# Lignite-derived activated carbon: A superior, low-cost alternative to coconut-shell GAC for tributyl phosphate (TBP) adsorption from wastewater

**Guk Chol Kim [1] *, Jong Hyok Kim[1], Yong A Choe [2], Jin Song O[1],**

[1] *Faculty of Energy Science,* ***Kim II Sung*** *University, Pyongyang 999093, Democratic People's Republic of Korea*

[2] *Analytical Measurement Laboratory,* ***Kim Il Sung*** *University, Pyongyang 999093, Democratic People's Republic of Korea*

* *Corresponding Author. E-mail: kgc19881116@163.com*
*Tel: 178-4316-3453*

## Abstract

This study examined the use of local lignite-based and walnut shell-based GACs as potential low-cost alternatives to the imported coconut shell-based GACs for the removal of TBP from wastewaters in Zr alloy production. The lignite-based GAC steam activated showed that the surface groups consisted of –OH, C=C, and C–O–C and that it had a predominantly mesoporous structure (65% mesopores and 20% micropores).

At a solid-to-liquid ratio of 1:100 and an initial concentration of 400 mg/L of TBP, the GAC derived from lignite adsorbed 38.7 mg/g with an efficiency of 96.2%. This result was comparable to the coconut shell GAC, which adsorbed 39.8 mg/g with an efficiency of 99.5%. The walnut shell GAC had a slightly higher adsorption capacity than the other two GACs, with 39.7 mg/g and an efficiency of 99.6%. In all cases, equilibrium was reached in 120 min, while the literature usually reports 150–180 min. This may be because the intraparticle diffusion is accelerated when the mesopore content is high; in this GAC, the mesopores accounted for 65% of the volume. This kinetic advantage distinguishes domestically produced GACs from predominantly microporous coconut-shell GAC. Economically, lignite-derived GAC showed superior cost-effectiveness, with a production cost less than one-fifth that of imported coconut-shell GAC. The economic effectiveness index clearly favoured domestically produced GACs.

Lignite-derived GAC, originally used almost exclusively for gas purification, was successfully validated for liquid-phase TBP removal, an application with no prior example. Thus, domestically produced lignite-derived GAC is an effective, low-cost alternative to imported coconut-shell GAC for TBP removal from Zr alloy production wastewater.

**Keywords:**

tributyl phosphate; lignite; GAC (granular activated carbon); adsorption amount; equilibration time; adsorption rate

## 1. Introduction

Various industrial processes, including the separation and leaching of valuable metals such as Zr and Hf, utilise organic solvents like tributyl phosphate (TBP) and methyl isobutyl ketone (MIBK). These processes generate substantial volumes of wastewater contaminated with TBP, often at concentrations exceeding its aqueous solubility (0.39–0.407 g/L at 25 °C). The National Environmental Protection Standard (2021) limits organic content in effluent from Class II titanium industries to below 3 ppm [1,2]. Quantitative analysis of TBP in aqueous solutions can be reliably performed using gas chromatography–mass spectrometry or spectrophotometric colorimetry, with an error of less than 2% in the concentration range of 1–400 ppm [3–5].

Various approaches have been explored for TBP removal from industrial wastewater, which can be broadly categorised into physical separation, chemical oxidation, membrane filtration, and adsorption. Physical separation methods, such as combined air-lift mixer-settler units, can reduce TBP concentration from 200 ppm to below 8 ppm (96% removal) but require complex, energy-intensive configurations [7]. Chemical oxidation using supercritical water effectively decomposes TBP yet demands high-pressure, high-temperature conditions, leading to significant operational costs [8]. Membrane-based techniques, including micellar-enhanced ultrafiltration, can simultaneously remove TBP, its degradation product dibutyl phosphate, and uranyl ions [9]; similarly, ozonation has been reported for treating brominated organic compounds [10]. While effective, these methods generally involve sophisticated technical requirements, specialized reagents, and high waste disposal costs, limiting their practical applicability, especially in resource-constrained settings.

Among the available technologies, adsorption remains one of the most traditional, cost-effective, and operationally simple methods for removing both inorganic and organic pollutants from wastewater [11,12]. Activated carbon, in particular, offers a highly hydrophobic surface, well-developed pore structure, and high selectivity, making it a widely used material for water purification in dyeing, food processing, and chemical industries [13,14]. However, most commercial granular activated carbons (GACs) used for organic wastewater treatment – especially coconut-shell-based GAC – are imported and expensive. Moreover, existing studies on activated carbon adsorption for TBP-containing wastewater are scarce, and most commercially available GACs have been originally designed for gas purification rather than for liquid-phase TBP removal. Specifically, the application of lignite-derived carbonaceous GAC (primarily intended for gas-phase applications) to TBP-contaminated wastewater has rarely been reported, and a systematic evaluation of its adsorption performance – including adsorption capacity, removal rate, equilibrium time, and economic viability – remains lacking.

