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Study on the adsorbing characteristics of expanded graphite for organic dyes

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ABSTRACT

The adsorbing characteristics of expanded graphite for dyes in single component solution have been investigated. Five reference sorbates were basic fuchsine with tritane structure, auramine lake yellow O with biphenyl structure and acid brilliant red 3B, oxamine blue GN(B) , methyl orange all with azobenzene structure. Expanded graphites were characterized by expanded volume, specific surface area and pore cubage. Sorption isotherm, Langmuir constants and free energy change ($\Delta G°$) were detected and calculated, respectively. Influence of pH on absorbency and adsorbance, and impact of NaCl, $NaSO_4$, $NaNO_3$ on adsorbance were investigated. It was demonstrated that adsorption of dye on expanded graphite was a spontaneous process. Both dyes' molecular weight and molecular structure affected sorption type and saturation adsorbance. Linear relationship was obtained between sorption capacity and specific surface area. Expanded graphite kept a stronger sorption for dyes with weak polarity than that with strong polarity. The presence of salts and the proper adjustment of pH would improve the sorption capacity. Contrastive adsorption experiment to sewage from woolen mill testified expanded graphite possessed a higher decolor rate to dyes than active carbon.

KEYWORDS

Expanded graphite;
Dyes;
Adsorbing thermodynamics;
Adsorbing isotherm;
pH;
Salt.

INTRODUCTION

Most of the industries such as textiles, paper, plastics, leather, food, cosmetic, etc, use dyes or pigments to color their final products. Such extensive use of color often possess problems in the form of colored wastewaters that require pretreatment for color prior to disposal into receiving water bodies or publicly owned treatment works. Most of the commercially used dyes are resistant to biodegradation, photodegradation and oxidizing agent. Unless properly treated, these dyes may significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of metals, chlorides, etc. While both biological and physical/chemical methods have been employed for dye removal, the former have not been very successful, due to the essential non-biodegradable nature of most of the dyes.

Adsorption is a kind of effective measure, active carbon[1-4], modified Al_2O_3[5], anion exchange resin[6], active sludge[7,8], peat, steel plant slag and fly ash have been reported to be employed for the treatment of dyes [9]. Expanded graphite is a kind of eco-material and possesses environmental consciousness and biological compatibility. Its abundant porous structure makes it have the capacity as adsorbent. According to Walker's adsorption experiment of acid dyes on active carbon[1], micropore structure was found to be redundant in the adsorption of large molecular weight compounds such as dyes, and only 14% of the total specific surface of the activated carbon is available for adsorption due to the high molecular area and aggregation of the dye.

However, expanded graphite particles have 4 levels with the size ranging from nanometer scale to micron scale[10], and most of them are open pores, only a few are close types. So it should have the capability to adsorb dyes. But its application in adsorbing of dyes from wastewater has been reported not so much. Wang pressed the worm-like particles into low-density plate of 0.1g/cm^3[11], then the plate was used to treat dye waste-water from woolen mill, and the optimum applying condition was tested. Beata guessed the possibility to remove dyes with expanded graphite from wastewater in the removal of engine oils[12]. Research group of Hebei normal university investigated the influencing factors in sorption process and indicated that the sorption capacity of expanded graphite was influenced by various factors, not only the expanded volume, primary concentration of dyes, contact time, but also the amount of expanded graphite, pH and temperature[13]. But they neglected the influence of pH both on absorbency and sorption capacity, and improper pH was used. At the same time, too high dosage of sorbents or too low primary concentration of dyes' solution caused that adsorption isotherms of the tested dyes were all type I, which could not reflect real adsorbing type on expanded graphite.

The objective of the present study was to do further research on adsorbing thermodynamics, adsorbing isotherm. Investigate the effect of pH, specific surface area and salt, such as NaCl, NaSO$_4$ or NaNO$_3$ presented in dye's solution on sorption capacity, and evaluate the decolor capacity of expanded graphite. In the research, basic fuchsine, auramine lake yellow O, acid brilliant red 3B, oxamine blue GN(B) and methyl orange were used as reference compounds.

