Utilization of Sewage Sludge from Beverage Industry as Dye Adsorption Materials

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Abstract. This sewage sludge from beverage industry mainly contains organic carbon that can be carbonized and functionalized to sludge char with enhanced porosity and surface area, suitable for utilization as quality adsorbent. Investigation on the adsorption behaviour of Rhodamine B (RhB) as cationic dye in aqueous solution, which represented wastewater from textile industry, onto activated char sludge was performed in this study. The sludge was chemically activated with KOH and subjected to further thermal process at temperature of 800°C for 60 min under nitrogen atmosphere. Adsorption kinetics, isotherms and temperature effect on Rhodamine B adsorption were investigated to evaluate the influence of activation parameters. The result showed that activated char sludge with KOH yielded the highest adsorption capacity of Rhodamine B. At this condition, the activation obviously increased specific surface area from 12.46 m²/g to 2,565 m²/g resulted in substantial enhancement of adsorption capacity. The adsorption equilibrium was represented by Freundlich isotherm model. The kinetic model that fits the experimental data was pseudo-second order. The result confirmed that sewage sludge from beverage industry could be used as an effective adsorbent.

1. Introduction
Sewage sludge, produced from wastewater treatment plant is important problem in beverage industry due to its high volume and prohibitive cost of disposal [1]. Normally, sewage sludge consists of high organic carbon content that can be used as active component of adsorbents. As a matter of fact, sewage sludge has been used as adsorbents on several ways such as direct use in form of dried sludge or pretreated via carbonization chemical and thermal activation processes. Conversion of sludge to sludge char by carbonization (500°C) and activation with activating agents (ZnCl₂, H₃PO₄ and KOH) can improve porosity and specific surface area of resulting materials which leads to high adsorption capacity. In previous studies, the sewage sludge from various sources were used as precursors to generate adsorbents. For example, activated cellulose sludge from paper industry activated with H₃PO₄ was used for methylene blue adsorption, yielding the adsorption capacity of 107.1 mg/g [2]. Municipal sludge was used for cadmium and phenol removal from wastewater by using ZnCl₂ activation [3]. However, utilization of sewage sludge from beverage industry as source for adsorbent has been not methodically reported. Consequently, this study aims to utilize sewage sludge from beverage industry as sludge char adsorbents for removal of RhB from aqueous solution using carbonization process and
chemical-thermal activation at different temperature and activating agents. The characteristic of each adsorbent was determined and RhB adsorption behavior were investigated via adsorption kinetic and adsorption isotherm.

2. Material and methods

2.1 Raw material
In this study, dewatered sewage sludge (DSS) collected from beverage industry wastewater treatment plant in Phra Nakhon Si Ayutthaya province, Thailand was used. Raw material was crushed with high speed ball mill and sieved through 150 µm sieve size, then dried inside a convention oven at 105°C until no further weight loss was detected and then stored in a desiccator.

2.2 Preparation of sludge adsorbents
In order to prepare carbonized sludge, DSS sample was placed on a crucible and then positioned in the center of tubular furnace to be heated at 500°C for 4 hr under nitrogen flow. After carbonization, carbonized sludge was chemical activated by mixing with KOH at weight ratio of 3:1 (KOH: carbonized sludge). Next, carbonized sludge, with and without chemical activation, were subjected to further thermal treatment in a tubular furnace at 800°C for 1 hr under nitrogen flow to produce activated sludge char (ASC) and sludge char (SC), respectively. After activation step, both ASC and SC were rinsed with 2M HCl to eliminate excess activating agent and soluble ash. Then, these samples were washed several times with deionized water until pH of rinsed water was similar to that of deionized water. The final product was filtered and dried in the oven at 105°C until weight constant was reached. These samples were then transferred to a desiccator for further characterization and adsorption experiments.

2.3 Adsorption kinetics
Rhodamine b (RhB, HiMedia Laboratories) as a cationic dye was used as an adsorbate [4]. Kinetics studies were performed by mixing 0.2 g of DSS, 0.2 g of SC or 0.05 g of ASC with 100 mL of 100 mg/L RhB solution in a flask at 25°C. The pH value of solution was controlled at 7 using 0.01 M NaOH or HCl solutions. Liquid samples from mixed solution were continuously collected at constant interval and filtrated using nylon syringe filter. RhB concentration was then measured by UV-visible spectrophotometer at 555 nm. Next, the adsorption capacity of RhB can be calculated by eq. (1).

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  

In eq. (1), \( C_0 \) and \( C_t \) are the initial concentration and concentration at time \( t \) of RhB (mg/L); \( V \) is the RhB solution volume (L); and \( m \) is the weight of adsorbent (DSS, SC, and ASC). Then, the different kinetic models, pseudo first and pseudo second order were evaluated to study the adsorption dynamic in relation to time for these adsorption processes.

