

Adsorption of Phenol Using Activated Carbon Derived from Polystyrene, Paper and Wood Mixtures

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Abstract

The removal of phenol from wastewater is essential due to its toxicity, persistence, and environmental risks. Among various treatment methods, activated carbon (AC) adsorption is widely preferred for its efficiency and cost-effectiveness. This study examines the production of AC from polystyrene (PS), paper, and wood – common components of refuse-derived fuel (RDF) – and evaluates their phenol adsorption capacity. The aim was to assess potential interactions during thermal treatment and their impact on adsorption performance. The results showed that for most mixtures, co-carbonization reduced adsorption capacity compared to separately activated components, indicating negative thermal interactions. However, a positive adsorption-related synergy was observed for the PS/wood mixture. BET surface area analysis revealed that paper-containing mixtures exhibited significantly lower surface areas than expected, likely due to the inhibition of gasification reactions, resulting in reduced adsorption performance. This study highlights how RDF components influence AC properties and provides insights for optimizing waste-derived adsorbents in wastewater treatment.

Keywords

adsorption, phenol, gasification, activated carbon

1 Introduction

Phenol, also known as carboic acid, is an organic compound consisting of a hydroxyl group attached to a benzene ring [1, 2]. It is widely used as a raw material in various industrial processes, including oil refining, polymeric resin production, pesticide manufacturing, pulp and paper processing, pharmaceuticals, and the textile industry [3–5]. However, due to its toxic and corrosive nature, phenol is a significant environmental pollutant [3, 6]. Its mutagenic and carcinogenic properties, combined with its persistence in the environment, pose serious risks to both human health and ecosystems [3].

The removal of phenol from wastewater can be achieved through physical, chemical, and biological methods. Each approach has advantages and limitations; for instance, biological treatment can be highly effective but is sensitive to phenol concentrations above 200 mg dm⁻³ [3, 7]. Conventional physical and chemical methods are effective but may be expensive, have slower kinetics, or cause undesirable environmental impacts [8]. Hybrid approaches, particularly adsorption coupled with biological treatment are often preferred due to their high efficiency, flexibility, and reduced

environmental footprint [8]. Adsorption is especially advantageous because it prevents toxic effects on microorganisms, making it a viable pre-treatment step in biological systems [9]. However, the effectiveness of adsorption depends on the availability of low-cost yet efficient adsorbents.

Waste-derived materials can serve as cost-effective precursors for adsorbent production. Refuse-derived fuel (RDF), which consists of the high-energy fractions of municipal solid waste (MSW), is a potential raw material for activated carbon (AC) production [10–12]. Utilizing RDF for this purpose offers environmental benefits, but only if the feedstock consists of non-recyclable MSW components. Currently, global MSW generation is approximately 2.01 billion tonnes per year and is expected to rise to 3.40 billion tonnes by 2050 [13]. In many countries, a significant proportion of waste is still landfilled — more than 50% in Hungary in 2023 [13, 14]. Even in modern landfills, waste decomposition leads to methane emissions, which have a global warming potential 34 times greater than carbon dioxide [13].

Several studies have explored the potential of producing AC from RDF, targeting a range of applications including

the removal of dioxins and furans from flue gases [15], as well as the adsorption of contaminants such as gold [16], NO_x [17], copper [18], and lead [19]. These investigations span various activation methods, including both physical (e.g., steam) [20] and chemical (e.g., HNO₃, HCl, NaCl, KOH, ZnCl₂) [16, 18, 20, 21] techniques. While some RDF-based ACs have demonstrated comparable performance to commercial ACs [16], others, though less efficient, remain promising due to their low production cost and waste-to-resource value [17]. Phenol adsorption onto ACs is governed by several factors, including surface area, pore structure, and surface functional groups—particularly oxygen-containing ones, which can enhance adsorption through specific interactions [22]. In addition, operational conditions, especially pH, significantly influence adsorption efficiency; for instance, Abas et al. [23] reported maximum phenol uptake by peanut shell-based AC at pH 8. Despite the growing interest in RDF-based ACs, only one study, conducted by Nakagawa et al. [21], specifically addressed phenol adsorption. Their work evaluated RDF sourced from MSW in a Japanese city, finding that HCl pre-treatment substantially increased the BET surface area from 230 to 520 m²/g. Interestingly, the phenol adsorption capacities of both untreated and pre-treated RDF-based ACs were comparable to that of commercial AC, suggesting that surface chemistry and pore structure, rather than surface area alone, play a critical role in determining adsorption performance.

