                   | MO initial concentration 40 mg/L  | 80.4 | 171.1 |
|                                   | MO initial concentration 100 mg/L | 86.6 | 172.3 |

<sup>b</sup> Experimental temperature 20 °C

#### Adsorption and competitive adsorption isotherm constants

To provide a description of dye concentration and possible conformation in the interfacial region, Langmuir Equation and Freundlich isotherm Equation were used to treat the isotherm data with the same methodology that reported in literature [9]. As shown in Table 4, these two models can all be used to describe the adsorption and competitive adsorption behavior, the correlation coefficient  $r$  are all above 0.9. According to results listed in Table 4, MO saturation adsorbance  $q_0$  in MO-DDB binary solution is smaller than that in MO single solution, and it decreases with the increase of DDB concentration. Accordingly, the results illustrate there are competitive adsorption for the same adsorbing sites on EG and replacements of DDB for MO. Whereas for DDB in DDB-MO binary solution, the adsorbance is bigger than that in DDB single solution, it increases with the increase of MO concentration. It can be seen the adsorption of EG for MO and DDB are selective.

#### Influence of EG specific surface area on absorption and competitive adsorption adsorbance

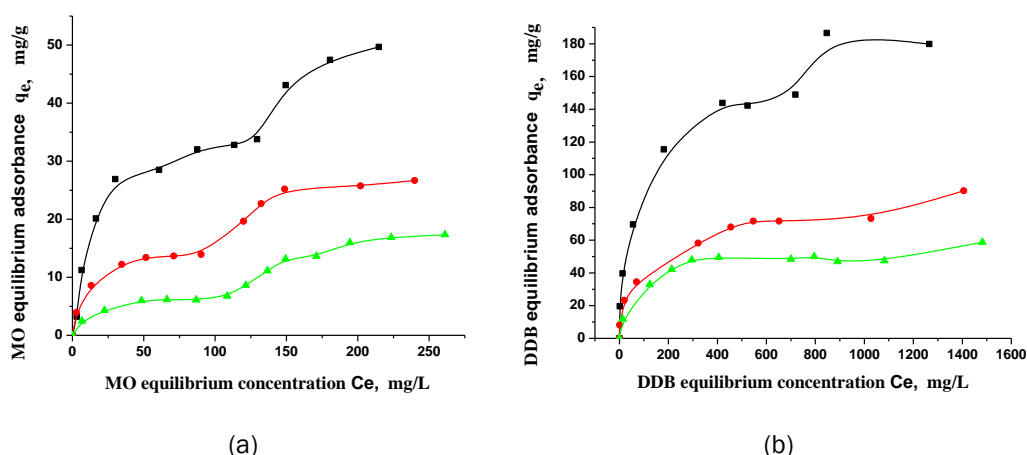
As shown in Figure 2, the larger the specific surface area is, the higher the adsorbance for MO or DDB is in single and binary aqueous solution. EG with large granularity possesses of higher expanded volume and higher specific surface area (as shown in Table 1). Accordingly, it is in favor of improving EG adsorption capacity to increase its specific surface area and expanded volume. Hereby, in all the adsorption and competitive adsorption of MO or DDB is in single and MO-DDB binary aqueous solution, EG with an EV of 400 mL/g was used as adsorbent.

Table 4: Langmuir and Freundlich isotherm constants of DDB and MO on EG <sup>c</sup>

| Adsorbates |              | Langmuir equation          |               |        | Freundlich equation |        |        |
|------------|--------------|----------------------------|---------------|--------|---------------------|--------|--------|
|            |              | q <sub>0</sub><br>(mmol/g) | A<br>(mmol/L) | r      | K <sub>F</sub>      | 1/n    | r      |
| MO         | DDB 0 mg/L   | 0.1220                     | 0.0155        | 0.9993 | 6.0449              | 0.3853 | 0.9611 |
|            | DDB 250 mg/L | 0.0723                     | 0.0376        | 0.9949 | 1.1711              | 0.5917 | 0.9950 |
|            | DDB 800 mg/L | 0.0471                     | 0.0184        | 0.9767 | 1.4255              | 0.4752 | 0.9866 |
| DDB        | MO 0 mg/L    | 0.1061                     | 0.0741        | 0.9909 | 5.9445              | 0.4491 | 0.9925 |
|            | MO 40 mg/L   | 0.1191                     | 0.0071        | 0.9784 | 17.8030             | 0.3248 | 0.9824 |
|            | MO 140 mg/L  | 0.2368                     | 0.2048        | 0.9845 | 4.2774              | 0.5940 | 0.9041 |

