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Dye adsorption on biosolid adsorbents and commercially activated carbon

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Abstract

This study reused biosolids to manufacture adsorbents (S500 and S600) and used for Chrysophenine (CH) and Orange II adsorption. In addition, a commercially activated carbon (F820) was selected and used in dye adsorption to enable comparison of the dye adsorption characteristics of biosolid adsorbents and commercially activated carbon. The Boehm titration method allows determination of the oxygen surface functional groups. Results indicated that the distribution of the surface functional groups of the two biosolid adsorbents was similar in spite of the fact that they were pretreated under different pyrolytic temperatures. Only a small amount of quinoid-type group existed on the surface of biosolid adsorbents, but it contributed substantially to the surface functional group on F820. The sequence of BET surface area was S600 (813 m^2/g) $\approx$ F820 (802 m^2/g) $>$ S500 (737 m^2/g). The commercially activated carbon had a high micropore volume and possessed a significant pore volume increment at the pore diameter $<$ 13 Å (a large pore volume peak in the vicinity of 9 Å). The pore volume of biosolid adsorbents was high in the vicinity of 500 Å (macropore) and 80 Å (mesopore). The sequence of CH adsorption capacity was S500 $>$ S600 $>$ F820 at different temperatures, indicating that the biosolid adsorbents were more suitable for CH adsorption than the commercially activated carbon. But for Orange II, the adsorption capacity of biosolid adsorbents was higher than F820 at 10 °C. When the adsorption temperature increases, the mass transfer increases and overcomes the adsorption energy barrier. Therefore, the Orange II molecule could transfer into micropores, and the adsorption capacity of F820 approached that of biosolid adsorbents. Moreover, the adsorption capacity of F820 could be higher than that of biosolid adsorbents at 60 °C.

Keywords: Adsorption; Chrysophenine; Orange II; Biosolid adsorbent; Activated carbon

1. Introduction

Treatment and disposal of biosolids generated from wastewater treatment processes is perhaps one of the most complex environmental problems facing the engineer. Furthermore, it is known that the cost of sludge disposal is greater than 50% of the total operation cost of wastewater treatment [1]. In the past years, sludge disposal methods included landfill, composite, incineration, and pyrolysis [2,3]. Pyrolysis is used to convert biomass and wastes into fuels that are regarded as a renewable resource [4,5]. Sewage sludge pyrolysis has advantages over other techniques, especially if the sludge contains heavy metals (excluding mercury and cadmium) [6]. Heavy metal leaching in pyrolytic ash is less than that in incineration ash [6].

Many studies in the literature have reported the selection of sewage sludge as raw material and the use of pyrolysis and chemical activation or physical activation processes as the treatment methods. $ZnCl_2$ is a popular activation agent for converting sludge [7–12] to adsorbents. In addition, sulfuric acid [13,14] and acetic acid [15] were also used as activation agents, but the surface areas of acid derived adsorbents were less than that of $ZnCl_2$ activation. A simple carbonization method was used to produce adsorbents, but its surface area was low [16]. $ZnCl_2$ activation processes seemed to generate

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a higher specific surface area of sludge-derived adsorbents than other activation methods, but these processes require immersing sludge into a high concentration (3–5 M) solution for about 1–2 h before pyrolysis. Therefore, this process could be improved to reduce the $ZnCl_2$ concentration and pyrolytic times. Sludge-derived adsorbents were used for the adsorption of VOCs [7], H_2S [9,13,16], and dyes [14,15].

The effluent wastewater from dyeing and finishing processes in the textile industry is known to contain color, high amounts of surfactants, dissolved solids, and possibly heavy metals [17]. The removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogenic and/or toxic [18]. The dyes are stable to light and heat and are biologically non-degradable. The conventional methods in use in wastewater treatment, such as primary and secondary treatment systems, are unsuitable [19]. Therefore, it is necessary to use tertiary treatment to remove color before discharge. Water-insoluble dyes generally exhibit good exhaustion properties, i.e., most of the dye bonds to fiber and can be removed by physical processes such as flocculation [20]. However, for the water-soluble dyes (reaction dyes) that are used extensively by the industry, conventional biological treatment processes are not able to achieve adequate color removal. Another important reason for the use of adsorption as a technique for treating wastewater containing reactive dyes is the failure of conventional physicochemical coagulation/flocculation methods [21].

