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PHYSICOCHEMISTRY PROPERTIES OF WATER TREATMENT SLUDGE (WTS) AS ADSORBENTS FOR DYES AND ANTIBIOTICS REMOVAL

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Abstract. Application of waste materials as adsorbent for water treatment has obtained special attention owning to their low cost and surface functionality. In this study the waste-treatment sludge (WTS) sludge was selected as based materials and used as adsorbents for dyes and antibiotic adsorption. The adsorbent was prepared by calcination of the washed and dried WTS adsorbent (S105) at 300 °C (S300) and 700 °C (S700). The morphology, elemental composition, functional groups, pH at point zero charged, and cationic exchange capacity were observed and evaluated to understand the adsorption performance capability of the adsorbents. Then, the adsorbents were test for dyes and antibiotic adsorption in aqueous solution. Adsorbent prepared at higher temperature have darker color. The FTIR peaks related to functional groups of organic compounds such as OH and CO were diminished when the WTS was calcined at 700 °C. Value of pHpzc of of S105, S300 and S700 were 5.43, 5.81 and 5.89, respectively. The value of CEC for S700 and S105 however lower than S300. Adsorption performance of WTS adsorbents towards cationic methylene blue (MB), anionic methyl orange (MO) and reactive red-120 was evaluated in aqueous solution. All adsorbents show high adsorption performance towards MO, but lower adsorption performance towards RR was observed. The calcination of WTS results the higher adsorption capacity observed for adsorption of anionic and cationic dyes. The S700 also show better adsorption performance towards OTC and TC. This study indicates that the WTS has a potential application as low-cost adsorbent to remove hazardous substances from aqueous solution.

Keywords: water treatment sludge (WTS), adsorbents, physiochemistry, dyes, antibiotics.

Introduction

Clean waste demand is increasing over a year due to increasing population. Due to industrialization and urbanization, the risk of consuming dirty water and dealing with its sanitation issues is growing. Therefore, cost-effective, and efficient wastewater treatment technologies are urgently needed. Conventional techniques such as chemical precipitation, carbon adsorption, ion exchange, evaporations and membrane processes for removing dissolved hazardous substances becoming inadequate to meet current stringent regulatory effluent limits or are increasing in cost (Rajasulochana & Preethy, 2016).

Adsorption is highly recommended technique due to its flexibility and simplicity of design, low initial cost, high insensitivity to toxic pollutants and ease of operation. Various materials, including alumina, carbons (Sabzehmeidani et al., 2021), clays (Gil et al., 2021; Adeyemo et al., 2017), silicas (Da'na, 2017; Saman et al., 2020), zeolites (Rad & Anbia, 2021; Lye et al., 2020), biomasses (Ali et al., 2021; Saman et al., 2018, 2019; Abdul Rahim et al., 2021; Johari et al., 2016), biochar (Baltrėnaitė-Gedienė et al., 2020, 2021) and polymeric matters (Sharma & Rajesh, 2016) have been employed as adsorbents for the elimination of contaminants in environmental water.

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In this study the waste-treatment sludge (WTS) sludge was selected as based materials and used as adsorbents for dyes and antibiotic adsorption.

The WTS basically is residue generated from purification of water for drinking water, which usually includes several processes such as screening, coagulation, flocculation, sedimentation, decantation, granular filtration, and chemical disinfection (He et al., 2021). The WTS product is rising annually along with the rapidly growing urban population, and its management has become a global concern. The sludge commonly contains of silicon oxide, aluminum oxide, calcium phosphates, and iron oxide (Wang et al., 2019; Ali et al., 2021). In some country, it is classified as a scheduled waste since it contains metals which causes its disposal to be expensive.

WTS is produced in massive amounts globally and there is very less solutions on how to utilize the sludge for the good of mankind. This paper aims to use modified WTS as adsorbent material, by determining the effects of calcined WTS with changes in their physicochemical properties and adsorption performance towards dyes and antibiotic in aqueous solution.

1. Materials and methods

1.1. Materials

The water treatment sludge (WTS) used in this study was collected from Syarikat Air Johor (SAJ) plant located at Skudai, Johor Bahru, Malaysia. In this study, the synthesized adsorbents were test for their potential adsorption towards dyes and antibiotics in aqueous solution. Chemicals used for adsorption process includes methyl orange (C.I.13025) manufactured by Merck Chemicals (Germany), methylene blue (C.I.52015) manufactured by Riendermann Schimidt (Germany) and Reactive Red-120 manufactured by Sigma Aldrich (China). Antibiotics solution was prepared using tetracycline hydrocholoride manufactured by EMD chemicals (USA) and oxytetracycline dihydrate produced by Sigma Aldrich (Germany). Molecular structure of dyes and antibiotics used in this study are shown in Figure 1.

