

DYE ADSORPTION ON BIOSOLID ADSORBENTS

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Abstract

This study was reused the biosolid to manufacture adsorbents (S5 and S6) and use for Orange II and Chrysophenine (CH) adsorption. In addition, a commercial activated carbon (F820) was selected and compared to biosolid adsorbents for dye adsorption. Results indicated the distribution of surface functional groups of two biosolid adsorbents were similar; in spite of they were pretreated with different pyrolytic temperature. Only a little quinoid-type group existed on the surface of biosolid adsorbents. But the quinoid-type group contributed a lot of surface functional group on F820. The sequence of BET surface area was S6 ($813 \text{ m}^2/\text{g}$) \approx F820 ($802 \text{ m}^2/\text{g}$) $>$ S5 ($737 \text{ m}^2/\text{g}$). The commercial activated carbon was major in the micropore size and possessed a significant pore volume increment at the pore diameter $< 13 \text{ \AA}$ (a large pore volume peak in the vicinity of 9 \AA). The pore volume of biosolid adsorbents was major in the vicinity of 500 \AA (macropore) and 80 \AA (mesopore). For Orange II, F820 seem imply the better adsorption capacity than biosolid adsorbents. The sequence of CH adsorption capacity was $S5 > S6 > F820$ at different temperatures that indicated the biosolid adsorbents was more suitable to use for CH adsorption than commercial activated carbon in this study.

Keywords: A. Activated carbon; B. Pyrolysis; C. Adsorption; D. Functional groups

1. Introduction

Wastewater treatment processes produce biosolids and their treatment and disposal is perhaps one of the most complex environmental problems facing the engineer. In addition, the disposal cost is greater than 50 % of the total operation cost [1]. In pass years, biosolid disposal methods have 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, thus providing for sustainable environmental

development [4-5].

In addition, dyeing and finishing processes in the textile industry are known to contain color, high amounts of surfactants, dissolved solids, and possibly heavy metals, which appear in the effluent wastewater [6]. The removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic [7].

Conventional biological treatment processes are no longer able to achieve adequate color removal as water soluble

dyes (reaction dyes) are used extensively in the industry. In addition, standard physicochemical coagulation/flocculation methods have failed [18]. Activated carbon has been the most effective and widely used adsorbent; it produces quality effluents, which are low in dissolved organic compounds, such as dyes from textile wastewater effluents.

Many studies have suggested using biosolids, via the proper treatment processes, to produce adsorbents and for volatile organic compound and acid gas adsorption [8-16]. Annadurai et al (2003), for example, obtained biosolid samples from a wastewater treatment plant and mixed them with acetic acid. The mixture was heated in a microwave oven to produce adsorbent (2.62 m²/g) for Rhodamine 6G dye removal. [17].

This study recycled biosolids to manufacture adsorbent for Orange II and Chrysophenine (CH) adsorption. In addition, a commercial activated carbon was selected for dye adsorption comparison. The oxygen surface functional groups and dye adsorption isotherms of the three adsorbents were investigated in this study.

2. Experimental

2.1 Raw material

Biosolid samples (S5 and S6) were obtained from a petrochemical industry's biological wastewater treatment plant in Taiwan. Biosolid cakes were taken from belt filter press dewatering equipment. In order to assure the stability of the biosolid cake composition, the 300-400 kg biosolid samples were taken at one time. The biosolid sample was stored at 4 °C in a laboratory refrigerator. Two kilograms of the biosolid sample were heated at 105 °C for 24 hours in each run. The dried

biosolid was immersed in a 1 M ZnCl₂ solution and mixed for 24 hours, then filtered out and dried at 105 °C for 24 hours. Each sample was brought back to the laboratory and kept in a desiccator for further utilization.

2.2 Pyrolytic processes

Forty g of the oven-dried biosolid was placed in the middle of a quartz reactor tube. High purity nitrogen, at 2 L/min, (99.995%) was used as the sample bed purge gas. The reactor was heated to the desired temperature in 15 K/min increments. When the furnace reached the reaction temperature, the reactor tube was put into the furnace for pyrolysis. Pyrolysis temperatures varied from 500 and 600 °C with 30-minute residence times. When the pyrolysis process was completed, the quartz tube was taken from the furnace. Nitrogen gas continued flowing to quench the residue temperature. After the residue was cooled to room temperature, it was removed from the reactor tube, weighed and characterized.