Many investigations have been conducted on physicochemical methods for the removal of color from textile effluents. Those studies included coagulation [22], oxidization [23], ultra-filtration [24], electro-chemical [25,26], and adsorption [27] techniques. Activated carbon is the most effective and widely used adsorbent; it has rapidly gained prominence as a treatment process that produces good-quality effluents with low concentrations of dissolved organic compounds, such as dyes from the wastewater effluent of textile industries.

Some studies have reported the effect of surface functional groups of activated carbon on dye adsorption. Al-Degs et al. [20] investigated the effect of carbon surface chemistry on the removal of Remazol reactive dyes from textile effluent. They attributed the high adsorption capacity of F400 to the net positive surface charge during the adsorption process. Pereira et al. [28] used HNO_3, H_2O_2, NH_3 and thermal treatment to modify the surface chemical groups of activated carbon under H_2 and N_2 gas. Anionic dyes exhibited a strong dependence on the surface basicity of adsorbents, whereas cationic dyes showed greater affinity toward the acid oxygen-containing surface groups. Surface characteristics are important factors of activated carbon in terms of dye adsorption capabilities. Yang and Al-Duri [29] also used activated carbon to remove reactive dyes and reported that activated carbon adsorption was an effective method for dye removal.

The objective of this study was to recycle the biosolid to adsorb Orange II and Chrysophenine (CH) from wastewater. A commercially activated carbon was also used in dye adsorption experiments. The dye adsorption characteristics of biosolid adsorbents and commercially activated carbon were compared. The biosolid adsorbent was characterized for its surface function groups, specific surface area, pore volume distribution, adsorption energy, and adsorption capacity.

2. Experimental

2.1. Raw material

Biosolid samples were obtained from a petrochemical biological wastewater treatment plant in Taiwan. Sludge cakes were taken from the belt filter press dewatering equipment. To ensure the stability of sludge cake composition, the sludge sample was taken in batches of 300–400 kg. The biosolid samples were refrigerated at 4 °C upon arrival in the laboratory. Two kilograms of the biosolid sample was heated at 105 °C for 24 h in each run. The dried biosolid was immersed in a 1 M $ZnCl_2$ solution and mixed for 24 h, then filtered to collect the solid, which was dried at 105 °C for 24 h. Each sample was brought back to the laboratory and kept in a desiccator for further utilization.

2.2. Pyrolytic processes

A 40-g sample of the oven-dried biosolid was placed in the middle of a quartz reactor tube. High-purity nitrogen (99.995%) flowed over the sample bed at a rate of 2 L/min. The reactor was heated to the desired temperature at a rate of 15 K/min. When the furnace reached the reaction temperature, the biosolid sample was put into the furnace for pyrolysis. Pyrolysis temperatures varied from 500 (S500) to 600 (S600) °C, and the residence time was 30 min. When the pyrolysis process was completed, the quartz reactor was removed from the furnace, and the nitrogen gas continued to flow to quench the residue temperature. After the residue was cooled to room temperature, it was removed from the reactor, weighed, and characterized.

2.3. Manufacture of biosolid adsorbent

$ZnCl_2$ immersed pyrolytic residue was put into a flask. HCl (3 N) was added to remove the $ZnCl_2$ from the pyrolytic residue. The solution was then filtered. The pyrolytic residue samples were washed with distilled water until the electric conductivity of the rinsed water reached that of distilled water. The pyrolytic residue was dried in an oven at 105 °C for 48 h and then transferred to a desiccator until use.

2.4. Commercially activated carbon

To compare the adsorption characteristics and confirm that the sludge adsorbent is able to remove dyes, a commercially activated carbon, F820 (Norit, 8–20 mesh), was selected.

2.5. Dyes

Orange II (Aldrich Chemical Company) and Chrysophenine (CH) (Aldrich Chemical Company) were used to assess the performance of sludge adsorbents and commercially activated carbon. Orange II and CH were analyzed by a UV/visible spectrometer (Lambda 12, model U-2001, Hitachi, Japan), with detection at 485 and 466 nm, respectively. The detection limits of Orange II and CH were 0.2 and 0.04 mg/l, respectively. The linear detection concentration range of Orange II and CH by the visible spectrometer is less than 80 mg/l (2.4×10^{-4} mol/l) and 110 mg/l (1.7×10^{-4} mol/l), respectively. Table 1 shows the properties of dye molecules. Molecular surface area and volume are determined using Connolly's program [30]. Dye molecule size including length, width, and thickness were measured by Molecular Mechanics 2 (MM2) using the Cambridge Soft Chem3D Ultra 8.0 interface [31,32].