In this study, ACs were prepared from polystyrene (PS), paper, and wood—common components of RDF. The adsorption capacity of the resulting ACs for phenol removal were investigated, along with the potential synergistic effects of these materials during thermal treatment and adsorption. Previously, we examined laboratory-prepared RDF mixtures [24] composed of up to seven different components to evaluate how RDF composition influences the properties of the resulting AC. However, the complexity of those mixtures made it difficult to clearly identify the role of each individual component. Therefore, in the present work, we reduced the number of components to three, selected based on two main criteria: (1) their higher char yield during pyrolysis and (2) their chemical and structural diversity. By focusing on two- and three-component mixtures, we aimed to better understand the interactions between materials during activation and adsorption, and to clarify their individual and combined contributions.

2 Materials and method

2.1 Materials

Paper (P), wood (W), and PS were selected as feedstock materials because they are common components of RDF. An important consideration in their selection was their diverse nature, as they represent different material types. The ultimate analysis of the samples was conducted, and the results, including ash content, are presented in Table 1.

The sulfur content in all materials was below the detection limit, which is beneficial since sulfur-containing compounds are undesirable in the gaseous products of carbonization and gasification processes. Among the three materials, paper exhibited a significantly higher ash content compared to wood and PS.

Using these materials, mixtures were prepared with compositions detailed in Table 2. The component ratios were determined according to their typical proportions in RDF produced in Hungary.

2.2 Activated carbon preparation

Carbonization was carried out in a laboratory batch reactor (Fig. 1) with an approximate capacity of 1 dm³ at 520 °C.

To ensure an inert atmosphere, the reactor was purged with nitrogen. The pyrolysis temperature was selected based on previous thermogravimetric analyses. The resulting chars were then subjected to physical activation in a laboratory-scale gasification reactor, with 15 g of char used per experiment.

The gasification reactor (Fig. 2) consisted of a steel tube and a tubular reactor, where steam was used as the gasifying agent. Distilled water was introduced into the system using a perfusion pump to generate steam. Activation was performed at 900 °C for 1 h, maintaining a char-to-steam mass ratio of 3:1.

Table 1 Ultimate analysis and ash content of samples [wt.%]

Material	C	H	N	S	O	Ash
Paper	33.8	4.5	<0.3	<0.2	40.9	20.7
Wood	45.9	6.0	<0.3	<0.2	47.8	0.2
PS	86.1	7.4	<0.3	<0.2	0.8	5.6

Table 2 Composition of material mixtures [wt.%]

Sample	Paper	PS	Wood
P/W	83.2	-	16.8
P/PS	90.0	10.0	-
W/PS	-	35.5	64.5
P/W/PS	76.2	8.5	15.4

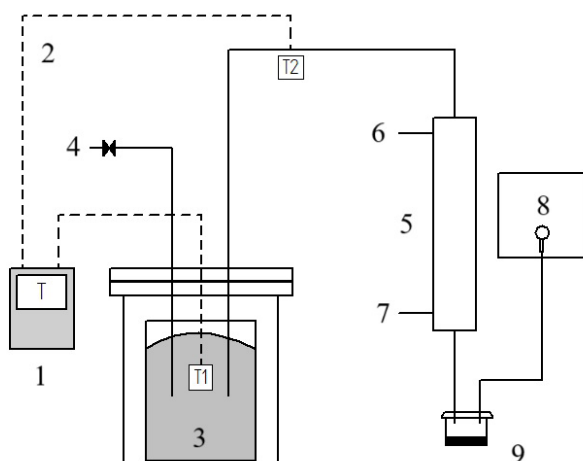


Fig. 1 Pyrolysis setup: 1. Data logger, 2. K-type thermocouple, 3. Reactor, 4. N₂ inlet, 5. Heat exchanger, 6. Cooling water in, 7. Cooling water out, 8. Multi-layer gas sampling bag, 9. Liquid collecting vessel