EXPERIMENTAL

Sorbents

Expandable graphite was firstly prepared according to literature[14], and then it was expanded in KSW heating oven(Huacheng Oven Factory of Tientsin) at 300°C, 400°C and 900°C, respectively. Sorbents with different expanded volumes were obtained. Structural parameters of expanded graphite were characterized by expanded volume, surface area, pore cubage and pore size distribution. Expanded volume was detected by the research group and was expressed in terms of the volume to mass ratio. Surface area, pore cubage, pore size distribution were offered by Chinese Academy of Science(CAS). Adsorbent surface area investigations were carried out using Quadrasorb SI specific surface area meter(Quantachrome Instruments,USA) from which the total surface area was calculated by the Brunauer–Emmett–Teller (BET) method by measuring the adsorbent's adsorption and desorption of nitrogen under varying pressures. Pore cubage investigations were carried out using PoreMaster 60GT (Quantachrome Instruments, USA) instrument under varying pressures. Detection results of structural parameters were listed in TABLE 1. Figure 1 shows the porous structure and wide pore size distribution of ex-

TABLE 1: Structural parameter of expanded graphite

Expanded volume (mL/g)	Specific surface area (m^2/g)	Total pore cubage(cm^3/g)	Distributing of pore diameter
90	24.03	28.67	4 nm~950μm
180	43.31	30.4	4 nm~950μm
240	79.92	66.73	4 nm~950μm

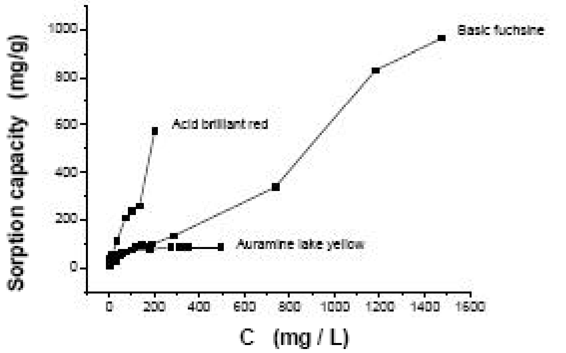
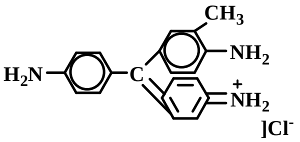
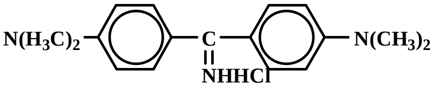
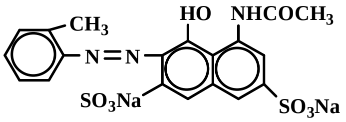
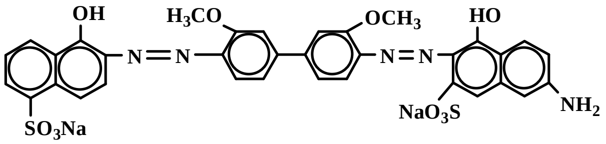
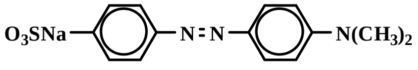


Figure 1 : Adsorption isotherm of basic fuchsine, acid brilliant red 3B and auramine lake yellow O at atmospheric pressure and 20^{0}C

TABLE 2: Chemical structure and molecular weight of dyes used for experiment

Dye	Structure	Molecular weight	λ_{max}(nm)
Basic fuchsine		338.5	543
Auramine lake yellow O		318.5	430
Acid brilliant red 3B		675.0	520
Oxamine blue GN (B)		773.7	560
Methyl orange		327.3	463

panded graphite ranging from nm to μm.

Sorbates

Five kinds of dyes were selected as reference compounds. They were basic fuchsine with tritane structure, auramine lake yellow O with biphenyl structure and acid brilliant red 3B, oxamine blue GN(B), methyl orange all with azobenzene structure. The dyes were supplied by Yuhua trade company, Tientsin, China. Molecular structures and molecular weight of these dyes are shown in TABLE 2.

Simulated dye wastewaters were prepared by dissolving the different dyes in distilled deionized water at various concentrations. All color measurements were made with a 722S spectrophotometer (Precision Instrument Limited Company of Shanghai) operating in the visible range on absorbance mode. Absorbance values were recorded at the wavelength for maximum absorbance(λ_{max}) corresponding to each dye, and each dye solution was initially calibrated for concentration in terms of absorbance units.