2.4 Adsorption isotherm
The adsorption isotherm of RhB was obtained by measuring the concentration of this simulated dye in flasks containing 50 mL of (20-500 mg/L) RhB solution with 0.2 g of DSS, SC or 0.05 g of ASC. These samples were shaken in water bath shaker at 25°C for 3 hr. Liquid samples were then collected and measured for final concentrations. The adsorption isotherms (Langmuir’s and Freundlich) were evaluated to gain further information on the adsorption mechanism of RhB with these adsorbates.
3. Results and discussion

3.1 Characterization of adsorbents

The chemical composition of DSS from beverage industry is shown in Table 1. The major content of DSS is organic matter (64%), inorganics (35.97%) which are predominantly SiO$_2$, P$_2$O$_5$ and CaO. High organic content in DSS is due to the fact that DSS was not decomposed by anaerobic digestion process. The results showed that DSS did not contain any harmful heavy metals and therefore suitable to be used as a precursor to develop adsorbent for removal of pollutants from wastewater.

In addition, the total pore volume, surface area, and pore size were shown in Table 2 indicated surface area of DSS was quite low (12.46 m$^2$/g) though the number increased to 276.5 m$^2$/g after carbonization at high temperature (SC). In addition, the surface area of ASC was greatly enhanced to 2,565 m$^2$/g, approximately nine times of SC. The total pore volume of each sample exhibited similar trend as the surface area. This activation yielded significant improvement when compared with using other chemical activating agents such H$_2$SO$_4$ activation, ZnCl$_2$ activation and CO$_2$ activation [2, 5, 6]. According to the resulting average pore diameters, the pore in DSS was nanopore (<2 nm) while those of SC and ASC were mesopores (2-50 nm).

| Organic content | SiO$_2$ | P$_2$O$_5$ | CaO | Al$_2$O$_3$ | SO$_3$ | Fe$_3$O$_3$ | K$_2$O | MgO | Na$_2$O | TiO$_2$ | MnO |
|-----------------|---------|-----------|-----|------------|-------|------------|------|-----|--------|--------|-----|
| 64.03           | 11.12   | 7.52      | 5.02| 3.51       | 2.75  | 2.40       | 1.75 | 0.85| 0.43   | 0.14   | 0.11|

Table 1. The chemical composition of dried sewage sludge, DSS (% wt).

| Adsorbent | $S_{BET}$ (m$^2$·g$^{-1}$) | $D_p$ (nm) | $V_{total}$ (cm$^3$·g$^{-1}$) |
|-----------|---------------------------|------------|-----------------------------|
| DSS       | 12.46                     | 1.479      | 0.0461                      |
| SC        | 276.5                     | 4.527      | 0.3129                      |
| ASC       | 2565                      | 2.460      | 1.577                       |

Table 2. Specific surface area of adsorbents from sewage sludge.

3.2 Adsorption kinetics

The adsorption kinetics of adsorbents is important, especially in water treatment process. The adsorption kinetic constant is a good indicator that is used when selecting an adsorbent. The adsorption kinetics can be studied between adsorption capacity at time of RhB adsorbed ($q_t$) and contact time. The results show that the adsorption capacity at time ($q_t$) of all adsorbents increased with contact time. Initially, adsorption rate increased rapidly due to higher vacant surface sites available in the initial stage of adsorption [7]. In this study ASC exhibits the highest adsorption capacity (199.86 mg·g$^{-1}$, at equilibrium). The adsorption equilibrium of RhB on DSS, SC and ASC were success within 120, 117 and 55 minutes, respectively.

The kinetics of adsorption was described as the rate of solid-liquid interaction. Usually, the mathematical models used to explain the adsorption kinetic were pseudo first order eq. (2) and pseudo second order eq. (3).

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]  

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

Where $q_e$ and $q_t$ are the theoretical equilibrium adsorption capacity and adsorption capacity at time (mg·g$^{-1}$), $k_1$ and $k_2$ are the adsorption rate constant of pseudo first order adsorption (min$^{-1}$) and second order adsorption (g·mg$^{-1}$·min$^{-1}$).
The results of adsorption kinetic were obtained for RhB adsorption on each adsorbent. The kinetic parameters obtained are shown in Table 3. Normally, the best fit model can be considered by using the correlation coefficient ($R^2$), Figure 1 and Figure 2. The $R^2$ value of all adsorbents indicated that pseudo second order model was suitable for explanation of the adsorption kinetic of RhB adsorption. The $q_e$ of each adsorbent in pseudo second order is close to $q_e$ from experiment which indicate that the adsorption of RhB on DSS, SC and ASC was proceeded by chemisorption process related with sharing of electrons between RhB and adsorbent surface [8].