2.3 Manufacture of biosolid adsorbent

ZnCl₂ immersed pyrolytic residue was put into a flask. 3N HCl was added to remove the ZnCl₂ from the pyrolytic residue. The solution was then filtered. The pyrolytic residue samples were washed with distilled water until the conductivity of the rinsed water reached that of distilled water. The pyrolytic residue was dried in an oven at 105 °C for 48 hours then transferred to a desiccator until used.

2.4 Commercial activated carbon

In order to compare the adsorption characteristics and confirm the biosolid dye adsorbency, F820 (Norit, 8-20 mesh) was selected as the commercial activated carbon adsorbent.

2.5 Dye

Orange II (C₁₆H₁₁N₂NaO₄S, Aldrich

Chemical Company) and Chrysophenine (CH) ($C_{30}H_{26}N_4Na_2O_8S_2$, Aldrich Chemical Company) was used to assess the performance of the biosolid adsorbents and F820. Orange II and CH were analyzed with a UV/Visible spectrometer (Lambda 12, Model U-2001, Hitachi, Japan), with detection at 485 and 466 nm, respectively. The linear detection concentration range of Orange II and CH by the visible spectrometer was less than 80 mg/l and 110 mg/l, respectively.

2.6 *Physicochemical characteristics of adsorbents*

2.6.1 *Surface area and pore volume*

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. Pore volume distribution was determined by the BJH method. Silica-alumina (surface area: $215 \pm 6 \text{ m}^2/\text{g}$, total pore volume: $0.61 \pm 0.08 \text{ cm}^3/\text{g}$, average pore diameter: $114 \pm 15 \text{ \AA}$), alumina (multipoint specific surface area $0.51 \pm 0.03 \text{ m}^2/\text{g}$) and molecular sieve (median pore diameter: $8.3 \pm 0.2 \text{ \AA}$) were obtained from Micromeritics and used in the quality assurance and quality control procedures.

2.6.2 *Surface chemistry*

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 base (0.1 N $NaHCO_3$, Na_2CO_3 , NaOH, and $NaOC_2H_5$) were used for the analysis of each surface functional group. Unless otherwise stated, strong acid (0.1 M $HClO_4$) and strong base (0.2 M NaOH) were used for all pH

adjustments.

Procedures for the oxygen functional group analysis follow those established by Boehm [19-21]. The activated carbon samples were first dried in a vacuum oven (10^{-2} - 10^{-3} mmHg, 105°C) for 24 hours. Twenty-five mL of an alkali solution (0.1 N $NaHCO_3$, Na_2CO_3 , NaOH, and $NaOC_2H_5$) were added to test tubes containing a given amount of the activated carbon sample (5g). The samples were mixed constantly with a vibrator (100 rpm) at 25°C for 100 hours to assure the surface functional groups reacted with alkali solution. A given amount of the supernatant (5 mL) was drawn from the test tubes and back titrated with HCl (0.1 N) solution. The Residual bases determined the concentrations of various functional groups after back titration as described by Boehm [19-21].

2.7 *Adsorption isotherm*

Orange II and CH concentration ranged from 30 to 80 mg/l. A 100 ml dye solution was put into a vial and then weighed. Then, 10 mg of adsorbent was added into the dye solution vial. The vial was put into a water bath tank and temperature ranged from 10 to 60°C . The vial was vibrated for 10 days to assure the dye contacted with adsorbent and reached equilibrium. After the adsorption, the solution was filtered out and put into a centrifuge to separate the adsorbent particles and end the reaction. Next, the solution was detected by a Visible spectrometer.