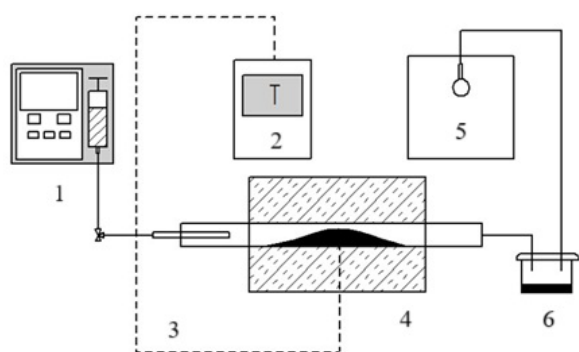


Fig. 2 Gasification setup: 1. Perfusion pump, 2. Data logger, 3. K-type thermocouple, 4. Tube furnace, 5. Multi-layer gas sampling bag, 6. Liquid collecting vessel

2.3 Adsorption experiments

Batch adsorption experiments were conducted at room temperature (approximately 25 °C) to investigate phenol uptake. In each experiment, 100 mg of adsorbent was added to 100 cm³ of phenol solution with an initial concentration of 20 mg dm⁻³. The mixtures were placed on a shaker and agitated for 20 h to ensure sufficient contact between the adsorbent and the adsorbate. After the adsorption process, the residual phenol concentration was determined according to the "ISO 6439:1990 Water quality – Determination of phenol index" standard [25].

Two approaches were investigated during the phenol adsorption experiments:

1. The components were carbonized and activated separately, then mixed before adsorption.
2. The components were carbonized and activated together, and the resulting ACs were used individually for adsorption experiments.

This approach allowed us to determine whether any interactions occurred between the materials during thermal treatment that could influence adsorption performance.

As the adsorbents reported in the literature were tested under varying conditions, it is difficult to directly compare their adsorption capacities. Therefore, we used a commercially available ≤ 2 mm granulated AC from Thermo Fisher Scientific, with an iodine number of 969 mg/g, as a reference.

2.4 Characterization of ACs and by-product gases

The ash content of solid samples was determined according to the ISO 21656:2021 standard (Solid Recovered Fuels – Determination of Ash Content) using an HK-45/12-V laboratory furnace [26]. Elemental analysis of the base materials was performed using a Carlo Erba EA1108 elemental analyzer. Nitrogen adsorption measurements were conducted with a TriStar 3000 instrument. The composition of the gas samples was analyzed using an Agilent 490 Micro GC gas chromatograph equipped with a thermal conductivity detector (TCD) and two columns (PoraPLOT U and CP-COX).

3 Results and discussion

3.1 Analysis of pyrolysis products

Fig. 3 presents the yields of pyrolysis products for the different material mixtures. The mixtures P+PS, P+W, and P+PS+W exhibited similar product distributions in terms of mass balance. In contrast, the PS+W mixture resulted in the lowest char and gas yields, while producing the highest amount of liquid fraction.

An estimation of char yield for material mixtures was calculated based on the individual pyrolysis data of each component. Specifically, the known char yields from the pyrolysis of each material were weighted according to their respective mass ratios in the mixture. By multiplying the char yield of each individual material by its proportion in the mixture and summing the results, an estimated overall

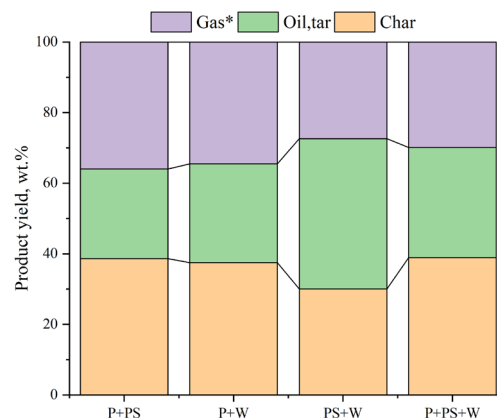


Fig. 3 Pyrolysis product yields

char yield for the mixture was obtained. The results are presented in Fig. 4 and were compared with the experimentally measured values. For the P+PS and P+W mixtures, no significant differences were observed between the estimated and measured char yields. However, for mixtures containing PS and wood, more char was produced than expected based on the estimation.