### 3.3 Adsorption isotherm

The adsorption isotherm is the relation between the equilibrium adsorption capacity of RhB ($q_e$) and equilibrium RhB concentrations at constant temperature. The maximum adsorption capacity was calculated from the experiment, depending on the mathematical model being applied. Usually, the mathematical models used to explain the adsorption isotherm were Langmuir isotherm eq. (4) and Freundlich isotherm eq. (5).

#### Table 3. Kinetic parameters for RhB adsorption using adsorbent

| Kinetic parameters | DSS     | SC      | ASC     |
|--------------------|---------|---------|---------|
| $q_e$ exp (mg·g$^{-1}$) | 13.4    | 22.59   | 199.86  |
| **Pseudo-first order** |         |         |         |
| $q_e$ cal (mg·g$^{-1}$) | 9.663   | 9.099   | 148.627 |
| $k_1$ (min$^{-1}$) | 3.52x10^2 | 2.72x10^2 | 6.20x10^2 |
| $R^2$ | 0.843   | 0.689   | 0.958   |
| **Pseudo-second order** |         |         |         |
| $q_e$ cal (mg·g$^{-1}$) | 13.568 | 22.472 | 204.082 |
| $k_2$ (g·mg$^{-1}$·min$^{-1}$) | 1.08x10^2 | 1.67x10^2 | 1.45x10^3 |
| $R^2$ | 0.997   | 0.999   | 0.992   |

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bqe_m}
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

In eqs. (4-5), $q_e$ is the adsorption capacity at (mg·g$^{-1}$), $C_e$ is the RhB concentration at equilibrium (mg·L$^{-1}$), $b$ is the Langmuir isotherm constant (L·mg$^{-1}$), $q_m$ is the maximum adsorption capacity (mg·g$^{-1}$).
$K_F$ constant is related to adsorption capacity ($L \cdot mg^{-1}$), and $n$ is the Freundlich adsorption constant (dimensionless) which indicates adsorption affinity of the adsorbent. The resulting isotherms displayed in Figure 3 of DSS, SC, and ASC exhibited shape resemble to type I isotherm which indicated monolayer adsorption. The adsorption capacity rapidly increased and eventually reached a plateau at high concentration [8].

Table 4 shows the related parameters of Langmuir and Freundlich isotherms. From the result, DSS was fitted to the Langmuir isotherm since it showed high correlation coefficient ($R^2$) and $q_m$ was 25.44 mg·g$^{-1}$. In addition, Freundlich isotherm was fitted to the SC and ASC experimental data following favorable correlation coefficient ($R^2$). When comparing adsorption ability of adsorbents using $K_F$, it is obvious that ASC maintains highest adsorption capacity. Obviously, carbonization, chemical activation with KOH as well as thermal activation at 800$^\circ$C improve porosity and surface area that suitable for RhB adsorption.

![Figure 3. Adsorption isotherm of RhB on DSS, SC, and ASC.](image)

Table 4. Langmuir and Freundlich isotherms for the RhB adsorption on various adsorbents prepared from sewage sludge.

| Adsorbent | Langmuir | Freundlich |
|-----------|----------|------------|
|           | $q_m$ (mg·g$^{-1}$) | $B$ (L·mg$^{-1}$) | $R^2$ | $K_F$ (L·mg$^{-1}$) | $n$ | $R^2$ |
| DSS       | 25.44    | 0.014      | 0.9844 | 0.739 | 1.577 | 0.9495 |
| SC        | 27.55    | 0.339      | 0.7569 | 9.209 | 4.292 | 0.9397 |
| ASC       | 303.03   | 2.200      | 0.7707 | 198.34 | 9.719 | 0.9309 |

### 4. Conclusions

The experimental results confirmed that sewage sludge from beverage industry could be converted and applied as an effective adsorbent for removal of RhB and similar compounds from wastewater. In particular, ASC activated with KOH at 800$^\circ$C may achieve high porosity and surface area of 1.577 cm$^3$·g$^{-1}$ and 2565 m$^2$·g$^{-1}$, respectively and present various beneficial functional groups on surface area. The adsorption capacity of ASC was relatively high of 381.81 mg·g$^{-1}$ at initial RhB concentration of 500 mg·L$^{-1}$. The kinetics of RhB adsorption on ASC was better represented by pseudo second order model. The Freundlich isotherm was described as a more fitted adsorption mode. It is feasible from the acquired data that this sewage sludge may be processes to quality adsorbent thus help reducing generated waste while adding value and utility of this waste sludge.
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