<sup>c</sup> Experimental temperature 20 °C

Figure 2: Influence of EG specific surface area on adsorption and competitive adsorption capacities



(a) Isotherm of MO (with DDB initial concentration of 250 mg/L)

(b) Isotherm of DDB (with MO initial concentration of 40 mg/L)

Graphite initial granularity (■) 0.30 mm; (●) 0.18 mm; (▲) 0.15 mm

### Influence of ionic strength on absorption and competitive adsorption capacities

In MO or DDB single aqueous solution and MO-DDB binary aqueous solution, NaCl and NaSO<sub>4</sub> aqueous solution were used to adjust ionic strength, respectively. Results prove that adsorbance of MO and DDB on EG increase slightly with the increase of ionic strength. Both electrostatic interaction and “salting-out effect” are often used to illuminate the results [17]. Accordingly, the electrostatic interaction between MO, DDB and EG decrease with the increase of ionic strength for the suppression of the electric double layer. On the other hand, hydrophobic attraction of MO and DDB increase due to the “salting-out effect”.

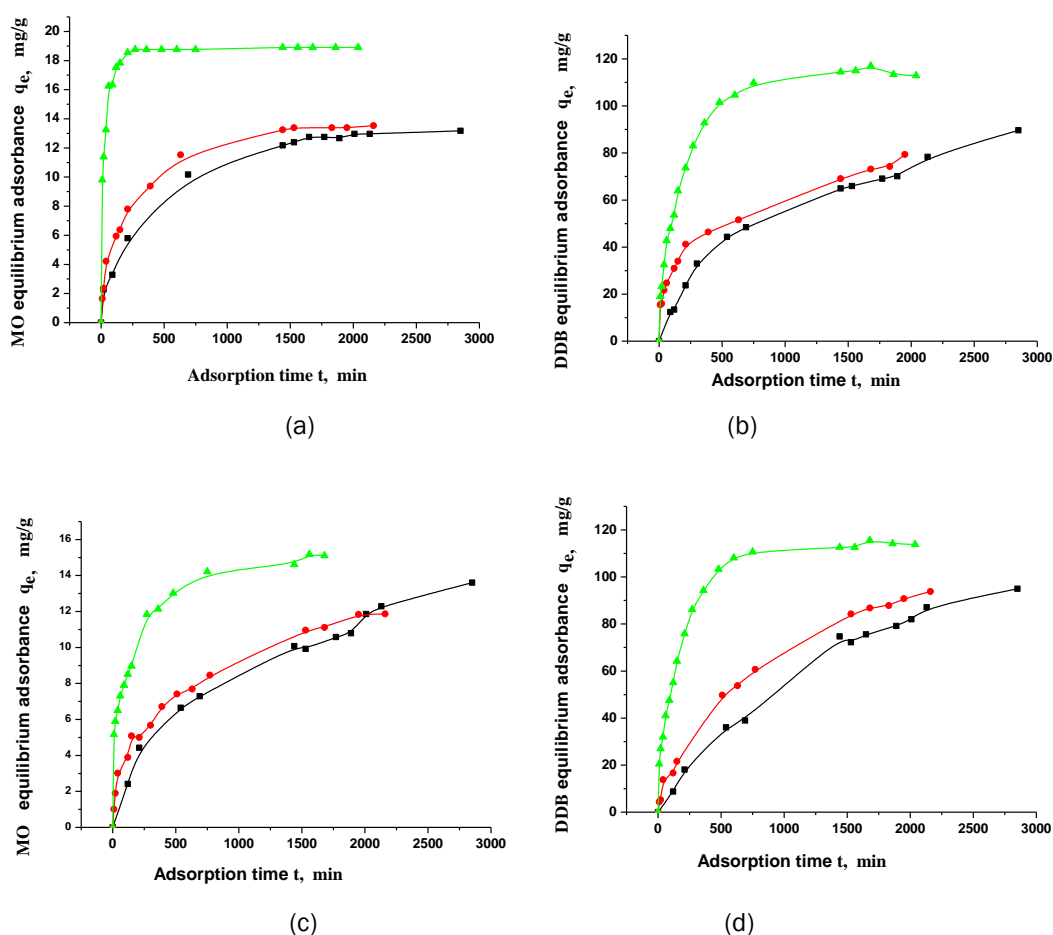
### Adsorption and competitive adsorption kinetics of EG for MO and DDB