This finding is consistent with a study published in 2018 [27], in which the authors reported a synergy between poplar and PS during pyrolysis. In their study, the difference between the expected and actual char yields was a maximum of 2.5 wt.%. The observed increase in char formation suggested that the presence of PS led to reactions resulting in secondary char formation, likely due to volatile condensation and repolymerization processes.

The results of gas chromatography measurements are presented in Fig. 5.

The pyrolysis gases of cellulosic materials contain a higher proportion of oxygenated compounds, including CO_2 , whereas plastic-derived pyrolysis gases are richer in hydrocarbons. In the paper/PS/wood mixtures, the PS

content varied between 0 and 28.4 wt.%, meaning that the gas composition was primarily influenced by the cellulosic components. The highest PS content was in the PS+W mixture; consequently, its pyrolysis gas had the lowest CO_2 concentration and the highest levels of CH_4 , C_2H_2 , and C_2H_6 .

3.2 Synthesis gas analysis

Following carbonization, the produced chars were subjected to steam gasification for physical activation. The resulting syngases were analyzed, and the results are presented in Fig. 6.

The overall gas compositions were similar, with only slight variations. A gradual increase in H_2 content was observed with increasing paper content in the mixture. A more significant difference was noted in specific gas production. As the paper content in the mixture decreased, the specific gas yield also decreased. The highest CO concentration was observed in the syngas produced from the PS-free sample. Overall, changes in the mixture composition had a much smaller impact on syngas composition compared to their effect on pyrolysis gas composition.

3.3 Characterization of ACs

Nitrogen adsorption analysis was performed under isothermal conditions, and the resulting adsorption-desorption isotherms for the Case B materials – where the components were carbonized and activated together – are shown in Fig. 7. In Fig. 7, P is the equilibrium pressure of nitrogen gas, and P_0 is its saturation vapor pressure at the measurement temperature (-196°C). The ratio P/P_0 represents the relative pressure.

Regardless of the base material, all isotherms exhibit a similar form. The International Union of Pure and Applied Chemistry (IUPAC) classifies adsorption isotherms based