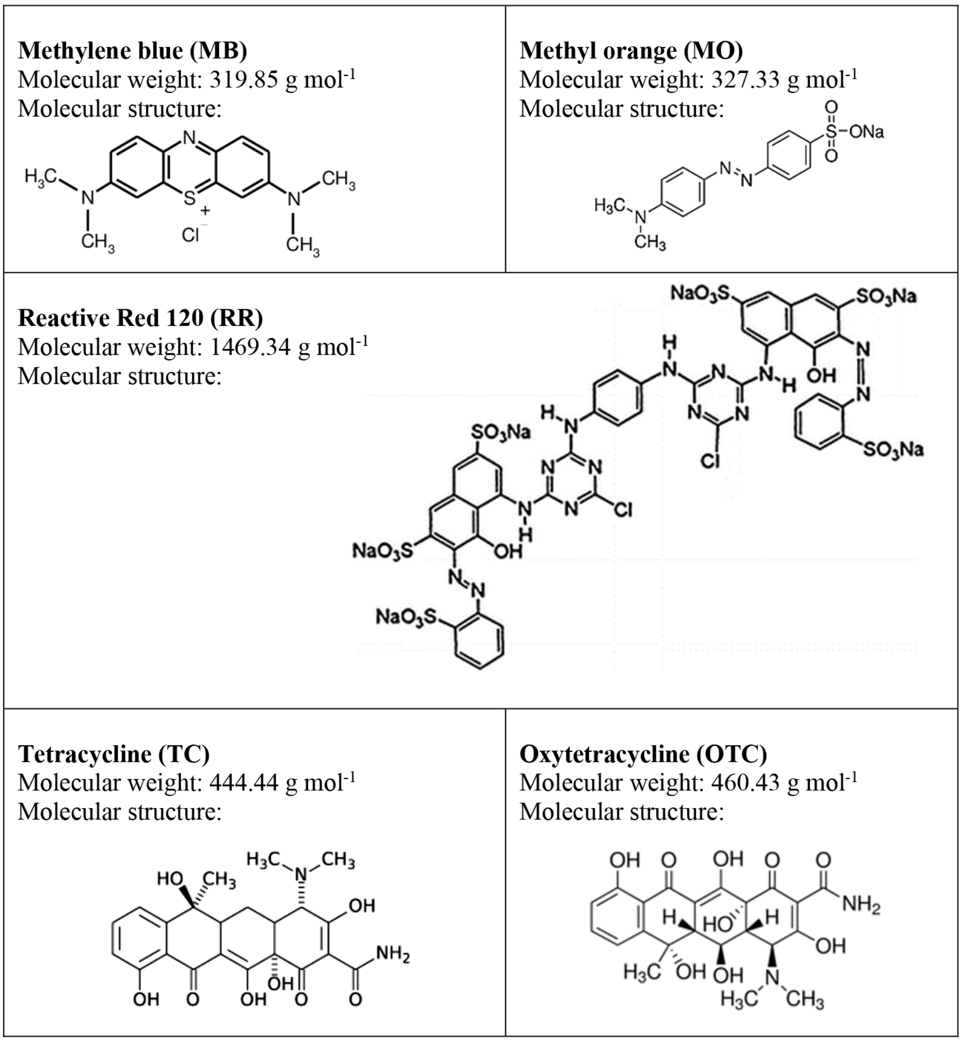

Figure 1. Molecular weight and molecular structure of dyes and antibiotics

1.2. Preparation of water treatment sludge (WTS) adsorbents

The water treatment sludge (WTS) was collected and washed with distilled water several times to remove stone, dirt, and foreign object that may be collected during sampling. Then, it was dry in an oven at 105 °C in an oven for 3 days This sample denoted as S-105. The dry S-105 sample was then calcined at 300 °C and 700 °C for 3 hr, and denoted as S-300 and S-700, respectively. The sample then were characterized and the potential used as adsorbents was evaluated using dyes and antibiotic compounds.