As shown in Figure 3 and Figure 4, adsorbance is a function of time, temperature and dye concentration, adsorption equilibrium time is about 25 h for MO and 36 h for DDB. In DDB single aqueous solution and DDB-MO binary aqueous solution, adsorption for DDB occurs more rapidly in high temperature, and equilibrium adsorbance increase with the increase of temperature and initial DDB (or MO) concentration. As for MO, the influence of time,

temperature and dye initial concentration on adsorbance are more complex. When the initial concentration of MO is 40 mg/L, the equilibrium adsorbance increases with the increase of temperature (as shown in Figure 3), and adsorption occurs more rapidly in the early stage. But when it is 140 mg/L, the adsorbance decreased with the increase of temperature and time (as shown in Figure 4).

The results might be caused by different influence of temperature on MO and DDB effective concentration in solution and replacement of DDB for MO. Within certain concentration range, the increase of temperature will cause the decrease of DDB effective concentration and increase of MO effective concentration in solution. At the same time, the existence of competitive adsorption for the same adsorbing sites on EG and the difference in adsorbing rate, MO adsorbance increases with adsorption time first, and then it decreases due to the replacement of DDB (as shown in Figure 4 (c)). The coexistence of DDB would finally causes the decreased of MO equilibrium adsorbance, which become more obvious at high temperature. Under the condition of high dye concentration and solution temperature, EG will show higher affinity and selectivity for DDB than for MO.

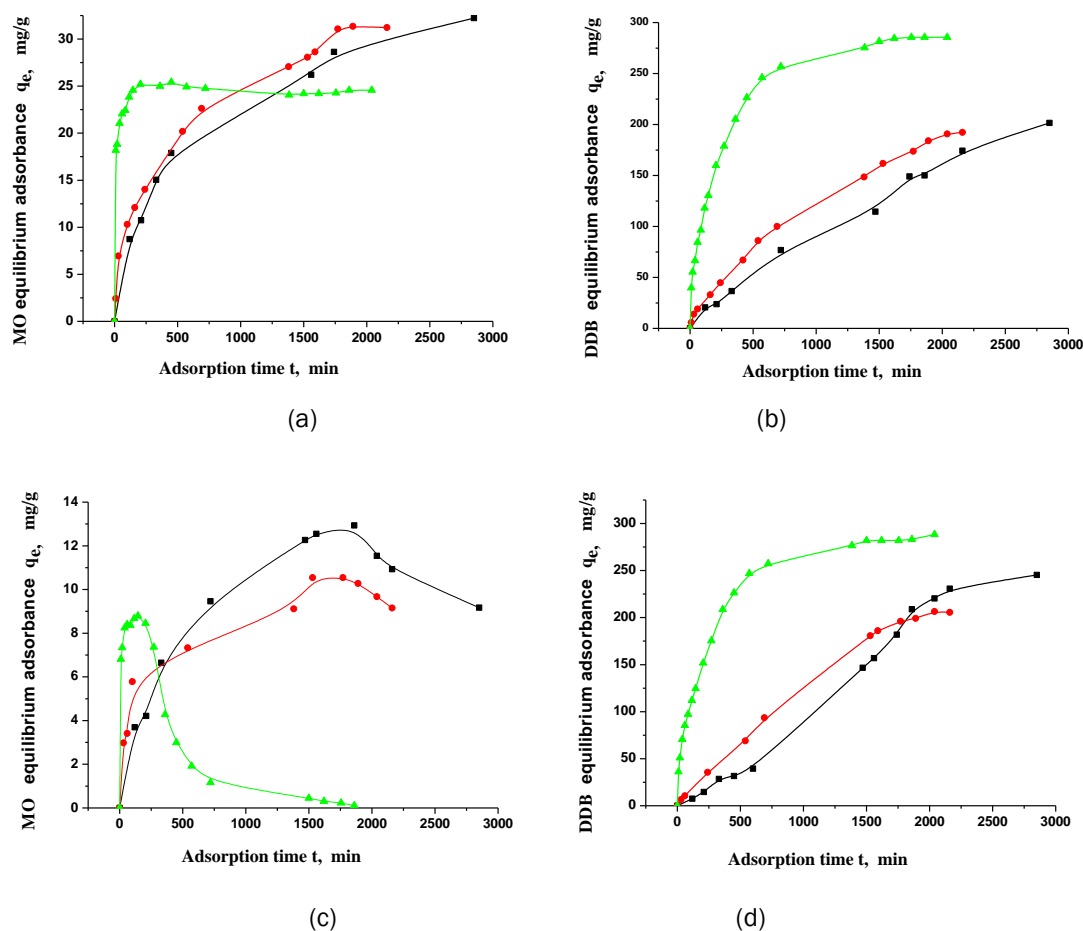
**Figure 3: Effect of the initial concentration and temperature on adsorption kinetics**