2.6. Physical characteristics of adsorbents

2.6.1. Surface area and pore volume distribution

The physical characteristics of the biosolid adsorbents, including specific surface area, pore volume distribution, and pore diameter were measured via N_2(g) adsorption in an ASAP 2010 micropore analyzer at 77 K in liquid N_2. Surface area was calculated by the BET method [33,34]. Pore volume distribution was determined by the BJH method [35,36]. Silica–alumina (surface area, 215 ± 6 m^2/g; total pore volume, 0.61 ± 0.08 cm^3/g; and average pore diameter, 114 ± 15 Å), alumina (multipoint specific surface area 0.51 ± 0.03 m^2/g), and molecular sieve (median pore diameter, 8.3 ± 0.2 Å) were obtained from Micrometrics and used in quality assurance and quality control processes.

2.6.2. Surface chemistry characteristics

All solutions were prepared from chemicals provided by Merck Chemicals Company, Germany. A pH meter (model 420A) was used for pH measurements. Strong acid (0.1 N HCl) and bases (0.1 N $NaHCO_3$, Na_2CO_3, NaOH, and $NaOC_2H_5$) were used for the analysis of surface functional groups. Unless otherwise mentioned, strong acid (0.1 M $HClO_4$) and strong base (0.2 M NaOH) were used for all pH adjustments.

2.6.3. Boehm titration

Procedures for the analysis of oxygen functional groups follow those established by Boehm [37–41]. The activated carbon samples were first dried in a vacuum oven (10^{-2}–10^{-3} mmHg, 105 °C) for 24 h. Twenty-five milliliters of an alkali solution (0.1 N $NaHCO_3$, Na_2CO_3, NaOH, and $NaOC_2H_5$) was added to the test tubes containing a given amount of the activated carbon sample (5 g). The samples were constantly mixed over a vibrator (100 rpm) at 25 °C for 100 h to ensure that the surface function groups reacted with the alkali solution. A given amount of the supernatant (5 ml) was drawn from the test tubes and back-titrated with HC1 (0.1 N) solution. The concentrations of various functional groups were determined by the residual bases after back-titration as described by Boehm [37–41]. Selective neutralization by equilibration with a series of bases of increasing strength (i.e., $NaHCO_3 < Na_2CO_3 < NaOH < NaOC_2H_5$) allows differentiation of the various acid groups on carbon as follows: $NaHCO_3$ neutralizes carboxyl groups; Na_2CO_3 neutralizes carboxyl groups and neutralizes lactone groups to open and form carboxyl groups; NaOH neutralizes carboxylic, lactone, and phenolic groups; and $NaOC_2H_5$ neutralizes carboxylic, lactone, phenolic and carbonyl (quinoid-type) groups.

Table 1
Properties of Orange II and Chrysophenine

Property	Orange II	Chrysophenine, CH
Molecular formula	$C_{16}H_{12}N_2O_4S$	$C_{30}H_{28}N_4O_8S_2$
Molecular weight (g mol^{-1})	328.35	636.71
Molecular volume (Å^3 molecule^{-1})	231.95	485.97
Molecular surface area (Å^2 molecule^{-1})	279.02	554.86
Width (Å)	7.3	8.0
Length (Å)	13.6	29.4
Thickness (Å)	2.3	5.7

2.7. Adsorption isotherm

Orange II and CH concentrations ranged from 30 to 80 mg/l. One hundred milliliters of dye solution was put into a vial and then 10 mg of adsorbent was added. The vial was put into a water bath tank with temperatures ranging from 10 to 60 °C and shaken at 100 rpm for 10 days to ensure that the dye came into contact with the adsorbent and reached the adsorption equilibrium. After adsorption, the solution was filtered out and put into a centrifuge to separate the adsorbent particle and end the reaction. After that, the solution was characterized using a visible spectrometer.

3. Results and discussion

3.1. Physical characteristics of adsorbents

Table 2 shows the physical characteristics of the adsorbents. The sequence of BET surface area was S600 ≈ F820 > S500. The micropore area of the three adsorbents was F820 (546 m^2/g) > S600 (503 m^2/g) > S500 (455 m^2/g). The pore volumes of F820, S500 and S600 were 0.430, 0.533, and 0.449 cm^3/g, respectively. Fig. 1 shows the nitrogen adsorption and desorption isotherms at 77 K. The results indicated that the sequence of nitrogen adsorption capacity was S600 > S500 > F820. Fig. 2 shows the pore size distribution of the adsorbents. The results indicated that the commercially activated carbon had a high micropore volume and evidenced a significant pore volume increment at pore diameter < 13 Å (a large pore volume peak in the vicinity of 9 Å). The pore volume of biosolid adsorbents was mostly in the vicinity of 500 Å (macropore) and 80 Å (mesopore). In addition, the micropore volume of S500 was a little greater than that of S600 at pore diameter between 10.5 and 13.5 Å and increased significantly at pore diameters between 9 and 10.5 Å.