3. Results and Discussion

3.1 *Physicochemical characteristics of adsorbents*

3.1.1 *Pore characteristics*

Table 1 shows the adsorbent physical characteristics. The sequence of the BET surface area was $S6 \approx F820 > S5$. But the

sequence in the micropore area of the three adsorbents was F820 ($546 \text{ m}^2/\text{g}$) > S6 ($503 \text{ m}^2/\text{g}$) > S5 ($455 \text{ m}^2/\text{g}$). The pore volume of F820, S-500 and S-600 was 0.430, 0.533, and $0.449 \text{ cm}^3/\text{g}$. Figure 1 and 2 illustrate the adsorbent pore size distribution.. Results indicated the commercial activated carbon was predominant in the micropore size and possessed a significant pore volume increment at the pore diameter < 13 \AA (a large pore volume peak in the vicinity of 9 \AA). The pore volume of the biosolid adsorbents was largest in the vicinity of 500 \AA (macropore) and 80 \AA (mesopore). In addition, the micropore volume of S5 was a little larger than S6 at pore diameters between $10.5\text{-}13.5 \text{ \AA}$ and significantly larger at pore diameters between $9\text{-}10.5 \text{ \AA}$.

3.1.2 Surface chemistry

Table 2 shows the pH and surface oxygen functional groups of the biosolid adsorbents and commercial activated carbon. Results indicated the pH was from 4.5 to 5.6, in the acid range. The Boehm's titration method allows the determination of the surface functional groups such as the phenolic group (-OH), lactone group (C=O), carboxylic group (-COOH) and carbonyl (quinoid-type) groups. The distribution of the two biosolid surface functional groups was similar although they were pretreated with different pyrolytic temperatures. Only a little quinoid-type group existed on the surface of the biosolid adsorbent. But the quinoid-type group contributed considerably to the surface functional group on F-820. When the surface basic group was neutralized by HCl; results indicated the concentration of the basic group of S5, S6 and F820 was 64, 84 and $52 \text{ meq}/100\text{m}^2$, respectively.

3.2 Adsorption isotherm

3.2.1 Orange II adsorption

Figure 1 shows the Orange II adsorption isotherms at different concentrations (30-80 mg/L) and temperatures ($10\text{-}60 \text{ }^\circ\text{C}$). Results indicated the adsorption capacity of F820 was from 78-102, 101-177 and 131-241 mg/g at 10, 30, and $60 \text{ }^\circ\text{C}$, respectively. In addition, the adsorption capacity of S5 and S6 was 96-121 and 98-159 mg/g, 103-154 and 119-184 mg/g, and 113-171 and 150-196 mg/g at 10, 30 and $60 \text{ }^\circ\text{C}$, respectively.

3.2.2 CH adsorption

Figure 2 displays the adsorption isotherms of CH on the three adsorbents at different temperatures. Results indicated the CH concentration was from 30 to 80 mg/L corresponding to the adsorption capacity of F820 at 10, 30 and $60 \text{ }^\circ\text{C}$ was 20-68 mg/g, 32-91 mg/g and 50-127 mg/g, respectively. In addition, the CH adsorption capacity of S5 was 39-87, 75-131, and 99-191 mg/g at 10, 30 and $60 \text{ }^\circ\text{C}$, respectively. Furthermore, the adsorption capacity of S6 ranged from 27 to 85 mg/g, from 75 to 107 mg/g, and from 101 to 187 mg/g at 10, 30, and $60 \text{ }^\circ\text{C}$, respectively. The sequence of CH adsorption capacity was $\text{S5} > \text{S6} > \text{F820}$ at different temperatures, which indicated the biosolid adsorbents was more suitable for CH adsorption than commercial activated carbon. This is attributed to CH being a large molecule that is not easy transported into the small pore. On the other hand, F820 is predominant in the micropore size, which confined the transportation of CH. Since the biosolid adsorbents are prevalent in the mesopore, the CH molecule is easy transported.

4. Conclusions

The pore size of the biosolid adsorbents is predominantly in the mesopore and the CH molecule is easily transported in the mesopore. The oxygen surface functional group is foremost in the carboxyl in this study. F820 is predominant in the micropore and CH is a large molecule that is confined in the smaller pores, prohibiting transportation. The CH adsorption capacity of the biosolid adsorbents was higher than F820's capacity.

