

Competitive and cooperative adsorption of heteroatom components from pyrolysis oil

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The increasing use of plastic, due to its advantageous properties, has led to a pressing challenge in the management of plastic waste. Despite extensive mechanical recycling efforts, only 9% of the total plastic waste was recycled in 2019 (OECD, 2022). Chemical recycling through pyrolysis emerges as a potential solution. However, the resulting plastic pyrolysis oil introduces complications, particularly in terms of heteroatom contaminants such as oxygenated, nitrogenated, and chloride components that cause several issues for downstream processing such as catalyst deactivation, corrosion, and fouling (Kusenbergh, Eschenbacher, Djokic, et al., 2022; Ragaert et al., 2017; Ristic et al., 2017). Consequently, upgrading post-consumer plastic pyrolysis oil is unavoidable because it allows for higher cracking rates than those currently practiced.

Although hydrotreatment offers a solution, its implementation demands operating conditions, exemplified by processes such as hydrodenitrogenation (Temperature: 450°C, Pressure: 150 bar) and hydrodeoxygenation (Temperature: 400°C, Pressure: 135 bar) (Kusenbergh, Eschenbacher, Delva, et al., 2022). Seeking a more energy-efficient alternative, numerous studies and patents have explored adsorption as a method to remove heteroatom contaminants from pyrolysis oil. However, these studies have limitations. Some use oversimplified model oils that contain only one hydrocarbon as a solvent and one heteroatom component as a contaminant (Jiang et al., 2021; Ma et al., 2016). Others employ real-field pyrolysis oil but face challenges in characterizing individual contaminants (Brunetti et al., 2021).

Central to our approach is the development of a model oil that representative to real-field pyrolysis oil while remaining feasible to analyze individual component using standard characterization methods. The pyrolysis oil comprises three components—n-nonane (paraffin), 1-hexene (olefin), and ethylbenzene (aromatic). The contaminants in the pyrolysis oil are represented by eight heteroatom components belonging to three groups: nitrogenated, chloride, and silicon (**Table 1**).

In this study, various adsorbents were initially tested by performing equilibrium experiments to identify the most effective adsorbent capable of removing a wide range of heteroatom. Subsequently, experiments were conducted with a pyrolysis oil model with multiple contaminants. The adsorption capacity of each heteroatom component was examined under two conditions: low background concentration and high background concentration. In this context, "background" refers to a group of other heteroatom contaminants that exclude the contaminant under consideration. Multicomponent mixtures were formulated with varying compositions for each heteroatom, at two levels of feed concentration for each heteroatom, as outlined in **Table 1**. The concentration of the model pyrolysis oil was analyzed using GC-FID to quantify the concentration of each contaminant before (C_i^0) and after equilibrium experiment (C_i^{eq}). The adsorption was evaluated using the following equation, at certain adsorbent mass (m_{ads}), and model pyrolysis oil volume (V_{liq})

$$q_i^{eq} = \frac{C_i^0 - C_i^{eq}}{m_{ads}} \times V_{liq} \quad (1)$$

In the context of our present findings, **Figure 1** illustrates the adsorption capacity (mg g^{-1}) of selected contaminants and the influence of background when activated carbon is used. Generally, with the exception of pyridine, all components exhibit competitive adsorption ($q_i^{m,Mix} < q_i^{m,Single}$), leading to a reduction in removal efficiency as the concentrations of other components increase. Notably, at lower background concentrations, pyridine exhibits

cooperative adsorption ($q_i^{m,Mix} < q_i^{m,Single}$) whereas it shifts to competitive adsorption at higher background concentrations.

Table 1 Components of the target heteroatom and their feed concentrations.

Components	Concentration	
	Lower Level (g L ⁻¹)	Higher Level (g L ⁻¹)
Pyridine	3	5
Benzonitrile	3	5
Chlorobenzene	1	2
Cyclopentanone	1	5
Phenol	3	5
Methacrylic acid	3	5
Benzoic acid	3	5
Hexamethylcyclotrisiloxane	0.5	1