Table 2
Physical characteristics of adsorbents

Adsorbents	BET surface area (m^2/g)	Pore volume (cm^3/g)	Micropore area (m^2/g)	Micropore volume (cm^3/g)	Pore diameter (Å)
S500	737 ± 65	0.449 ± 0.042	455 ± 49	0.21 ± 0.02	24.5 ± 0.77
S600	813 ± 13	0.533 ± 0.001	503 ± 14	0.23 ± 0.006	26.2 ± 0.49
F820	802 ± 27	0.430 ± 0.005	546 ± 7	0.24 ± 0.01	21.7 ± 0.77

3.2. Surface chemistry of adsorbents

Table 3 shows the pH and surface oxygen function groups of sludge adsorbent and commercially activated carbon. The results indicated that the pH ranged from 4.5 to 5.6. The Boehm titration method allows determination of the surface functional groups such as the phenolic group (–OH), lactone group (C=O), the carboxylic group (–COOH), and the carbonyl (quinoid-type) group. The results indicated that the distribution of the surface function groups of the two sludge adsorbents was similar in spite of different pyrolytic temperature during preparation. Only a small amount of the quinoid-type group was present on the surface of the biosolid adsorbents. But the quinoid-type group contributed significantly to the surface functional group of F820. The surface basic group was neutralized by HCl; the results indicated that the concentrations of the basic group of S500, S600 and F820 were 64, 84 and 52 meq/100 m^2, respectively.

3.3. Adsorption isotherm

3.3.1. Orange II adsorption

Fig. 3 shows the Orange II adsorption isotherms at different concentrations (0.9×10^{-4}–2.4×10^{-4} mol/l) and temperatures (10–60 °C). The results indicated that the adsorption capacity of F820 was from 0.24 to 0.31, from 0.31 to 0.54, and from 0.40 to 0.73 mol/kg at 10 °C, 30 °C, and 60 °C, respectively. In addition, the adsorption capacities of S500 and S600 were 0.29–0.37 and 0.30–0.48 mg/g, 0.31–0.47 and 0.36–0.56 mg/g, and 0.34–0.52 and 0.46–0.60 mg/g at 10 °C, 30 °C and 60 °C, respectively. The results indicated that the adsorption capacity of the biosolid adsorbent was higher than that of F820 at 10 °C. At the adsorption temperature of 30 °C, the adsorption capacity of sludge adsorbents and F820 was similar. In addition, at 60 °C, the adsorption capacity of F820 was higher than that of the biosolid adsorbents.

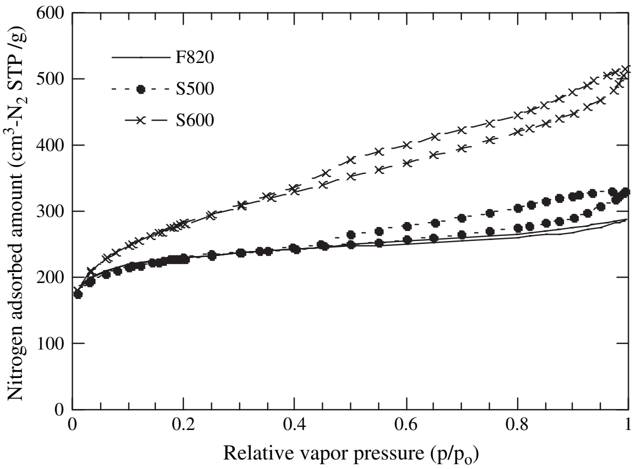

Fig. 1. Nitrogen adsorption and desorption isotherms of sludge adsorbents and F820 at 77 K.