Methods

1. Static adsorption and equilibrium adsorption amount

Batch equilibrium experiments were undertaken using a series of solutions of consecutively increasing initial dye concentration and of fixed volume 100.0mL which were placed in vessels where they were brought into contact with expanded graphite. The mass of adsorbent to volume of solution was standardized at M/V=0.05 g/0.lL=0.5g/L. The jars were sealed and placed in a shaker for 24h until equilibrium was reached. The samples were then analysed using standard spectrophotometry techniques. The temperature of the solution was held at 20°C. This was then used to calculate the solid phase dye concentration, Q(adsorption amount of adsorbate on adsorbent, mg/g) by a material balance on the adsorption system. The amount of adsorbate captured by the adsorbant was determined as follows:

$$Q=V(C_0-C)/M \qquad (1)$$

where: C_0: Initial concentration of dye in solution, mg/L; C: Equilibrium concentration of dye in solution, mg/L; M: Mass of adsorbent g

2. Adsorption isotherm and langmuir constant

The expanded graphite was equilibrated with the above reference dyes at a concentration ranging from 0.0 to 2000mg/L in 250mL flasks that were kept well mixed with a constant adsorbent. 24h was sufficient to reach equilibrium. After the equilibration period the flasks were sampled and the concentrations of the adsorbates in the solutions were determined by spectrophotometric measurements. Q was calculated according to equation (1). Isotherm was made from equilibrium concentration versus adsorbance. Then the experimental data which kept linear relationship were fitted with the Langmuir equation, and Langmuir constants were calculated from the intercept and slops of straight-line 1/Q versus 1/C[15].

3. Sorption capacity of expanded graphite in the influence of salt concentration, pH and expanded volume

NaCl, Na_2SO_4 and $NaNO_3$ were used to investigate their influence on sorption capacity of expanded graphite. Batch equilibrium experiments were undertaken by using a 100mg/l of different dye solutions which contained different salt at a concentration ranging from 0 to 50mg/L. The mass of adsorbent to volume of solution was standardized at 0.5g/L, and equilibrium adsorption amount was calculated according to equation (1).

In the range of 2 to 12, pH of the dye solutions was adjusted by HCl or NaOH, then detected with pHS-3C acidimeter (Weiye Instrument Company of Shanghai). The absorbencies under different pH were detected. The dye whose absorbency did not change along with pH was chosen to study the influence of pH on sorption capacity.

Three kinds of adsorbents with different expanded volume of 90mL/g, 180mL/g and 240mL/g were used respectively to determine the influence of expanded volume on sorption capacity. The mass of adsorbent to volume of solution was standardized at 0.5g/L.

RESULTS AND DISCUSSION

Investigation of adsorption isotherm and thermodynamic parameters

Static sorption capacities of expanded graphite corresponding to different equilibrium concentrations of basic fuchsine, acid brilliant red 3B and auramine lake yellow O were measured. Figure 1 illustrate a typical adsorption isotherm for the adsorption of basic fuchsine, acid brilliant red 3B and auramine lake yellow O onto expanded graphite with an expanded volume of 240mL/g, as a plot of solid phase equilibrium adsorbance versus liquid phase equilibrium concentration. Adsorption types of Basic fuchsine and acid brilliant red 3B were both type II. Sorption capacity increased quickly with increasing equilibrium concentration, which might be a result of multiplayer sorption of molecules[16]. Sorption isotherm for auramine lake yellow O was type I, of which molecule has a planar structure, so that its multiplayer sorption might not occur. In this case, large molecules adsorbed might form certain kinds of conformation on the surface of expanded graphite, which might reduce the adsorbed sites and make further sorption difficult. In the adsorbing research of biomedical molecules[17], such as ovalbumin, serum albumin, bovine serum albumin, lysine and herring sperm DNA, similar results were obtained. Sorption isotherms for ovalbumin, serum albumin, bovine serum albumin, lysine were type II, respectively, and that of linear herring sperm DNA was type I.

In the condition of monolayer adsorption, adsorption constant could be obtained from Langmuir equation[15]:

$$Q=Q_0\cdot C/(A+C) \qquad (2)$$

where: Q_0: The maximum adsorption amount of dye on expanded graphite in forming complete monolayer coverage on the surface; mg/g, A: The equilibrium concentration of dye corresponding to half saturation adsorbance; mg/mL

Equation (2) could be changed as the following form:

$$1/Q = 1/Q_0 + A\cdot/(Q_0\times C) \qquad (3)$$

Based on equation (3), the values of $1/Q_0$ and A could be calculated from the intercepts and slopes of the straight lines. Smaller A should indicate lower equilibrium concentration of dye at the half saturation adsorbance. In a word, the adsorbing intensity of adsorbent to sorbate was stronger. The dye holding bigger A should have a weak adsorption with expanded graphite.