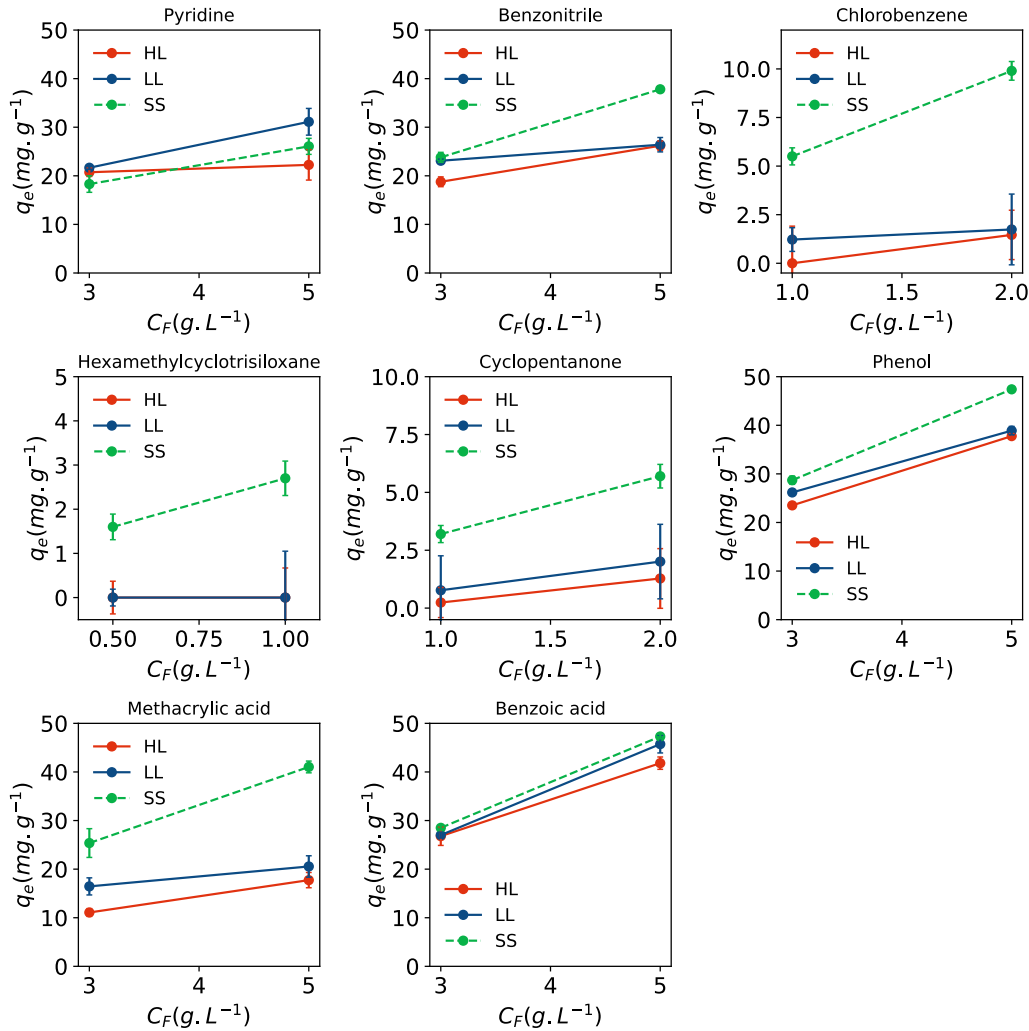


Figure 1 Plot between feed concentration and adsorption capacity of adsorbate in activated carbon at low level concentrations of other components (LL) and high level concentrations of other components (HL) in model pyrolysis oil at 298K±1K for activated carbon. The green dashed line (SS) represents removal efficiency in single contaminant model oil.

References

- Brunetti, F. G., Pinkos, R., SHEVCHENKO, G. A., PILARSKI, O., Haupt, S., Mueller, C., KOEPKE, D., Oliveira, A. L. D., & Iffland, G. (2021). *Process for purifying a crude pyrolysis oil originating from the pyrolysis of plastic waste* (Canada Patent CA3182517A1). <https://patents.google.com/patent/CA3182517A1/en>
- Kusenberg, M., Eschenbacher, A., Delva, L., De Meester, S., Delikonstantis, E., Stefanidis, G. D., Ragaert, K., & Van Geem, K. M. (2022). Towards high-quality petrochemical feedstocks from mixed plastic packaging waste via advanced recycling: The past, present and future. *Fuel Processing Technology*, 238, 107474. <https://doi.org/10.1016/j.fuproc.2022.107474>
- Kusenberg, M., Eschenbacher, A., Djokic, M. R., Zayoud, A., Ragaert, K., De Meester, S., & Van Geem, K. M. (2022). Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate? *Waste Management*, 138, 83–115. <https://doi.org/10.1016/j.wasman.2021.11.009>
- OECD. (2022). *Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options*. OECD. <https://doi.org/10.1787/de747aef-en>
- Ragaert, K., Delva, L., & Van Geem, K. (2017). Mechanical and chemical recycling of solid plastic waste. *Waste Management*, 69, 24–58. <https://doi.org/10.1016/j.wasman.2017.07.044>
- Ristic, N. D., Djokic, M. R., Konist, A., Van Geem, K. M., & Marin, G. B. (2017). Quantitative compositional analysis of Estonian shale oil using comprehensive two dimensional gas chromatography. *Fuel Processing Technology*, 167, 241–249. <https://doi.org/10.1016/j.fuproc.2017.07.008>