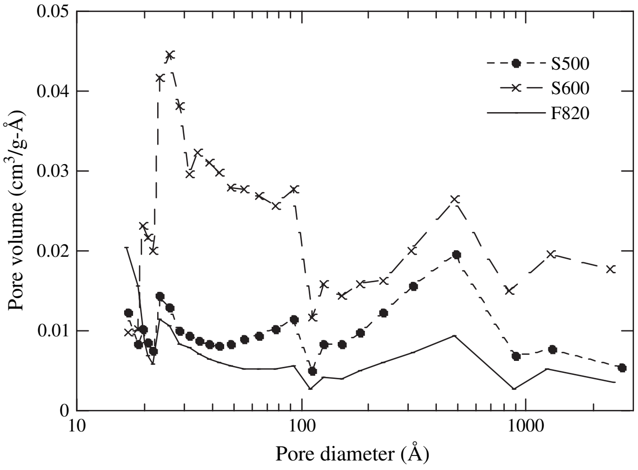

Fig. 2. Pore size distributions of sludge adsorbents and F820.

3.3.2. CH adsorption

Fig. 4 shows the adsorption isotherms of CH on three adsorbents at different temperatures. The results indicated that the CH concentration was from 0.5×10^{-4} to 1.5×10^{-4} mol/l corresponding to F820 adsorption capacities of 0.03–0.11, 0.05–0.14 and 0.08–0.20 mol/kg, respectively, at 10 °C, 30 °C and 60 °C. In addition, the CH adsorption capacity of S500 was 0.06–0.14, 0.12–0.21, and 0.16–0.30 mol/kg at 10 °C, 30 °C and 60 °C, respectively. Furthermore, the adsorption capacity of S600 ranged from 0.04 to 0.13, 0.12 to 0.17, and 0.16 to 0.29 mol/kg at 10 °C, 30 °C, and 60 °C, respectively. The sequence of CH adsorption capacity was S500 > S600 > F820 at different temperatures, indicating that the biosolid adsorbents were more suitable for use in CH adsorption than commercially activated carbon. This can be attributed to the large CH molecule that is not easily transported into the small pores. On the other hand, F820 is mostly occupied by micropores that impeded the transport of CH. In contrast, the sludge adsorbent possessed mostly mesopores; as a result, it is suitable for CH adsorption. The CH molecule is easily transported in mesopores. Gou et al. [42] and Namasivayam and Kavitha [43] used activated carbon to adsorb dyes and reported that the adsorption capacity increased with the increase of temperature. Mohan et al. [44] used fly ash to remove the dye from wastewater and found that the adsorption capacity of crystal violet and rosaniline increased with temperature. They indicated that the increase of adsorption capacity that occurred with an increase in temperature was due to the internal-diffusion-controlled adsorption reaction.

Table 3
Surface functional groups and pH of sludge adsorbents and commercially activated carbon (meq/100 m^2)

Adsorbents	pH	$NaOC_2H_5$	NaOH	Na_2CO_3	$NaHCO_3$	HCl
S500	5.6 ± 0.37	90 ± 2.03	90 ± 0.77	66 ± 1.54	46 ± 0.77	64 ± 0
S600	5.2 ± 0.26	100 ± 0	96 ± 2.78	62 ± 1.54	57 ± 1.33	84 ± 2.04
F820	4.54 ± 0.17	90 ± 0.77	32 ± 3.85	31 ± 3.56	2 ± 2.83	52 ± 0

3.4. Adsorption thermodynamics

The adsorption isotherms of Orange II and CH can be described by the Freundlich equation:

$$q = KC_e^n \tag{1}$$

where q is the amount of adsorption, C_e is the equilibrium concentration, K is the equilibrium constant, and n is a constant.

The Gibbs free energy can be expressed as follows:

