

Removal of Contaminants in the Dissolution Recycling of Plastic by means of Adsorption

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Introduction

The plastic recycling industry is facing a considerable challenge. With only 14% of plastic waste that is currently being collected for recycling on a global scale, the general consensus demands an increase in plastic recycling rates [1]. In general, a distinction is made between three types of plastic recycling: mechanical, chemical and dissolution or solvent-based recycling. Mechanical recycling is unable to remove persistent contaminants and plastic additives that are incorporated in the polymer matrix, while suffering from thermal-mechanical degradation and immiscibility of different polymer types. Chemical recycling is able to process plastic waste that is difficult to treat mechanically, yet also suffers from the presence of impurities and additives, leading to operational issues such as coking, catalyst poisoning and corrosion [2]–[6]. Dissolution recycling is an alternative method in which solid-liquid extraction and dissolution-precipitation are the most prominent types. However, the removal of undissolved contaminants in solid-liquid extraction methods is fairly limited as the migration of such suspended particles in the polymer matrix is restricted in its solid state [7], [8]. Furthermore, dissolution recycling techniques typically propose filtration as a technique to remove (undissolved) contaminants, yet, in case of dissolved contaminants (e.g. non-polar organic substances which include many additives), these would migrate through the filter together with the polymer and the solvent.

To avoid these drawbacks, this study explores the potential of adsorption in non-aqueous environment as a novel approach for the dissolution recycling of plastic. The main objective of this work is to provide a first evaluation of adsorption as an additive extraction technique by studying the adsorption behavior of a prevalent plastic additive in different polymer solutions. Due to the critical impact of colorants on the quality of the recycled product [9], the food-contact approved amino ketone-based dye Solvent Red 135 was selected. A screening of different types of commercially available adsorbents, revealed that the performance of activated charcoal was superior. Herein, a comprehensive study on the adsorption mechanism of the dye Solvent Red 135 was conducted in polystyrene (PS) solutions. For this, three different organic solvents were used, being *o*-xylene, butyl acetate and limonene. Next to classical isotherm models, the performed adsorption experiments were also analysed using statistical physics models, allowing for a thorough analysis of the adsorption phenomena at a molecular scale.

Materials and methods

In a first scenario, adsorption isotherm experiments of the dye and polymer were independently conducted in the three organic solvents at 293 ± 1 K. Initial concentrations were varied from 1 to 50 mg L⁻¹ and from 1 to 50 g L⁻¹ for Solvent Red 135 and PS, respectively. In a second scenario, solutions of 1.0 wt% PS were prepared with varying dye concentrations from 1 to 50 mg L⁻¹. For both scenarios, solutions of 100 mL were mixed with a fixed adsorbent mass of 10 mg and subsequently stirred at 300 rpm for at least 12 h to reach an equilibrium state. Samples were centrifuged at 4000 rpm and the supernatant was analysed via the UV-Vis spectrophotometer to determine the equilibrium concentration of the adsorbate.

Adsorption kinetics of the dye (with PS) were also studied in the three organic solvents at 293 ± 1 K. Solutions of pure PS were not considered due to the negligible adsorption capacity derived from preceding adsorption experiments. Initial dye concentrations were set to 40 mg L⁻¹. In a first stage, no PS was added. In a second stage, the solutions were adjusted to hold 1.0 wt% PS. Solutions of 100 mL were analogously mixed with an adsorbent mass of 10 mg and stirred at 300 rpm. The adsorption time was varied until equilibrium was obtained.

Finally, adsorption experiments were performed with increasing adsorbent dose to evaluate the effect on the removal efficiency of the plastic dye. The adsorbent dose was varied from 0.1 to 10 g L⁻¹. In a first case, Solvent Red 135 solutions were prepared without the addition of PS. The initial dye concentration was set

to 40 mg L⁻¹ for all three solvents. In a second case, the red dye was dissolved in 1.0 wt% PS solutions. The Solvent Red 135 concentration was again 40 mg L⁻¹, ensuring a realistic concentration of the dye in the polymer matrix of approximately 0.5 wt% [10], [11]. In a third and final case, the PS concentration was increased to 10.0 wt%, allowing evaluation in terms of practical feasibility. For comparison reasons, the concentration of the dye was maintained at 40 mg L⁻¹. All experiments were triplicated and conducted on all three solvents.