(a) MO single solution, MO concentration 40 mg/L; (b) DDB single solution, DDB concentration 250 mg/L; (c) MO-DDB binary solution, concentration of MO and DDB are 40 mg/L and 250 mg/L, respectively; (d) MO-DDB binary solution, concentration of DDB and MO are 250 mg/L and 40 mg/L, respectively

(■) 5 °C; (●) 20 °C; (▲) 45 °C

Figure 4: Effect of the initial concentration and temperature on adsorption kinetics



(a) MO single solution, MO concentration 140 mg/L; (b) DDB single solution, DDB concentration 800 mg/L; (c) MO-DDB binary solution, concentration of MO and DDB are 140 mg/L and 800 mg/L, respectively; (d) MO-DDB binary solution, concentration of DDB and MO are 800 mg/L and 140 mg/L, respectively

(■) 5°C; (●) 20°C; (▲) 45°C

Subsequently, the dynamic data corresponding to adsorption and competitive adsorption were characterized by pseudo-first-order model (Equation 1) and pseudo-second-order model (Equation 2) [18, 19]. Compare experiment data ( $q_{e,exp}$ ) with kinetic model data ( $q_{e,cal}$ ) and line curve fit coefficient  $r^2$ , we can see that: whether adsorption in MO single solution (Table 5) or competitive adsorption in MO-DDB binary solution (Table 6), the pseudo-second-order model gives better result than the pseudo-first-order model. As for the adsorption and competitive adsorption for DDB (Table 7 and Table 8), the pseudo-first-order model gives better result than the pseudo-second-order model at 5°C, 20°C. Specially, the pseudo-second-order model gives better result than the pseudo-first-order model at 45°C. For the adsorption of DDB on EG, temperature is the main influence factor, and its increases can cause the increase of adsorption rate constant  $k$  in single and binary aqueous solution. A higher adsorption temperature is good for the elimination of DDB.

$$\text{First-order model: } \ln(q_e - q) = \ln q_e - kt \quad (1)$$

$$\text{Second-order model: } t/q = 1/(k q_e^2) + t/q_e \quad (2)$$

$k$  –adsorption rate constant ( $\text{min}^{-1}$  for first-order adsorption,  $\text{g} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$  for second-order adsorption);  $t$ –adsorption time (min)

