THE REUSE OF BIOSLUDGE AS AN ADSORBENT FOR BENZENE AND DYE ADSORPTION
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ABSTRACT
Bioadsorbent generated from wastewater treatment processes and its treatment and disposal is one of the most complex environmental problems facing the engineer. Therefore, the disposal of biosludge is an important issue of wastewater treatment plant. This study reuses biosludge as an adsorbent raw material that was selected from a wastewater treatment plant of petrochemical industry. Biosludge was immersed in different concentration of ZnCl₂ solutions and pyrolyzed at different temperatures and times. Results indicated that the 1 M ZnCl₂ immersed biosludge pyrolyzed at 500 °C for 30 min could be reused and were optimal for benzene adsorption. Pore size analysis indicated the mesopore contributed more than the macropore and micropore in the pyrolyzed residue. The benzene adsorption capacity of the biosludge adsorbent was 65 and 55 % of the G206 and BPL activated carbons (commercial activated carbons), respectively. In addition, the biosludge adsorbent is also used for Chrysophenine (CH) and Orange II adsorption. CH adsorption capacity on biosludge adsorbent was higher than F820 (commercial adsorbent) at 10-60 °C that indicated the biosludge adsorbents was more suitable to use for CH adsorption than commercial activated carbon. Furthermore, the Orange II adsorption capacity of biosludge adsorbent was higher than F820 at 10 °C. But the Orange II adsorption capacity of F820 could be higher than sludge adsorbents at 60 °C. Results indicated the biosludge could be reused as a adsorbent for gas and liquid pollutant adsorption after the proper pretreated procedures.
INTRODUCTION

Biosludge treatment and disposal is perhaps one of the most complex environmental problems facing the engineer, and the disposal cost is greater than 50% of the total operation cost\(^1\). Biosludge disposal methods include landfill, composite, incineration, and pyrolysis\(^2-3\). Pyrolysis is used to convert biomass and wastes into fuels that are regarded as a renewable resource for the sustainable development of the environment\(^4-5\).

Many literatures selected the biosludge as raw material and used the pyrolysis and chemical activation or physical activation processes. ZnCl\(_2\) is popular activation agent for sludge\(^6-11\) to manufacture adsorbents. In addition, sulfuric acid\(^12-13\) and acetic acid\(^14\) were also used for activation, but the surface areas of acid derived-adsorbent were less than that of ZnCl\(_2\) activation. Biosludge-derived adsorbents were used for VOCs\(^6\), H\(_2\)S\(^8,12,15\), and dyes\(^13-14\) adsorption.

Benzene, a critical toxic pollutant and carcinogenic compound, is used as a raw material in the petrochemical industry. Adsorption is an appropriate method to control volatile organic compounds at a low concentration level. To achieve the target of zero-discharge, it might be worthwhile to produce biosolid adsorbent from the petrochemical sludge.

Dyeing and finishing processes in textile industry are known to contain color, high amounts of surfactants, dissolved solid and possibly heavy metals in the effluent wastewater\(^16\). The removal of synthetic dyes is great concern, since some dyes and their degradation products may be carcinogens and toxic\(^17\). The conventional methods in-use in wastewater treatment, such as primary and secondary treatment systems are unsuitable\(^18\). Therefore, it is necessary to use tertiary treatment to remove color before discharge. Activated carbon is the most effective and widely in-use adsorbent and can rapidly gaining prominence as treatment processes which produce good quality effluents which are low in concentration of dissolved organic compounds, such as dyes from a wastewater effluent of textile industries.

This study was recycled the biosludge to manufacture adsorbent and used for benzene, Orange II and Chrysophenine (CH) adsorption. Compare the benzene and
dye adsorption characteristics of biosludge adsorbents and commercial activated carbon.

