Valorisation of char derived from industrial pyrolysis of mixed plastic waste through methylene blue adsorption

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Introduction

In the last years, pyrolysis and gasification were identified as methods used to sustainably manage plastic and biomass waste, producing chemicals suitable for energy production or further industrial uses, in accordance with circular economy principles (Dogu *et al*, 2021). However, pyrolysis and gasification still leave solid residues, known as char (Dogu *et al*, 2021). To valorise biomass-derived char, various applications have been studied. Among those, its use as sorbent material for pollutants removal has been widely studied. On the other hand, the number of similar studies regarding plastic-waste-derived char is limited, when compared to studies focused on biomass-derived chars. (Singh *et al*, 2021)

The present work focused on analysing methylene blue MB adsorption performance of a char derived from an industrial process of pyrolysis of mixed plastic waste. The analysed char was therefore a by-product of a process already valorising a different kind of waste. The present work therefore expands the available literature on plastic-waste-derived chars and investigates the feasibility of valorising by-product chars, not obtained in conditions tailored to enhance their sorbent properties.

Materials and methods

The analysed char (PW-C) derived from mixed plastic waste pyrolyzed at 650 °C. The influence of initial methylene blue (MB) concentration, PW-C dose, contact time, agitation speed and temperature on adsorption performance was investigated. To assess the adsorption performance, two parameters were considered, being relative removal of MB from solution, expressed as removal relative to the initial MB concentration, and adsorption capacity, expressed as mass of MB adsorbed per mass of employed char. Also, thermodynamics, kinetics and mechanism of the adsorption were investigated.

The adsorption was carried out on a 200 ml MB solution, whose concentration depended on the tests, using a variable mass of PW-C. The solution concentration during the adsorption was monitored by periodically taking samples and analysing them through UV-vis spectrophotometry at 664 nm wavelength. PW-C functional groups were determined using a Fourier-transform infrared (FT-IR) analysis. PW-C superficial area, pore dimension and volume were determined using Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively.

Results and discussion

PW-C BET and BJH analyses resulted in a 13.6 m^2/g superficial area, 0.0298 cm^3/g pore volume and 18.9 nm pore width, identifying PW-C as a mesoporous material. FT-IR analyses revealed the presence of mainly aromatic compounds (mainly phenolic and aromatic ether groups), and possibly unsaturated aliphatic chains. Relatively low presence of carboxylic groups was also observed. A possible sorption mechanism was therefore proposed, involving carboxyl ionic groups and aromatic groups in the process.

Figure 1-a and 1-b show the influence of PW-C dose and initial MB concentration on relative removal of methylene blue from solution. Figure 1 shows that increasing PW-C dose at constant 20 mg/L initial concentration, resulted in an increase in MB removal from 60 % to 97 %, despite showing a decrease in adsorption capacity (not shown) from 4.8 mg/g to 1.5 mg/g. On the other hand, an increase in initial MB concentration at constant 2 g PW-C mass, resulted in a decrease of relative MB removal from 96 % to 61 %, whereas adsorption capacity (data not shown) increased from 1.9 mg/g to 6 mg/g. These trends were explained by adsorption equilibrium. An increase in PW-C dose led to an increase in available adsorption sites, whereas an increase in MB concentration implied a higher driving force; both increases leading to reaching equilibrium at higher MB adsorbed mass. However, the relative increase in adsorbed MB mass was not as high as the relative increase in PW-C dose or MB concentration, thus leading to decrease in adsorption capacity and relative MB removal, respectively.

The study of Langmuir and Freundlich isotherms revealed Langmuir isotherm (Figure 1-d) best fitted the experimental data, suggesting a monolayer adsorption mechanism.

The kinetics studies showed pseudo-second order model to best fit the experimental data (Figure 1-c), possibly suggesting a chemisorption mechanism and influence of external and internal diffusion as rate-limiting steps. Boyd and intra-particle diffusion models (not shown) confirmed the influence of both external and internal transport phenomena on rate-limiting steps (Fu *et al*, 2015; Travália and Forte, 2020).