With respect to the modelling analysis of the adsorption isotherms, this work included six classical models and three statistical physics models. The classical models are the Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Redlich–Peterson, and BET model, while the statistical physics models represent a monolayer, a double layer and a multi-layer model [12]–[17]. For the adsorption kinetics, the pseudo-first-order, pseudo-second-order, Elovich, and Weber–Morris model were considered, which are the most extensively used in adsorption studies [18]–[21].

Results

Modeling results for the classical isotherm expressions indicate that the Langmuir model performed best for all three solvent. This suggests a monolayer coverage of the dye molecules with homogeneous distribution over the activated charcoal adsorbent surface, with little interaction between dye molecules [22]. This is confirmed by the statistical physics modelling analysis where it was found that the monolayer expression described the adsorption process most accurately for all three solvents. Following the latter model, the adsorption capacity at saturation was 20.05, 60.91 and 136.30 mg g⁻¹ for o-xylene, limonene and butyl acetate as acting solvent, respectively. Hence, the adsorption capacity of the activated charcoal for the dye is largest in butyl acetate, while the lowest adsorption capacity is observed with o-xylene. This means that the dye experiences a relatively strong attraction towards o-xylene as opposed to butyl acetate. Results of the adsorption kinetics show that adsorption equilibrium for all three solvents was reached after less than 120 min. The performance of the pseudo-second-order model appears dominant for all three solvents. The corresponding rate constant is highest for o-xylene solutions, indicating a faster overall adsorption process.

Figure 1 illustrates the results of the removal efficiency study of Solvent Red 135. In general, the efficiency increases with the adsorbent dose as expected, due to the increase in available adsorption sites. Furthermore, the amount of dye molecules adsorbed for a particular adsorbent dose is significantly higher for butyl acetate as acting solvent compared to limonene and o-xylene. This is in agreement with the modelling results. When dealing with mixtures of the dye and 1.0 wt% PS in butyl acetate, a removal efficiency of 99% was achieved at an adsorbent dose of 2.0 g L⁻¹. However, when the PS concentration in the solvent increased to 10 wt%, the required adsorbent dose rose to 3.3 g L⁻¹.

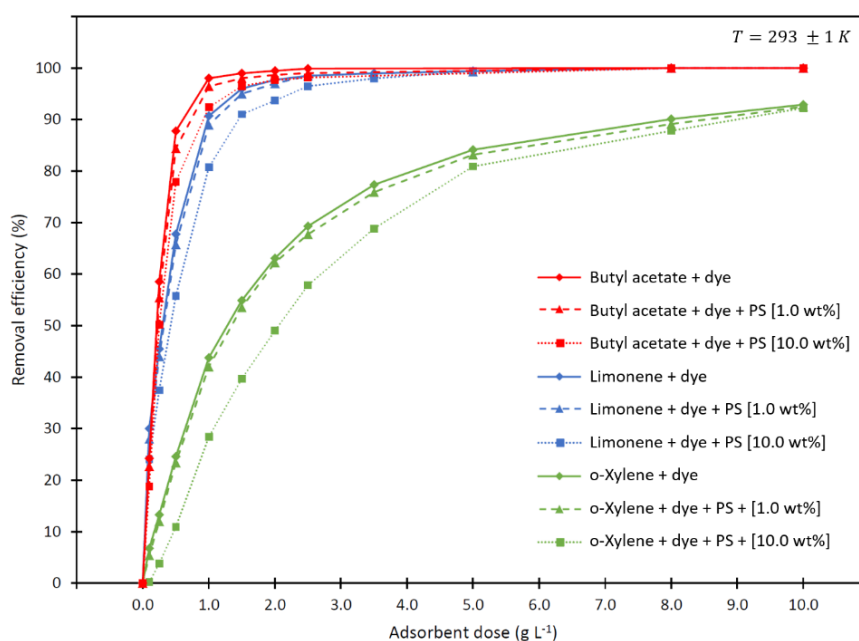


Figure 1. Removal efficiency of Solvent Red 135 at 40 mg L⁻¹ by activated charcoal in o-xylene (green), limonene (blue) and butyl acetate (red) at 293 ± 1 K as a function of adsorbent dose. Solutions of 100 mL with only dye (solid diamond lines), with a mixture of dye and 1.0 wt% PS (dashed triangle lines), and with a mixture of dye and 10.0 wt% PS (dotted square lines) are included.

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