Acknowledgements

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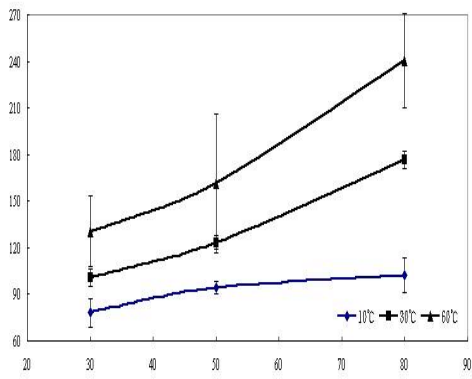
Table 1 Physical characteristic of the three adsorbents

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)
S5	737 ± 65	0.449 ± 0.042	455 ± 49	0.21 ± 0.02	24.5 ± 0.77
S6	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

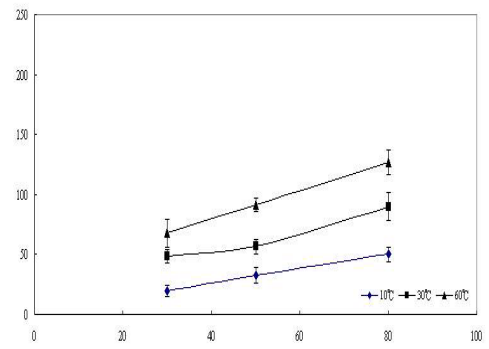
Table 2 Surface functional groups and pH of sludge adsorbents and commercial activated carbon (meq/100m²)

Adsorbents	pH	NaOC ₂ H ₅	NaOH	Na ₂ CO ₃	NaHCO ₃	HCl
S5	5.6 ± 0.37	90 ± 2.03	90 ± 0.77	66 ± 1.54	46 ± 0.77	64 ± 0
S6	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

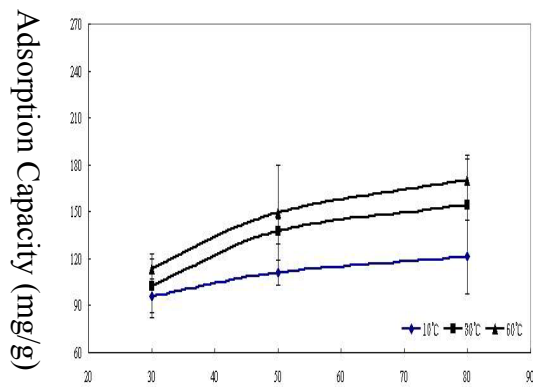
(a) F820



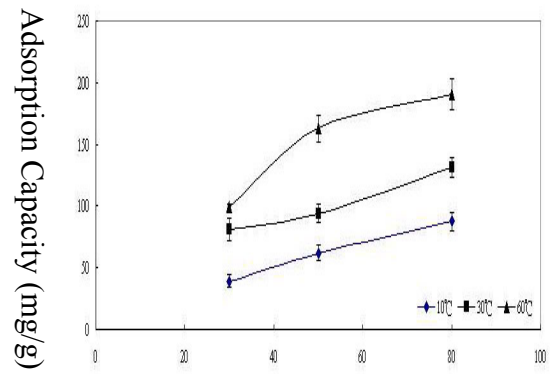
(a) F820



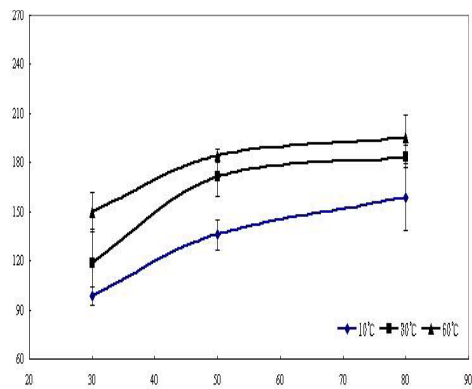
(b) S5



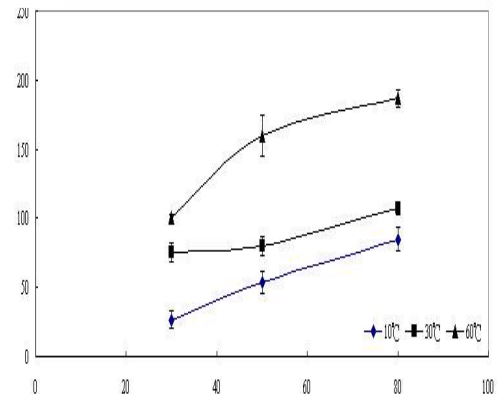
(b) S5



(c) S6



(c) S6



Concentration (mg/l)

Figure 1 Adsorption isotherm of Orange II on different adsorbents

Figure 2 Adsorption isotherm of Chrysophenine on different adsorbents