$$\Delta G^\circ = -RT \ln K \tag{2}$$

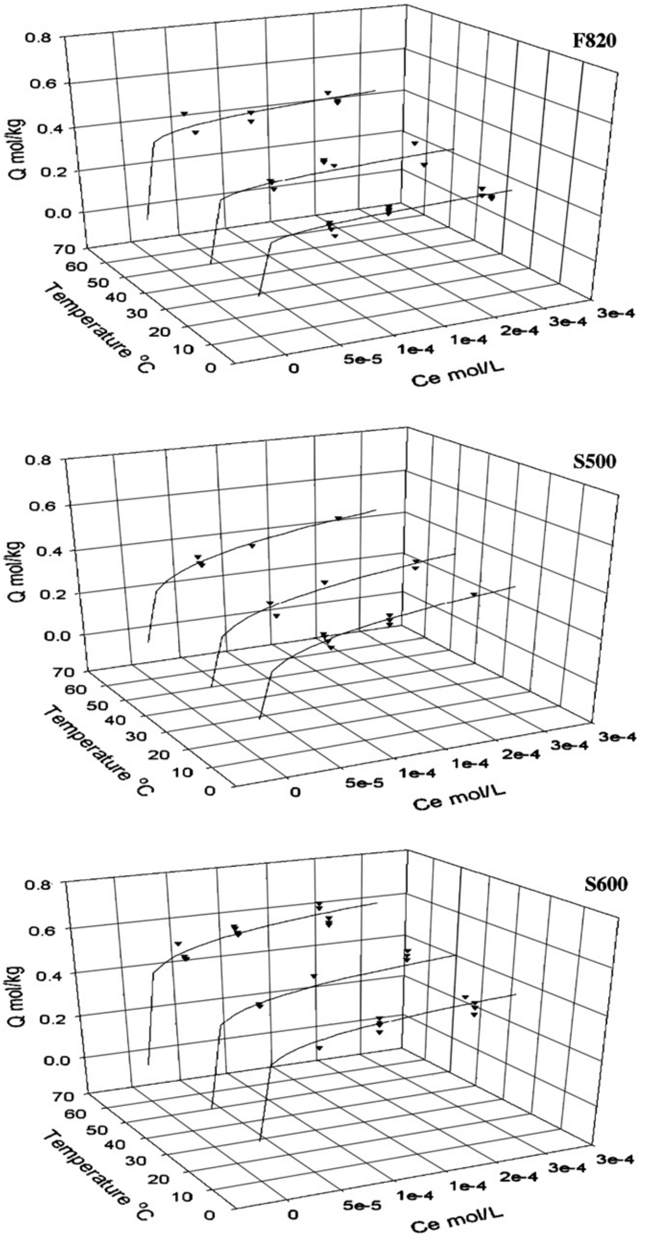

Fig. 3. Orange II adsorption isotherms at different temperatures for F820, S500 and S600.

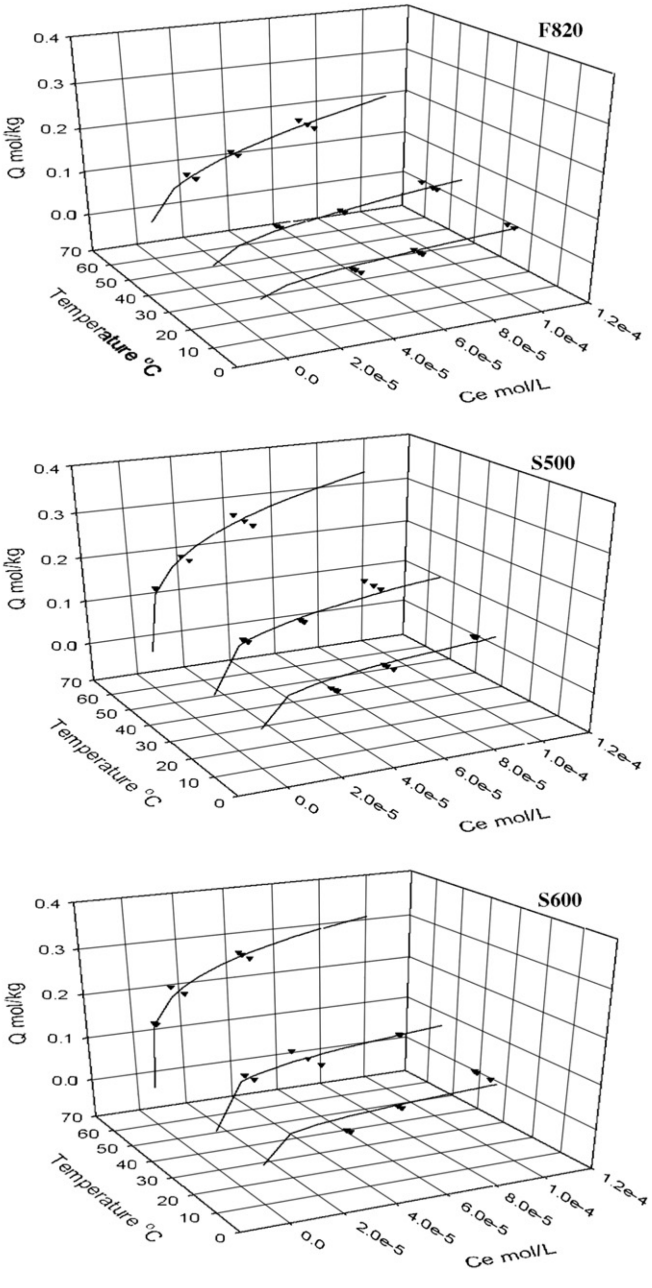

Fig. 4. Chrysophenine adsorption isotherms at different temperatures for F820, S500 and S600.