Experimental
Raw Material

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

Pyrolytic Processes

40 g of the oven-dried biosludge was placed in the middle of a quartz reactor tube. Two L/min of high purity nitrogen (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 sludge sample was put into the furnace for pyrolysis. Pyrolysis temperatures varied from 500 (S500) and 600 (S600) °C and residence times was 30 minutes. When the pyrolysis process was completed, the quartz reactor was taken out from the furnace and the nitrogen gas continued flowing to quench the residue temperature. After the residue was cooled to room temperature, it was removed from the reactor, weighed and characterized.

Manufacture of Biosludge 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 electric 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.
**Commercial activated carbon**

In order to compare the adsorption characteristics and confirm the biosludge adsorbent is able to use for dye adsorption, the F820 (Norit, 8-20 mesh), G206, and BPL were selected to be commercial adsorbents.

**Dye**

Orange II (Aldrich chemical Company) and Chrysophenine (CH) (Aldrich chemical Company) are used to assess the performance of sludge adsorbents and commercial activated carbon. Orange II and CH were analyzed by an UV/visible spectrometer (Lambda 12, model U-2001, Hitachi, Japan), with detection at 485 and 466 nm, respectively. The detection limit of Orange II and CH was 0.2 and 0.04 mg/l. 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.

**Surface area, and pore volume distribution of Adsorbent**

The physical characteristics of the sludge 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$^{19-20}$. Pore volume distribution was determined by the BJH method$^{21-22}$. Silica-alumina and molecular sieve were obtained from Micromeritics and used in quality assurance and quality control processes.

**Benzene adsorption isotherm**

The adsorption column was a U-type tube that was 110 mm in length and 15.8 mm in diameter. In order to avoid the influence of adsorbent particle size in the transport of benzene, the original adsorbent was ground into small particles (average particle size: 0.63 mm). The influent concentration of benzene was varied from 190 to 2800 ppm. The selected concentration range was based on petrochemical industry and paint plant VOC emission concentrations. Nitrogen was selected as the carrier gas. The inflow rate of the benzene vapor stream was set at 2.0 L/min and the adsorption temperature was maintained at 25-60 °C. The adsorption kinetic test was repeated four times for each different concentration. The benzene concentration was
determined by a gas chromatography and equipped with a BD-1 fused silica capillary column connected to a FID detector (Varian, 3300, USA). Quality control and quality assurance procedures were applied to the experiment, such as benzene retention time, method detection limit and reproducibility and spike recovery.

**Dye Adsorption isotherm**

Orange and CH concentration ranged from 30 to 80 mg/l and 100 ml dye solution was put into a vial and then weighted 10 mg of adsorbent added into the dye solution vial. The vial was put into a water bath tank that temperature was from 10 to 60 °C and shook with 100 rpm for 10 days to assure the dye contacted with adsorbent and reached the adsorption equilibrium. After the 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 detected by a visible spectrometer.

**Results and Discussion**

**Physical characteristics of adsorbents**

Table 1 is shown the physical characteristics of adsorbents. The sequence of BET surface area was G206>BPL>BA600 ≈ F820 > BA500. But the micropore area of three adsorbents was BPL (553 m²/g) > F820 (546 m²/g) > BA600 (503 m²/g) > BA500 (455 m²/g) > G206 (185 m²/g). The pore volume of G206, BPL, F820, BA500 and BA600 was 0.73, 0.44, 0.43, 0.53, and 0.45 cm³/g, respectively. Figure 1 is shown the pore size distribution of adsorbents. Results indicated the commercial activated carbon was major in the micropore size 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 sludge adsorbents was major in the vicinity of 500 Å (macropore) and 80 Å (mesopore).

**Adsorption of benzene**

Figure 2 shows the benzene adsorption isotherms of these three adsorbents at different temperatures. The benzene feed concentration ranged from 187 to 2829 ppm. The adsorption temperature was set from 25 to 60 °C. At 25 °C and a benzene
relative vapor pressure of 0.0226, the results indicated that the benzene adsorption
capacity of G206 (369 mg/g) was similar to BPL (358 mg/g) while the biosludge
adsorbent had the lowest benzene adsorption capacity.

