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Hydrothermal conversion of urban food waste to chars for removal of textile dyes from contaminated waters

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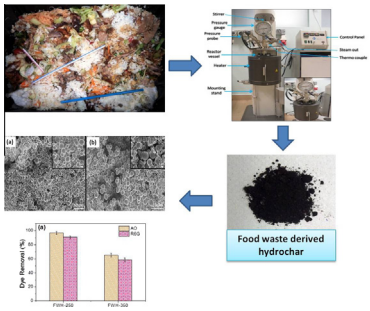
HIGHLIGHTS

- HTC of food waste yields novel hydrochar materials for dye adsorption.
- Microstructure and chemical properties of hydrochars were evaluated.
- Substantial increase in adsorption with increasing functional groups on hydrochar.
- Adsorption mechanism was elucidated using kinetic and thermodynamic analysis.
- An ANN-based model is also developed to predict adsorption capacity of hydrochar.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrothermal carbonization of urban food waste was carried out to prepare hydrochars for removal of Acridine Orange and Rhodamine 6G dyes from contaminated water. The chemical composition and microstructure properties of the synthesized hydrochars were investigated in details. Batch adsorption experiments revealed that hydrochars with lower degree of carbonization were more efficient in adsorption of dyes. Operational parameters such as pH and temperature had a strong influence on the dye uptake process. The adsorption equilibrium data showed excellent fit to the Langmuir isotherm. The pseudo-second-order kinetic model provided a better correlation for the experimental kinetic data in comparison to the pseudo-first-order kinetic model. Thermodynamic investigations suggested that dye adsorption onto hydrochars was spontaneous and endothermic. The mechanism of dye removal appears to be associated with physisorption. An artificial neural network (ANN)-based modelling was further carried out to predict the dye adsorption capacity of the hydrochars.

1. Introduction

The adsorption characteristics of biochars (pyrogenic black carbon derived from incomplete combustion of biomass) have been investigated for the removal of a variety of contaminants, including heavy metals, nutrients, aromatic compounds, pesticides and herbicides in wastewater (Cabrera et al., 2011; Chen and Chen, 2009; Inyang et al., 2012; Yao et al., 2011; Zheng et al., 2010). Hydrothermal carbonization (HTC) is gaining worldwide attention as a viable technology for conversion of waste biomass to carbon-rich, energy-dense, value-added solid hydrochar materials (Sevilla et al., 2011). HTC is carried out at relatively low temperatures (180–350 °C) in the presence of water under autogenous pressures, and does not require the drying of traditionally wet feedstocks for waste conversion. Also, a large percentage of the carbon in the original feedstock actually remains integrated within the hydrochar,

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Nomenclature

A	Arrhenius constant
C_a	equilibrium dye concentration on the adsorbent (mg L^{-1})
C_e	equilibrium dye concentration in solution (mg L^{-1})
C_o	initial dye concentration (mg L^{-1})
C_t	dye concentration in solution at any time, t (mg L^{-1})
E	mean free energy of adsorption per mole of adsorbate (kJ mol^{-1})
E_a	activation energy (kJ mol^{-1})
$\Delta G^{\#}$	free energy of activation (kJ mol^{-1})
ΔG^{O}	Gibbs free energy change (kJ mol^{-1})
$\Delta H^{\#}$	standard enthalpy of activation (kJ mol^{-1})
ΔH^{O}	enthalpy of reaction (kJ mol^{-1})
ΔH_X	isosteric heat of adsorption (kJ mol^{-1})
h	Planck's constant (6.626×10^{-34} J s)
K_C	distribution coefficient for adsorption
K_F	Freundlich isotherm constant (mg g^{-1}) (L $g^{-1})^{1/n}$
K_L	Langmuir isotherm constant (L mg^{-1})
k	reaction rate constant
k_B	Boltzmann constant (1.380×10^{-23} J K^{-1})
k_i	intra-particle diffusion rate constant (min^{-1})
k_1	pseudo-first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant (g mg^{-1} min^{-1})
m	mass of adsorbent (g)
N	number of data points
n	characteristic constant related to degree of favorability of adsorption
p	number of parameters in the model equation
q_e	equilibrium dye uptake per g of adsorbent (mg g^{-1})
$q_{e,exp}$	experimental equilibrium dye uptake per g of adsorbent (mg g^{-1})
$q_{e,cal}$	calculated equilibrium dye uptake per g of adsorbent (mg g^{-1})
$q_{e,pred}$	ANN predicted equilibrium dye uptake per g of adsorbent (mg g^{-1})
q_m	maximum adsorption capacity (mg g^{-1})
q_t	amount of dye adsorbed at any time, t (mg g^{-1})
R	universal gas constant (8.314 J mol^{-1} K^{-1})
R^2	correlation coefficient
$\Delta S^{\#}$	standard entropy of activation (J mol^{-1} K^{-1})
ΔS^{O}	entropy of reaction (J mol^{-1} K^{-1})
s	number of neurons per input value in a layer
T	temperature (K)
t	time (min)
V	volume of test solution (mL)
X_i	input or output variable X
X_{max}	maximum value of variable X
X_{min}	minimum value of variable X
X_{norm}	normalized value of variable X