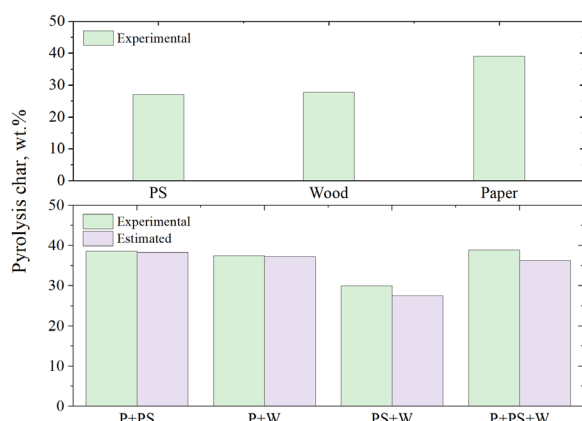


Fig. 4 Remaining char during 520 °C pyrolysis experiments

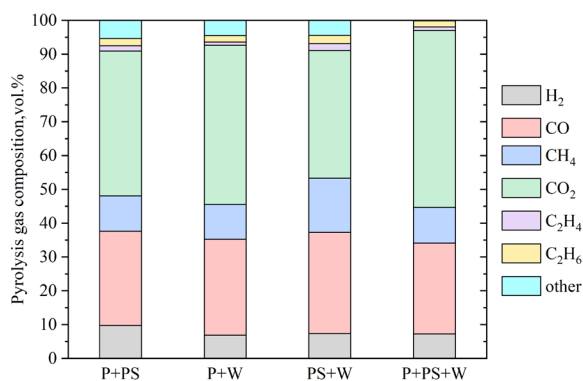


Fig. 5 Results of gas chromatography analysis

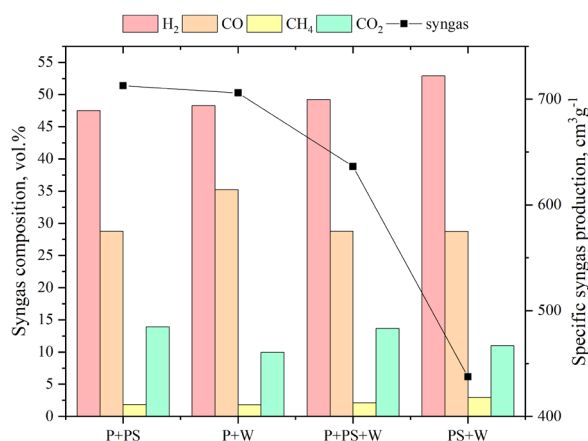


Fig. 6 Composition and production rate of synthesis gases

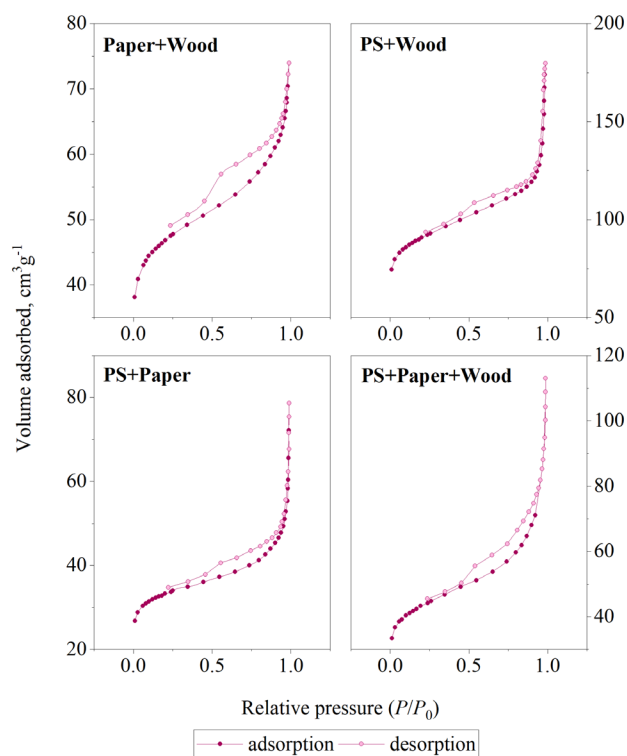


Fig. 7 Nitrogen adsorption and desorption isotherms

on their shapes. According to the IUPAC classification, the isotherms of our samples exhibit a transitional Type IV(a)–Type II behavior, suggesting the presence of both mesopores and macropores in the material structure [28].

Additionally, open hysteresis loops were observed, which is a common phenomenon in nitrogen adsorption analysis of biochars [29]. Biochars typically have a complex pore structure with pores of varying shapes and sizes. During adsorption, nitrogen molecules enter these pores, but some become trapped during desorption. As the pressure decreases, capillary forces retain certain nitrogen molecules inside the pores, preventing their release. This phenomenon results in desorption and adsorption isotherms that do not fully overlap [30].

IUPAC also classifies hysteresis loops based on their shape. The hysteresis loops observed in our samples most closely resemble the H3 type, which suggests the presence of wedge-shaped pores [31].

Fig. 8 presents the phenol uptake in weight percent for different mixtures under three conditions: Case A, where adsorption was performed with separately carbonized and activated components that were mixed before adsorption; Case B, where adsorption was carried out using ACs produced through co-carbonization and co-activation; and the estimated values (est), which were calculated based on previous single-component adsorption experiments.