1.3. Adsorbent characterization

The morphology of adsorbents was observed using Field-Emission Scanning Electron Microscope, (FE-SEM) coupled with energy dispersive X-ray (EDX). A small portion of the samples was mounted on the copper stub and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination. The samples were examined at a power voltage of 5–10 kV and magnifications power of 10000x.

In order to determine the ion-exchange properties of adsorbents, the cation exchange capacity (CEC) was determined. First, the adsorbents were saturated with barium by treating it with three times with 0.1 M barium chloride solution followed by an equilibration with a 0.01 M barium chloride solution. Then a known excess of 0.02 M magnesium sulphate was added. After equilibration with a 200 rpm shaker for 2 days, the liquid was retained and tested for magnesium content.

The functional group was determined using Fourier Transform Infrared Red (FTIR). The test was conducted using the KBr disc method. A small amount of the adsorbent will be grinded together with KBr followed by a compression between steel cylinders. This forms a transparent layer of the adsorbent which can be directly used for the scanning purposes. The measurement were carried out at 4000–370 cm^{-1}.

The zero point charge (pH_{PZC}) of the adsorbent was determined by the solid addition method. 0.25 mL of 0.3M KNO_3 solution was transferred into a series of Erlenmeyer flasks. The pH_0 values were adjusted to 2.0, 4.01, 6.02, 7.00, 9.01 and 11.01 respectively by adding 0.1 M HNO_3 and NaOH solutions. The pH_0 of the solutions were accurately noted and 0.05 g of adsorbent was added into each flask and was securely capped immediately. The suspensions were then shaken and allowed to equilibrate for 48 hours. The final pH of the solution was noted accurately. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_e$) was plotted against the final pH (pH_e). The point of intersection of the resulting curve at which $\Delta pH = 0$ gives the value of pH_{pzc}.

1.4. Dyes and antibiotics concentration determination

The concentration of the dyes and antibiotics in aqueous sample was determined using UV-VIS spectrophotometer, Perkin Elmer model Lambda 35. The standard calibration curve of each type of dyes were obtained by plotting absorbance versus concentration. The dye concentration determination was carried out in triplicate and the average value was presented.

1.5. Adsorption performance evaluation

In this study, the adsorbents were also tested on their capabilities to adsorb dyes and antibiotics compounds. Three type of dyes namely cationic methylene blue (MB), anionic methyl orange (MO) and reactive red-120 (RR) and two types of antibiotics compound namely oxytetracycline (OTC) and tetracycline (TC) were used for the adsorption studies. 0.05 mmol/L of dyes solution were prepared and used for the adsorption studies.

50 mg adsorbent was suspended in 50 mL aqueous solution and the mixture was shaken at 200 rpm using a shaker temperature of 30 °C. The mixture was shaken for 2 days to ensure equilibrium of the adsorption. After that, the mixture was filtered using nylon membrane filters (0.80 μm) and the concentration of dyes or antibiotic in the solution were measured. Adsorption capacity at equilibrium, Q_e of the adsorption process was calculated using Eq. (1):

$$Qe = \frac{(Ci - Ce)V}{m},$$

where C_i is the initial concentrations (mg/L), C_e is the concentrations at equilibrium (mg/L), V is the volume of solution (L), and m is the mass of the adsorbent (g).

2. Results and discussions

2.1. Adsorbents characterization

Figure 2 shows the photograph and SEM images for the synthesized adsorbents. The colour of sample become darker as the temperature used during the

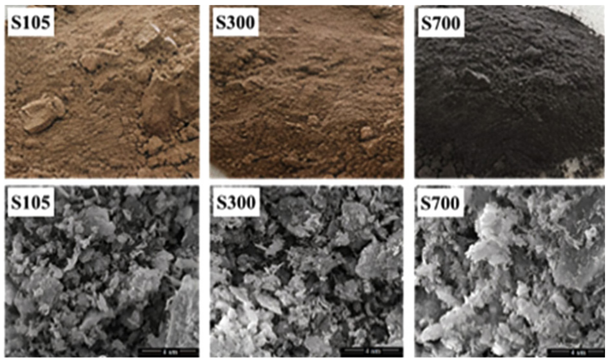

Figure 2. Photograph (above) and SEM (below) images of adsorbents

sample preparation increased. As it can be seen, there are no significant different present in the SEM images, except that the powder structure seemed to become denser as the preparation temperature of the samples is increased.