**Orange II adsorption**

*Figure 3(a)* indicates the Orange II adsorption isotherms at different
concentrations ($0.9 \times 10^{-4}$-$2.4 \times 10^{-4}$ mol/l) and temperatures (10-60 °C). Results
indicated the adsorption capacity of F820 is from 0.24-0.31, 0.31-0.54 and 0.40-0.73
mol/kg at 10, 30, and 60 °C, respectively. In addition, the adsorption capacity of
BA500 and BA600 is 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, 30 and 60 °C, respectively. Results
indicated the adsorption capacity of sludge adsorbent was higher than F820 at 10 °C.
The adsorption temperature was at 30 °C, the adsorption capacity of sludge adsorbents
and F820 was similar. In addition, the temperature at 60 °C, the adsorption capacity
of F820 was higher than sludge adsorbents.

**CH adsorption**

*Figure 3(b)* is shown the adsorption isotherms of CH on three adsorbents at
different temperatures. Results indicated the CH concentration was from $0.5 \times 10^{-4}$ to
$1.5 \times 10^{-4}$ mol/l corresponding to the adsorption capacity of F820 at 10, 30 and 60 °C
was 0.03-0.11, 0.05-0.14 and 0.08-0.20 mol/kg, respectively. 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, 30
and 60 °C, respectively. Furthermore, the adsorption capacity of S600 ranged from
0.04 to 0.13 mol/kg, from 0.12 to 0.17 mol/kg, and from 0.16 to 0.29 mol/kg at 10, 30,
and 60 °C, respectively. The sequence of CH adsorption capacity was S500 > S600
> F820 at different temperatures that indicated the sludge adsorbents was more
suitable to use for CH adsorption than commercial activated carbon. It is attributed
to the CH is a large molecule that is not easy transported into the small pore. On the
other hand, F820 is major in the micropore size that is confined the transportation of
CH. But the sludge adsorbents are major in the mesopore that is suitable to use for
CH adsorption. CH molecule is easy transported in mesopore. Gou et al.²³ and
Namasivayam and Kavitha²⁴ used activated carbon to adsorb dyes; results indicated
the adsorption capacity increase with the increase of temperature. Mohan et al used the fly ash removing the dye from the wastewater; results indicated the adsorption capacity of crystal violet and rosaniline increase with temperature. They indicated the adsorption capacity increase with the increase of temperature that is due to adsorption reaction is control by internal diffusion.

Conclusions

According to the pore volume distribution analysis, mesopores are predominant in the biosolid adsorbent. The benzene adsorption capacities on the biosolid adsorbent are 0.65 and 0.55 of G206 and BPL, respectively. Benzene adsorption experiments demonstrate that the biosolid adsorbent could be used in the control of volatile organic compounds, although, the adsorption capacity of the biosolid adsorbent is less than G206 and BPL. Molecular weight of CH is higher than Orange II, relatively; the adsorption capacity of CH is higher than Orange II. The sequence of BET surface area is BA600 ≈ F820 > BA500. Biosludge is developed to be a mesopore adsorbent after the pretreated procedures. The increase of adsorption temperature is corresponding to the increase of dye adsorption capacity on adsorbents. In addition, the mesopore sludge adsorbents seem to be more suitable use for dye adsorption than that of F820.

Literature Cited


### Table 1 Physical characteristics of adsorbents

<table>
<thead>
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<th>Adsorbents</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Micropore area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Pore Diameter (Å)</th>
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</tbody>
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#### Figure 1: Pore size distribution of adsorbents

- BA500
- BA600
- F820
- BPL
- G206

Figure 1 pore size distribution of adsorbents
Figure 2 Benzene adsorption capacity of G206, BPL, and BA500 at different temperatures
Figure 3 Orange II and CH adsorption capacity of BPL, BA500 and BA600