The adsorption free energy change ($\Delta G°$) could be calculated according to equation (4)[18]:

$$\Delta G° = -RT\ln b \qquad (4)$$

where: b-Langmuir equation constant; mL/mg, and b=1/A; $\Delta G°$-Free energy change in the adsorption. Negative of free energy indicated adsorption was spontaneous.

Based on experimental data, Langmuir constants

TABLE 3: Adsorption constants and thermodynamic parameter of basic fuchsine, acid brilliant red 3B, auramine lake yellow O[a]

Dye	Molecular weight (g/mol)	Q_0 (mg/g)	A (mg/mL)	ΔG° (kJ)
Acid brilliant red 3B	675.0	235.85	0.031	-8.46
Basic fuchsine	338.5	85.69	0.0089	-11.27
Auramine lake yellow O	318.5	64.31	0.0071	-11.79

[a] The experiment was carried out at atmospheric pressure and 20^{0}C

TABLE 4: Adsorption constants and thermodynamic parameter of acid brilliant red 3B, oxamine blue GN (B), methyl orange[a]

Dye	Molecular weight (g/mol)	Q_0 (mg/g)	A (mg/mL)	ΔG° (kJ)
Acid brilliant red 3B	675.0	235.85	0.031	-8.46
Methyl orange	327.3	52.11	0.0032	-13.67
Oxamine blue GN(B)	773.7	80.0	0.017	-9.74

[a] The experiment was carried out at atmospheric pressure and 20^{0}C

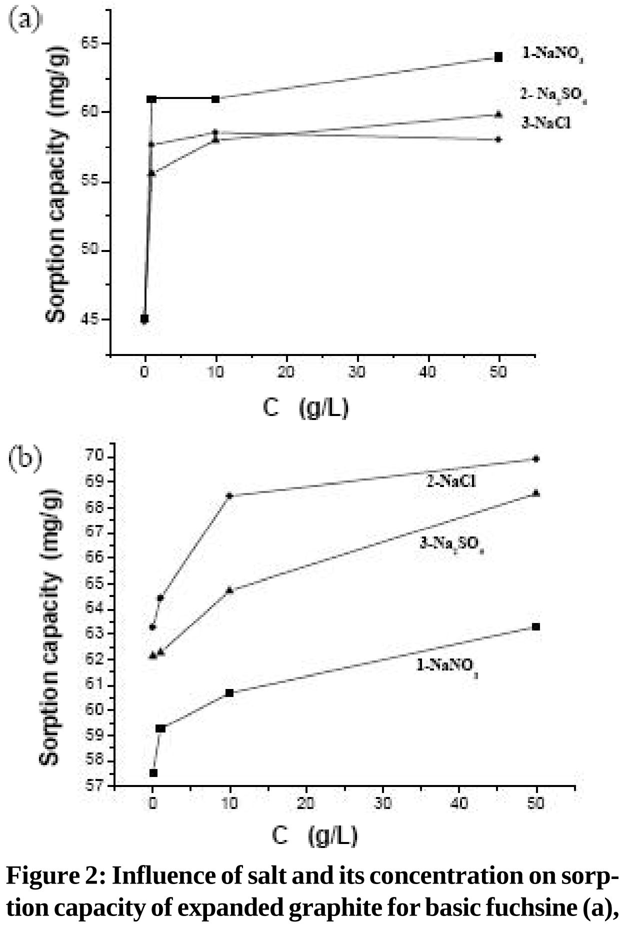


Figure 2: Influence of salt and its concentration on sorption capacity of expanded graphite for basic fuchsine (a), acid brilliant red 3B (b), auramine lake yellow O (C) at atmospheric pressure and 20^{0}C

for basic fuchsine, acid brilliant red 3B, auramine lake yellow O, oxamine blue GN (B) and methyl orange are shown in TABLES 3 and 4, respectively. Negative ΔG° indicated that adsorption of the reference compounds on expanded graphite were all spontaneous. Sorption to basic fuchsine and auramine lake yellow O were stronger than that to acid brilliant red 3B. The results were caused by the lipophilic nature of expanded graphite and polarity difference of dye' molecular. Comparing with basic fuchsine and auramine lake yellow O, acid brilliant red 3B possessed weaker affinity with expanded graphite, because it contained sulfo-group in its molecule.

Data listed in TABLE 3. indicated that saturation adsorption amount of expanded graphite for dyes had a same change order as that of the dyes molecular weight, and molecular weight was the main factor influencing adsorbance. Acid brilliant red 3B had a larger saturation adsorption amount than that of basic fuchsine and auramine lake yellow O.