The relationships of Gibbs free energy, enthalpy, entropy and temperature are as follows:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{3}$$

Combining Eqs. (1)–(3), one has

$$K = \mathrm{e}^{-\Delta H^{\circ}/RT}\,\mathrm{e}^{\Delta S^{\circ}/R} \tag{4}$$

Assumptions are as follows:

$$\alpha = \mathrm{e}^{\Delta S^{\circ}/R} \tag{5}$$

$$\beta = -\Delta H^{\circ}/R \tag{6}$$

One has

$$K = \alpha\,\mathrm{e}^{\beta/T} \tag{7}$$

The Freundlich equation can be expressed as follows:

$$q = \alpha\,\mathrm{e}^{\beta/T} C_{\mathrm{e}}^{n} \tag{8}$$

where R is a gas constant, ΔS° is the reaction entropy, ΔH° is the reaction enthalpy, ΔG° is the Gibbs free energy, and T is the temperature.

Table 4 shows the thermodynamic parameters of dye adsorption. Adsorption isotherms of CH and Orange II on biosolid adsorbents and activated carbon could be described by the Freundlich equation. The adsorption capacity increased with the increase of adsorption temperature; therefore, the dye adsorption was an endothermic reaction in this study. The entropy of dye adsorption was positive, which revealed that the degree of disorder was increased by the adsorption reaction. CH adsorption energy and entropy were higher than those of Orange II, which can be attributed to the difference of molecular weight.

Generally, physical adsorption is an exothermic reaction due to the fact that when a molecule is mixed in gas or liquid, it evidences a higher degree of disorder than when it is adsorbed on the surface of an adsorbent. Therefore, the potential energy of the system should reduce to compensate for the loss of entropy in an exothermic process. In this study, dyes were adsorbed on the adsorbent surface and the entropy increased, revealing an exothermic reaction. It is different from the traditionally physical adsorption in that the adsorption capacity decreases with the increase of temperature. But the enthalpy was less than 5 kcal mol^{-1}. Therefore, dye adsorption is at the state between physical and chemical adsorption. The case could be explained by the exchange of entropy. $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$, ΔH° is always positive (e.g., exothermic); for adsorption to proceed, ΔG° must be negative (a case of 25 °C is shown in Table 4). A large ΔS° means that adsorbed species are very tightly adsorbed, that is, very well organized on the surface. Similar endothermic reactions were reported for the adsorption of DDT, lindane, heptachlor and PCB, which were hydrophobic compounds [45,46]. Non-polar compounds in the aqueous phase are repulsed by the hydrogen bond between water molecules and the surface, which could promote the adsorption of non-polar compounds onto the non-polar surface of the adsorbent. The non-polar molecules are transported from the water constraint to the absorbent surface spontaneously to gain entropy. Therefore, changes in entropy and enthalpy could compensate the adsorption energy of the system. Some ion exchange adsorptions were observed to be endothermic reactions, for example, the ion exchange of Ca^{2+} and Na^{+} wherein one mole of Ca^{2+} is adsorbed and two moles of Na^{+} are released. There are more molecules to obtain entropy in the ion exchange system [47]. The thermodynamic characteristics of dye adsorption are similar to those reported in the studies reported above.

The surface of adsorbents is acidic with some oxygen functional groups on the surface. It is proposed that a large proportion of the active sites of the adsorbent would be occupied by water molecules via hydrogen bonds. Furthermore, the molecular size of dye is larger than that of water; therefore, one dye molecule adsorbed on active sites would replace more than one surface water molecule. Water molecules replaced should overcome the hydrogen bonding between water molecules and adsorbent surface. Dye molecules adsorbed on the surface released energy that was not strong enough to overcome the strong hydrogen bonding between the dye molecules and the adsorbent. Therefore, the overall adsorption reaction would absorb energy from the surrounding solution, which yields an endothermic reaction. Fig. 5 illustrates the conceptual model of dyes adsorbed on the surface of the adsorbents.