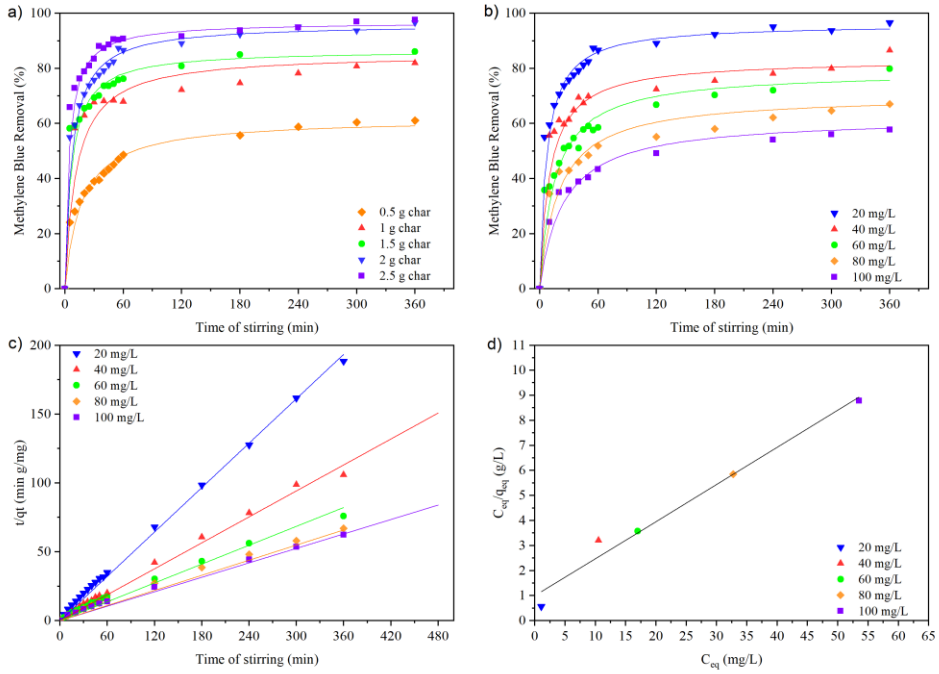

Figure 1 Study of MB adsorption on PW-C. a) influence of PW-C dose on MB relative removal; b) influence of initial MB concentration on MB relative removal; c) influence of MB initial concentration on adsorption kinetics; d) Langmuir isotherm fitting of equilibrium data. a) data were collected at 20 mg/L initial MB concentration. b), c), d) data were collected at 2 g PW-C dose. All data were collected at room temperature.

Thermodynamic studies (not shown), conducted in a temperature range between 20 and 55 °C, revealed negative values of Gibbs free energy (ranging from -26 to -30 kJ/mol) and positive adsorption enthalpy equal to 4.7 kJ/mol, identifying the adsorption as a spontaneous, endothermic mechanism primarily characterized by physisorption (Fu *et al*, 2015), even if part of the adsorption happened through chemisorption, as suggested by pseudo-second order kinetics.

Conclusions

An adsorption performance assessment was conducted on a char derived from an industrial pyrolysis process, investigating influence of char dose and adsorbate initial concentration on adsorbate removal and adsorption capacity, also conducting thermodynamics, kinetics and mechanism studies to support the assessment. The PW-C performance assessment showed good relative removal of MB at lower initial MB concentration and higher PW-C mass, despite a decrease in adsorption capacity. However, char production as by-product of a different valorisation process and absence of pre-treatment, makes the char a low-cost, non-expensive material, making the lower adsorption capacity not an economical issue. The analysed char could therefore be ideal to be used in conjunction with other sorbent materials. This work findings pose as basis for future works aimed to activate the analysed char, to improve its surface reactivity or superficial area and increase its adsorption capacity.

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