Table 5: Adsorption kinetic parameters of MO on EG in MO single solution

| C <sub>0</sub><br>mg/L | T<br>°C | q <sub>e,exp</sub><br>mg/g | Pseudo-first-order         |                            |                | Pseudo-second-order        |                                |                |
|------------------------|---------|----------------------------|----------------------------|----------------------------|----------------|----------------------------|--------------------------------|----------------|
|                        |         |                            | q <sub>e,cal</sub><br>mg/g | k<br>10 <sup>-3</sup> /min | r <sup>2</sup> | q <sub>e,cal</sub><br>mg/g | k<br>10 <sup>-3</sup> g/g/ min | r <sup>2</sup> |
| 40                     | 5       | 13.17                      | 9.95±<br>1.087             | 1.78±<br>0.073             | 0.9741         | 14.28<br>±0.002            | 0.309±<br>0.050                | 0.9878         |
|                        | 20      | 13.53                      | 11.11±<br>1.097            | 2.36±<br>0.101             | 0.9695         | 14.65<br>±0.001            | 0.371±<br>0.042                | 0.9933         |
|                        | 45      | 18.90                      | 11.29±<br>1.130            | 16.51±<br>0.947            | 0.9744         | 19.02<br>±0.000            | 4.951±<br>0.580                | 0.9999         |
| 140                    | 5       | 32.22                      | 26.25±<br>1.234            | 1.38±<br>0.115             | 0.9119         | 34.07<br>±0.001            | 0.114±<br>0.023                | 0.9743         |
|                        | 20      | 31.35                      | 26.00±<br>1.034            | 1.40±<br>0.037             | 0.9909         | 34.49<br>±0.001            | 0.100±<br>0.012                | 0.9863         |
|                        | 45      | 25.42                      | 12.59±<br>1.200            | 19.32±<br>1.830            | 0.9407         | 24.43<br>±0.000            | 4.479±<br>0.950                | 0.9985         |

Table 6: Competitive adsorption kinetic parameters of MO on EG in MO-DDB binary solution <sup>d</sup>

| C <sub>0</sub><br>Mg/L | T<br>°C | q <sub>e,exp</sub><br>mg/g | Pseudo-first-order         |                            |                | Pseudo-second-order        |                                |                |
|------------------------|---------|----------------------------|----------------------------|----------------------------|----------------|----------------------------|--------------------------------|----------------|
|                        |         |                            | q <sub>e,cal</sub><br>mg/g | k<br>10 <sup>-3</sup> /min | r <sup>2</sup> | q <sub>e,cal</sub><br>mg/g | k<br>10 <sup>-3</sup> g/g/ min | r <sup>2</sup> |
| 40                     | 5       | 13.60                      | 10.74±<br>1.065            | 0.84±<br>0.055             | 0.9348         | 13.60±<br>0.004            | 0.210±<br>0.042                | 0.9583         |
|                        | 20      | 11.84                      | 9.91±<br>1.050             | 1.42±<br>0.060             | 0.9725         | 12.79±<br>0.003            | 0.281±<br>0.034                | 0.9824         |
|                        | 45      | 15.18                      | 7.38±<br>1.235             | 1.78±<br>0.240             | 0.7744         | 15.24±<br>0.001            | 1.005±<br>0.193                | 0.9969         |
| 140                    | 5       | 13.39                      | 14.53±<br>1.177            | 2.81±<br>0.243             | 0.9243         | 13.44±<br>0.004            | 0.332±<br>0.093                | 0.9553         |
|                        | 20      | 10.98                      | 8.92±<br>1.081             | 0.57±<br>0.068             | 0.8132         | 10.61±<br>0.004            | 0.719±<br>0.243                | 0.9765         |
|                        | 45      | 8.79                       | 3.49±<br>1.426             | 30.3±<br>5.81              | 0.6633         | 9.11±<br>1.600             | 19.31±<br>3.811                | 0.9970         |

<sup>d</sup> At 45°C and initial concentration of DDB is 250 mg L<sup>-1</sup> when MO initial concentration is 40 mg L<sup>-1</sup>; initial concentration of DDB is 800 mg L<sup>-1</sup> when MO initial concentration is 140 mg L<sup>-1</sup>