Figure 3 shows the EDX analysis of the WTS adsorbents. The materials basically composed of element Al, Si, O, and C. Element C is decreasing as the materials undergoes calcination process (S300 and S700). Element Au detected for all three adsorbent is due to coating materials used to prevent electrostatic interaction during the examination process.

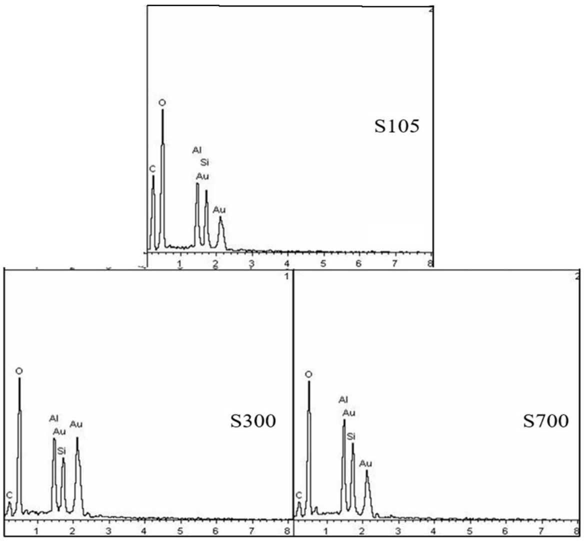

Figure 3. EDX-spectra of adsorbents S105, S300 and S700

The FTIR spectra of the sample is shown in Figure 4. The figure shows that adsorbent that prepared at higher temperature (S700) has less functional group compared to adsorbents prepared at lower temperature.

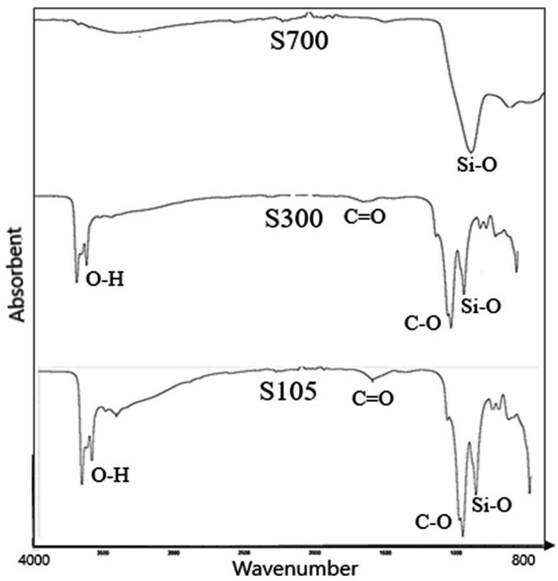

Figure 4. FTIR spectra of WTS adsorbents

The functional groups, including OH, and CO functionalities as well as fingerprint region (at wavelength below 800 cm^{-1}) diminished or have low percentage of absorption with increased calcination temperature. These results shows that the organic compounds were degraded during the calcination process.

The cation exchange capacity (CEC) values determine the ability of adsorbent to hold and release various ions and compounds at the active functional groups in the adsorbent. The values of CEC for S105, S300 and S700 were 737319.6 cmol+/kg, 821817.9 cmol+/kg and 718146.3 cmol+/kg, respectively. The S300 has the highest CEC values compared to other adsorbents. This result indicate that the 300 has higher potential to form interaction by ion-exchange mechanism compared to other two adsorbents.

The pH at point of zero charge, H_{PZC} values is determined the pH condition on the adsorbent where number of negative charges is equal to the number of positive charges on the adsorbent surface. The values of pH_{PZC} for S105, S300 and S700 were 5.43, 5.81 and 5.89, respectively. The adsorption capacity of cations is favored at pH higher than pH_{PZC} because their surfaces might be negatively charged under this condition, while the adsorption of anions is favored at pH lower than the adsorbent pH_{PZC} value.

2.2. Adsorption experiments

2.2.1. Dyes adsorption evaluation

Figure 5 shows the adsorption capacity of dyes adsorbed onto the synthesized adsorbents. All adsorbents basically have higher adsorption performance towards MO. The MO adsorption capacity onto S105, S300 and S700 were 0.027 mmol/g, 0.028 mmol/g and 0.029 mmol/g, respectively. For the MB, the S105 resulted the highest adsorption capacity, followed with S700 and the adsorption of MB onto S300 was the lowest.