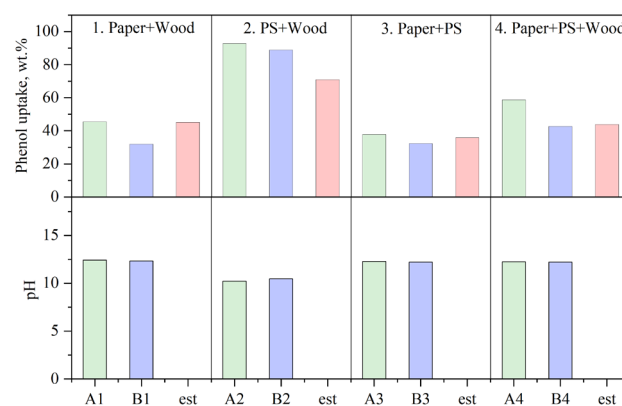


Fig. 8 Comparison of phenol uptake capacity and pH of the solutions

In all cases, the phenol uptake in Case B is consistently lower than in Case A, suggesting that interactions between the components during carbonization and activation negatively affected the adsorption capacity of the resulting ACs. In contrast, Case A values closely match the estimated values for most mixtures, confirming that when the components were activated separately, their adsorption behavior followed the expected trends based on single-component experiments. However, a notable exception was observed in the PS+W mixture, where the adsorption capacity in Case A exceeded the estimated value. This suggests that some factor related to the adsorption process, rather than the thermal treatment, enhanced phenol uptake.

A possible explanation for this is the influence of pH on adsorption efficiency. The initial pH of the solution was approximately 5.8. The pH of the solution after adsorption for single-component carbons was 6.9 for wood, 13.2 for paper, and 12.4 for PS. In the case of the PS+W mixture, the final pH was measured between 10.2 and 10.5, indicating that the combination of these materials altered the solution conditions. This intermediate pH may have contributed to a more favorable environment for phenol adsorption, leading to higher uptake than predicted. These findings highlight the dual role of both thermal treatment effects, which negatively impacted adsorption in Case B, and adsorption-related factors, such as pH-dependent interactions, which enhanced uptake in Case A for the PS+W mixture.

Fig. 9 shows the remaining char rate after activation and the BET specific surface area of the ACs. The highest BET surface area was measured for the PS+W mixture (308 m²/g), which is nearly half that of the reference AC (736 m²/g). This is consistent with the phenol uptake results, which were also highest for the PS+W mixture. The P+W (160 m²/g) and P+PS+W (149 m²/g) samples showed similar surface areas, while the P+PS mixture had the lowest specific surface area.

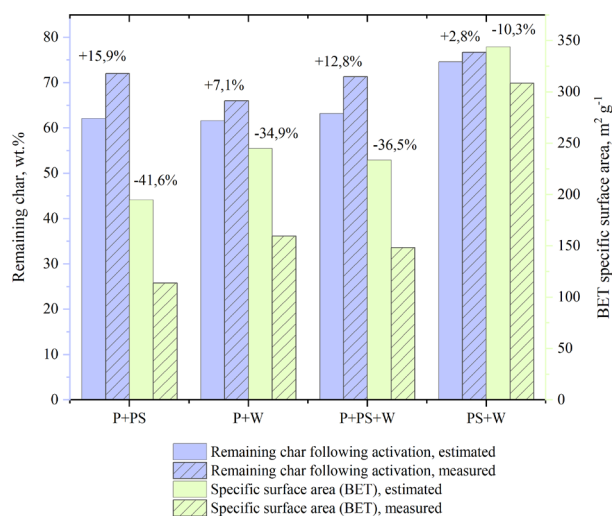


Fig. 9 Remaining char rates and specific surface area of the produced ACs

Both measured and estimated values are presented, where estimations were based on single-component experiments. The relative difference between the measured and estimated values is notably higher for mixtures containing paper.

For the remaining char, the relative difference was +2.8% for the paper-free mixture, whereas for paper-containing mixtures, it ranged between +7.1% and +15.9%. In terms of specific surface area, the relative difference was –10.3% for the paper-free mixture but significantly larger for paper-containing mixtures, ranging from –34.9% to –41.6%.

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The lower specific surface area resulted in weaker phenol adsorption capacity, indicating that the presence of paper hinders gasification reactions. This limitation likely leads to reduced pore development, ultimately decreasing both surface area and adsorption performance.

4 Conclusion

In this study, ACs were prepared from PS, paper, and wood mixtures, and their phenol uptake capacity was evaluated. The results showed that co-carbonization generally reduced adsorption capacity; however, a positive adsorption-related synergy was observed for the PS+W mixture, where phenol uptake exceeded the estimated values. BET surface area analysis revealed that paper-containing mixtures had lower surface areas than expected and also produced more residual char than predicted. This suggests that the presence of paper inhibits gasification reactions, ultimately leading to AC with a lower phenol uptake capacity than anticipated.

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