Table 7: Adsorption kinetic parameters of DDB on EG in DDB single solution

| C <sub>0</sub><br>Mg/L | T<br>°C | q <sub>e,exp</sub><br>mg/g | Pseudo-first-order         |                            |                | Pseudo-second-order        |                               |                |
|------------------------|---------|----------------------------|----------------------------|----------------------------|----------------|----------------------------|-------------------------------|----------------|
|                        |         |                            | q <sub>e,cal</sub><br>mg/g | k<br>10 <sup>-3</sup> /min | r <sup>2</sup> | q <sub>e,cal</sub><br>mg/g | k<br>10 <sup>-3</sup> g/g/min | r <sup>2</sup> |
| 250                    | 5       | 89.69                      | 76.07±<br>1.045            | 0.83±<br>0.039             | 0.9660         | 93.20<br>±0.001            | 0.023±<br>0.004               | 0.9508         |
|                        | 20      | 79.83                      | 74.22±<br>1.213            | 1.82±<br>0.190             | 0.8351         | 81.97<br>±0.000            | 0.054±<br>0.010               | 0.9705         |
|                        | 45      | 117.01                     | 67.78±<br>1.173            | 1.87±<br>0.184             | 0.8663         | 121.65<br>±0.081           | 0.074±<br>0.006               | 0.9983         |
| 800                    | 5       | 201.55                     | 204.80±<br>1.055           | 0.78±<br>0.055             | 0.9389         | 240.93<br>±0.939           | 0.003±<br>0.000               | 0.5493         |
|                        | 20      | 192.27                     | 208.49±<br>1.079           | 1.42±<br>0.080             | 0.9576         | 266.67<br>±0.000           | 0.004±<br>0.000               | 0.8624         |
|                        | 45      | 285.57                     | 248.33±<br>1.066           | 3.09±<br>0.102             | 0.9850         | 309.60<br>±0.036           | 0.020±<br>0.001               | 0.9979         |



**Table 8: Competitive adsorption kinetic parameters of DDB on EG in MO-DDB binary solution <sup>e</sup>**

| C <sub>0</sub><br>Mg/L | T<br>°C | q <sub>e,exp</sub><br>mg/g | Pseudo-first-order         |                            |                | Pseudo-second-order        |                               |                |
|------------------------|---------|----------------------------|----------------------------|----------------------------|----------------|----------------------------|-------------------------------|----------------|
|                        |         |                            | q <sub>e,cal</sub><br>mg/g | K<br>10 <sup>-3</sup> /min | r <sup>2</sup> | q <sub>e,cal</sub><br>mg/g | k<br>10 <sup>-5</sup> g/g/min | r <sup>2</sup> |
| 250                    | 5       | 95.00                      | 93.73<br>±1.049            | 0.981±<br>0.042            | 0.9718         | 125.63<br>±0.001           | 0.732±<br>0.083               | 0.8911         |
|                        | 20      | 93.79                      | 97.00<br>±1.055            | 1.54±<br>0.058             | 0.9760         | 121.65<br>±0.001           | 1.130±<br>0.113               | 0.9240         |
|                        | 45      | 115.65                     | 72.45<br>±1.120            | 2.05±<br>0.127             | 0.9487         | 120.92<br>±0.000           | 7.926±<br>0.646               | 0.9986         |
| 800                    | 5       | 245.34                     | 290.07<br>±1.110           | 1.06±<br>0.094             | 0.8940         | 584.80<br>±0.000           | 0.045±<br>0.005               | 0.5838         |
|                        | 20      | 206.52                     | 248.94<br>±1.093           | 1.65±<br>0.097             | 0.9575         | 331.13<br>±0.001           | 0.219±<br>0.003               | 0.7148         |
|                        | 45      | 288.36                     | 213.53<br>±1.072           | 2.15±<br>0.079             | 0.9773         | 309.60<br>±3.813           | 1.987±<br>0.144               | 0.9976         |

e At 45 °C and initial concentration of MO is 40 mg/L when DDB initial concentration is 250 mg/L; initial concentration of MO is 140 mg/L when DDB initial concentration is 800 mg/L

### CONCLUSIONS

This study has provided an insight into the adsorption and competitive adsorption of MO and DDB in single and binary aqueous solution. The results allow us to assume that:

An increase in the adsorbance of MO or DDB might be caused by the increase of initial dye concentration, ionic strength or EG specific surface area. In MO-DDB binary aqueous solution, the coexistence of DDB can obviously decrease adsorbance of MO on EG for the competition for the same adsorbing sites and the replacement of DDB for MO. On the contrary, there is a synergic effect of MO for the adsorption of DDB; the coexistence of MO can bring new adsorbing sites being more propitious to the adsorption of DDB. For MO-DDB binary solution, adsorption on EG is selective. Adsorption and competitive adsorption processes of MO on EG can all be described with pseudo-second-order kinetic model, the main influence factors are MO concentration and temperature. As for the adsorption and competitive adsorption of DDB on EG, the main influence factor is temperature. The pseudo-first-order model gives better result in low temperature; the pseudo-second-order model gives better result in high temperature.

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