As shown in TABLE 4, different azoic dye had a different A and different saturation adsorption amount. Methyl orange possessed the smallest A, the strongest affinity between it and expanded graphite was caused by their similar weak polarity. Although oxamine blue GN (B) held the highest molecular weight compared with that of acid brilliant red 3B and methyl orange, its planar structure and larger molecular area might reduce the number adsorbed on expanded graphite's surface, and then presented a smaller adsorbance than that of acid brilliant red 3B.

Influence of salt and its concentration on sorption capacity

To investigate the influence of NaCl, Na_2SO_4, $NaNO_3$ on sorption capacity of expanded graphite for basic fuchsine, acid brilliant red 3B and auramine lake yellow O, adsorbing research was carried out using a 100 mg/l of different dye solutions which contained different salt at a concentration ranging from 0 to 50 mg/l. The results are shown in figure 2. It indicated that the presence of NaCl, Na_2SO_4, $NaNO_3$ enhanced the sorption of expanded graphite for dyes. The possible reason might be: Absolute ionization of NaCl, Na_2SO_4, $NaNO_3$ in dye's solution made them form negative and positive ions, so there did not exist competitive adsorp-

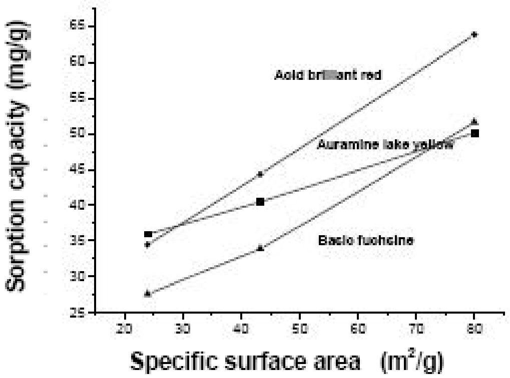


Figure 3: Soak absorbing capacity to dyes of expanded graphite with different expanded volume at atmospheric pressure and 20°C

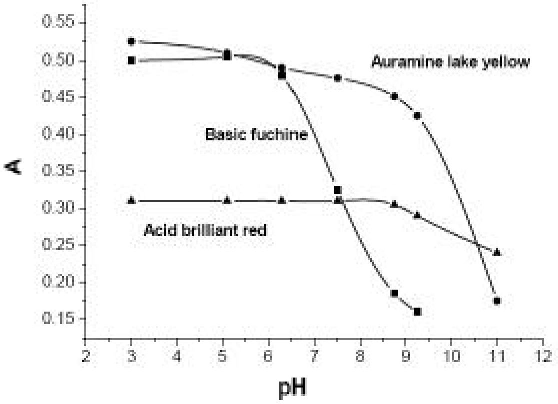


Figure 4: Influence of pH on dye' absorbency

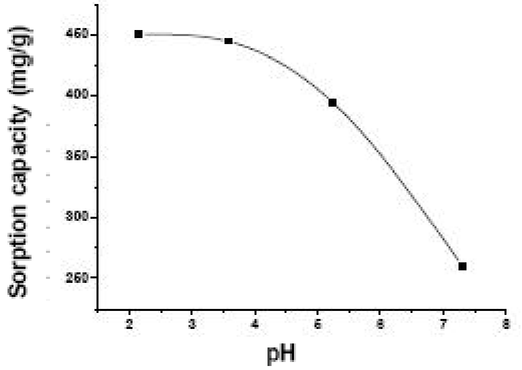


Figure 5: Influence of pH on sorption capacity of expanded graphite for acid brilliant red 3B at atmospheric pressure and 20°C

tion with dye molecule on absorbent. On the other hand, electrostatic interaction between dye and adsorbent decreased with the increase in ionic strength probably because of the suppression of the electric double layer[19], and hydrophobic attraction increases due to the "salting-out" effect. Over a range of 5.0g/L to 50.0g/L, the adsorbance of basic fuchsine and auramine lake yellow O increased slightly. But the change of acid brilliant red 3B was correspondingly obvious. For different dyes, the influences of NaCl, Na_2SO_4, $NaNO_3$ on sorption capacity were different.