Besides pore structure characteristics, the surface chemical characteristics are also important factors affecting the dye adsorption capacity. The pH ranges of Orange II and CH solution at different concentrations were 5.90–6.01 and 7.12–7.97, respectively. Table 3, which shows the pH of adsorbents, indicates that the surface acidity of F820 was higher than that of S500 and S600. Most of the quinoid-type carbonyl group on

Table 4
Thermodynamic parameters of dye adsorption

Dye	Adsorbent	n	K (25 °C)	ΔH° (kcal mol^{-1})	ΔS° (cal mol^{-1} K^{-1})	ΔG (kcal mol^{-1})	r^2	d.f[a]
CH	F820	0.49	9.20	4.6	19.9	−1.33	0.95	26
	S500	0.29	2.50	4.1	15.6	−0.55	0.93	25
	S600	0.22	1.13	4.5	16.2	−0.33	0.92	26
Orange II	F820	0.09	0.75	1.4	5.89	−0.36	0.84	29
	S500	0.24	3.32	0.7	4.64	−0.68	0.81	17
	S600	0.13	1.54	1.3	4.41	−0.21	0.80	30

[a] Degree of freedom.

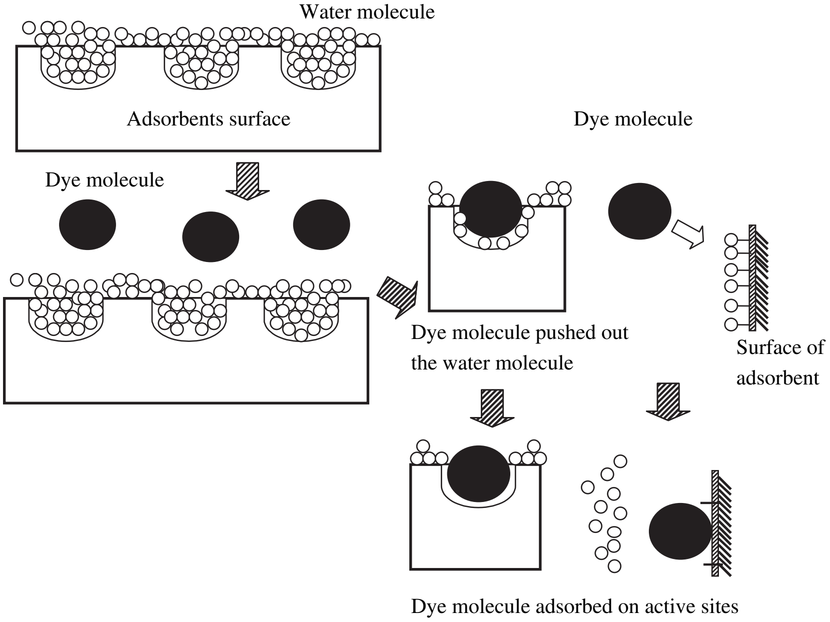

Fig. 5. Conceptual model of dye adsorbed on the surface of adsorbent.

the surface of F820 possesses strong bonding to compare to other acid groups. Little phenolic and carboxylic groups were measured on the surface of F820. Therefore, the quinoid-type carbonyl group is less amenable to interacting with the dye solution, which may be one of factors causing the lower adsorption of dye solution on F820. In addition, carboxylic, lactone and phenolic groups were significant on the surface of biosolid adsorbents. These functional groups may enhance dye adsorption by biosolid adsorbents. Khraisheh et al. [48] reported that the basicity of diatomite surface could affect the anionic dye, which is in agreement with the fact that the dye adsorption capacity of F820 was lower than that of the biosolid adsorbents.

4. Conclusions

The molecular weight of CH is higher than that of Orange II; the adsorption capacity of CH is higher than that of Orange II. The oxygen surface functional groups of sludge adsorbents were mainly in the NaOH titratable entities (i.e. carboxylic, lactone and phenolic groups). In addition, F820 possesses mostly the $NaOC_2H_5$ titratable, especially in carbonyl group (quinoid type). The high surface acid and quinoid-type carbonyl group might cause low dye adsorption capacity on F820. The sequence of BET surface area is $S600 \approx F820 > S500$. Biosolid is developed to be a mesopore-adsorbent after the pretreatment procedures. Dye molecules are easier to transport into the mesorpore biosolid adsorbents than F820. The increase of adsorption temperature corresponds to the increase of dye adsorption capacity on adsorbents, the reason may obtain the entropy from dye-adsorbent adsorption system. In addition, the mesopore-biosolid adsorbents seem to be more suitable for dye adsorption than F820.

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