Greek letters

β	coefficient related to the mean free energy of adsorption (mol^2 J^{-2})
ε	Polanyi potential (J mol^{-1}) = $RT \ln (1 + 1/C_e)$
χ^2	Chi-square test

ultimately minimizing greenhouse gas emission (Parshetti et al., 2013). Hydrochars differ from biochars in that they are generally less aromatic, consisting of mostly alkyl moieties (Cao et al., 2009). Work conducted by Sun et al. (2011, 2012) showed that hydrothermally produced hydrochars have the potential to adsorb a greater number of polar and nonpolar organics in water more effectively than biochar, demonstrating the use of hydrochars as a useful adsorbent for decontamination of wastewaters. However, mostly agricultural wastes and by-products are employed as feedstock's for hydrochar production.

A wide range of natural and waste materials are currently available for the production of hydrochar-based adsorbents, among which food waste is of considerable interest. According to the Global Food Losses and Food Waste report published in 2011 by the Food and Agriculture Organization of the United Nations, about 1.3 billion tonnes, or one third of the total food produced in the world for human consumption are lost or wasted every year throughout the various stages of the food supply chain (production, processing, distribution, consumption, and disposal). According to the waste statistics from Singapore's National Environment Agency (NEA), the annual generation of food waste in Singapore was 542,700 tonnes in 2006 and reached about 640,500 tonnes in 2010, which is around 10% of the total waste output in Singapore (Rajagopal et al., 2013). A recent report indicated that the amount of food waste generated in Singapore hit a record high of 703,200 tonnes in 2012 (NEA, 2012).

Conventional disposal methods such as landfills and ocean dumping emit methane, which has 20–25 times stronger warming effect than CO_2 on a molecular basis, thereby contributing significantly to climate change (Nahman et al., 2012). HTC as a hydrothermal conversion technique has the potential to overcome many of the challenges associated with the conventional disposal methods and/or biological treatment of discarded food. Carbonization offers the advantages of smaller footprint/land area required, efficient conversion of mixed wastes, and greater waste volume reduction. As HTC is a thermochemical technique, mixed wastes are not as significant an operational issue as in composting and anaerobic digestion. In addition, because of the moisture requirement, food waste is more suitable for conversion via HTC than other common dry thermal conversion techniques.

The overarching objective of this study was to (i) prepare solid carbonaceous hydrochars by HTC of food waste at two different temperatures i.e. 250 and 350 °C, (ii) examine the microstructure and chemical composition of the produced hydrochars by ultimate analysis, scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area analysis, X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma optical emission spectrometry (ICP-OES) and (iii) evaluate the potential practical application of the hydrochars as an adsorbent for removal of cationic dyes from contaminated waters. Acridine Orange (AO) and Rhodamine 6G (R6G) were selected as the model pollutants due to their extensive use in textile manufacturing, leather processing, printing inks and lithography, and their reported mutagenic effects in humans (Sadhasivam et al., 2007; Zubieta et al., 2012). The adsorption behavior was modelled using standard isotherm equations and the associated kinetics and thermodynamics were analyzed. Finally, the experimental adsorption data were used to predict the dye adsorption profile by applying an artificial neural network (ANN)-based model, because of its ability to capture the non-linear relationships existing between variables in complex systems.

2. Methods

2.1. Materials

Food waste was collected from the National University of Singapore restaurants. Visual observation of the food waste indicated