Influence of sorbent' specific surface area on sorption capacity

The sorption capacities of sorbents with different expanded volume of 90 mg/l, 180mg/l and 240mg/l were measured, respectively. The results for basic fuchsine, acid brilliant red 3B and auramine lake yellow O are shown in figure 3. It can be seen that there was a linear relationship between the sorption capacity and the specific surface area of expanded graphite. This is due to the abundant porous structure of graphite adsorbent. Commonly, dyes belong to big molecule substance, and they are easy to be adsorbed in the middle pores and the macropores[1]. The bigger the expanded volume of expanded graphite possessed, the larger the specific surface area and pore cubage it would hold, especially middle pores and macropores as shown in TABLE 1. Correspondingly, adsorbance increased linearly along with expanded volume. However, the adsorption characteristic of expanded graphite was different from active carbon in adsorbing dyes. Active carbon has higher ability in monolayer adsorption, but there was no obvious relationship between specific surface area and sorption capacity to dye[20]. While, the adsorption of acid brilliant red 3B and basic fuchsine on expanded graphite was multilayer.

Influence of pH on absorbency and sorption capacity

Ionic dyes upon dissolution release colored dye anions/cations in solution, and their absorbency changed along with the existence form, which was influenced by pH. So it is important to know how the pH affected absorbency and what the range of pH was before the study of pH on sorption capacity. Figure 4 indicates that acidity led to a change of absorbency under a certain wavelength. So pH studies could not be conducted on basic fuchsine and auramine lake yellow O. As for acid brilliant red 3B, the change of pH from 2.0 to 7.0 had no noticeable impact on absorbency, and the influence of pH on sorption capacity was investigated.

TABLE 5: Decolor rate of expanded graphite for acid brilliant red 3B

Experiment	Adsoption capacity mg/g	Decolor rate %
Reference experiment	122.2	61.09
Normal experiment	191.9	95.97

***Reference experiment: 20°C, acid brilliant red 3B initial concentration 100mg/L; Normal experiment: 20^{0}C, pH 2.0, NaCl concentration 20g/L, acid brilliant red 3B initial concentration 100mg/L**

TABLE 6: Contrast of decolor rate for sewage from woolen mill

Adsorbent	CODc$_r$ before adsorption mg/L	CODc$_r$ after adsorption mg/L	Adsorbance mg/g	Decolor rate %
Expanded graphite	186.7	167.0	394.0	10.27
Active carbon	186.7	179.1	152.0	4.05

***Condition: Dosage of adsorbent was 0.05g and the temperature was controlled at 20^{0}C**

Figure 5 gives a degressive relationship between equilibrium adsorbance and pH. This might be caused by the decrease of molecule of brilliant red 3B. The decreasing H$^+$ enhanced ionization of dyes in solution, and reduced the amount of unionized molecules. The lipophilic nature of the adsorbent led to the degressive adsorbance.

Evaluation of adsorption capability of expanded graphite for dye's waste water

Decolor rate of expanded graphite for acid brilliant red 3B simulated waste water was detected under the condition of dye concentration 100 mg/L, pH 2.0, NaCl concentration 20g/L, which was determined according to the above research results about the influence of salt's concentration, pH and expanded volume of the adsorbent on sorption capacity. The results as listed in TABLE 5. were collated with reference experiment which was carried out with no pH and salt's concentration adjustment. The existence of salts and properly adjustment of pH would improve the decolor rate of expanded graphite for dyes.

Meanwhile, the contrast of adsorption capacity between expanded graphite and active carbon with the same size was put in practice in dealing with real sewage from woolen mill with an initial chemical oxygen demand (COD$_{Cr}$) of 186.7 mg/L. The results were listed in TABLE 6. Expanded graphite possessed a higher adsorption capacity than active carbon because it's multilayer adsorption ability to dyes.

CONCLUSIONS

This study has provided an insight into the adsorption isotherm and thermodynamic parameter of expanded graphite for different dyes. Adsorption of dye on expanded graphite was a spontaneous process. The adsorption types of basic fuchsine, acid brilliant red 3B and auramine lake yellow O were type II, type II and type I, respectively. Saturation adsorption amount of dyes lied on its molecular weight and molecular area. Adsorption process was influenced by multifactors, not only the expanded volume, initial concentration of dyes, the amount of expanded graphite, salt and pH, but also the molecular structure of dyes. Expanded graphite preferred adsorbing dyes with weak polarity(such as auramine lake yellow O and methyl orange) to dyes with strong polarity(such as acid brilliant red 3B). pH of the solution not only impacted absorbency of dye, but also influenced its adsorbance on expanded graphite. Salts played an important role in influencing the sorption capacity of expanded graphite to dyes.

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