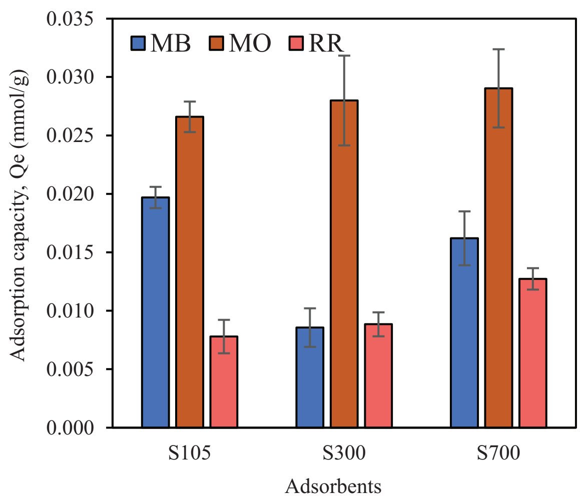

Figure 5. Adsorption capacity of MB, MO and RR WTS adsorbents

Adsorption performance of dyes is related to the physiochemistry properties of the adsorbent as well as dyes properties. MB is classified as cationic dyes which is preferable to be adsorbed onto negatively charged adsorbents through electrostatic interactions. While, methyl orange and reactive red however is anionic dye, thus highly attracted towards positively charged adsorbents. These dyes also known as a polycyclic aromatic compound hence can have electron donor-acceptor interactions with adsorbents with some amount of aromaticity such as biochar and carbonaceous adsorbents (Iwuozor et al., 2021). The electrostatic interaction and hydrogen bonding between nitrogen (N), oxygen (O) and hydrogen (H) functional groups of dye's and adsorbent's structure are also expected (Al-Ghouti & Al-Absi, 2020; Iwuozor et al., 2021; Jawad et al., 2019).

High affinity of methyl orange among other dyes is probably due to presence of –SO3Na that can interact through ion-exchange with Al+ at the adsorbents which is ascribed as the higher CEC values. The adsorption of RR onto all three adsorbents is not very promising. This result might be due to the bulkiness of the RR compounds (see Figure 1).

2.2.2. Antibiotic dyes adsorption evaluation

The adsorption capacity of antibiotics, namely tetracycline (TC) and oxytetracycline (OTC) are shown in Figure 6. The adsorbents show higher adsorption performance towards OTC compared to TC and adsorbent prepared at higher temperature resulted better performances.

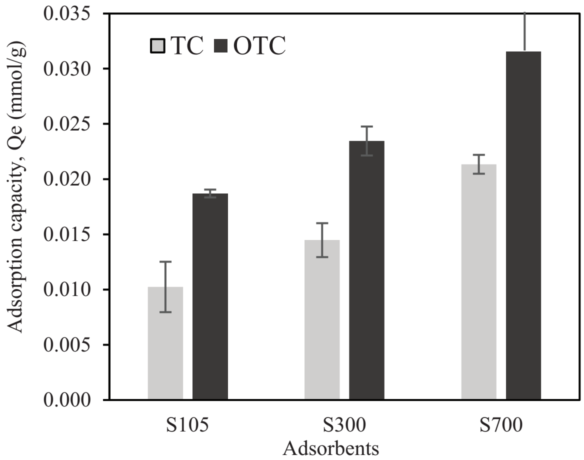

Figure 6. Adsorption capacity of TC and OTC onto WTS adsorbents

Compared with TC, OTC exhibited higher adsorption onto all three adsorbents, which is ascribed to additional OH groups of the OTC. This indicates that H-bonding between functional groups of the this type of antibiotic and the WTC adsorbent were significant. Other studies also provide evidence for the involvement of these groups in complex formation with the adsorbent (Yang et al., 2011; Lye et al., 2017).

Conclusions

1. The WTS-based adsorbents show a potential application to remove hazardous substances from aqueous solution.
2. The physiochemistry properties of the WTS changed when heat treatment is applied, thus affect the adsorption performance towards various hazardous substances.
3. For dyes adsorption performance, the three adsorbents have high affinity towards MO.
4. For antibiotic adsorption performance, the adsorbent that prepared at higher temperature resulted better adsorption performance.
5. In order to understand the adsorption mechanism, details adsorption studies at equilibrium and kinetic adsorption needs to be carried out.

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Disclosure statement

Authors declare that there are no competing financial, professional, or personal interests from other parties.

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