To address this gap, the present study introduces two domestically produced granular activated carbons: (i) lignite-derived carbonaceous GAC, produced by steam activation of carbonised lignite and originally developed for gas purification, and (ii) walnut-shell-derived GAC. The novelty of this work lies in three aspects. First, it extends the application of lignite-derived GAC – previously limited to gas-phase adsorption – to the liquid-phase removal of TBP from industrial wastewater, an application for which no prior example exists. Second, it provides the first comprehensive comparison of lignite-derived GAC, walnut-shell GAC, and commercial coconut-shell GAC in terms of TBP adsorption amount, adsorption rate, equilibrium time, and a composite economic effectiveness index. Third, it demonstrates that domestically produced GACs, particularly lignite-derived carbonaceous GAC, are not merely cheaper substitutes but can achieve superior overall cost-effectiveness compared to imported coconut-shell GAC.

Therefore, the specific objectives of this study are as follows: (1) to evaluate the

TBP adsorption behaviour of lignite-derived carbonaceous GAC and walnut-shell-derived GAC in terms of adsorption amount (mg/g), adsorption rate (%), and equilibrium time (min); (2) to compare their adsorption performance with that of commercial coconut-shell GAC under identical experimental conditions (TBP concentration: 400 ppm; solid-liquid ratios: 1:10, 1:50, and 1:100; contact time: up to 600 min); (3) to assess the economic effectiveness of the three GACs by integrating production cost, transport cost, durability, recyclability, and disposal requirements into a single economic effectiveness index; and (4) to determine whether lignite-derived carbonaceous GAC – originally designed for gas purification – can serve as a low-cost, high-performance alternative to imported coconut-shell GAC for the treatment of TBP-contaminated wastewater generated during Zr alloy production.

## 2. EXPERIMENTAL METHOD

### 2.1 Materials

To prepare the stock solution, 300 mL of distilled water and 0.42 mL of industrial-grade TBP (ρ = 0.9737 g/㎤, 99.3% purity) were placed in an Erlenmeyer flask, and the final volume was made up to 1 L with distilled water.

The solution was shaken at 150 rpm for 5 h using a shaker (LE-208). The emulsion formed was then neutralized by the addition of 0.1 M NaOH and left to stand for 12 h. To prepare and sample the supersaturated stock solution of TBP, the surface layer of the vessel wall or the emulsion should be avoided, and only the intermediate layer should be used.

GAC samples: Three GAC samples—coconut shell-based keratinous (produced in Malaysia), lignite-based carbonaceous (produced domestically), and walnut shell-based keratinous (produced domestically)—were prepared via hydrothermal carbonization. These samples were then placed in a thermostatic drying oven (SPT-200) at 110–120 °C for 2 h to remove the moisture.

### 2.2. Analytical methods

Fourier-transform infrared (FTIR) spectroscopy (Nicolet 6700, SHIMADZU) and gas chromatography-mass spectrometry (GC-MS, QP2010SE, SHIMADZU) were used to perform qualitative and quantitative analyses on commercial pure TBP solutions.

Surface pore structures of GAC samples were examined with scanning electron microscopy (SEM, JEOL JSM6610A, SHIMADZU), and surface functional groups were characterized by Fourier-transform infrared (FTIR) spectroscopy based on the General Regulations (15683:2016) of our country.

Specific surface area and pore distribution were determined by the BET apparatus using the nitrogen isotherm adsorption method, and ash content was determined by LOI.

TBP concentrations in the sample solutions before and after adsorption were measured by a gas chromatograph (GC-14B, SHIMADZU) equipped with a flame ionization detector (FID).

## 2.3. TBP adsorption experiments

GAC samples were weighed precisely to 1.000 ± 0.001 g using an analytical balance (LIBROR AEG-120, SHIMADZU) and placed in a beaker. Then, 400 ppm stock solutions were added according to the expected solid-liquid ratios (SLRs). Each sample solution was stirred at room temperature for specific time periods (5, 10, 30, 60, 120, 300, and 600 min) using a magnetic stirrer. The supernatant was filtered through an inorganic syringe filter (MREDA, 0.45 μm nylon) to determine the TBP concentration using gas chromatography. The TBP adsorption amounts and rates of several sorbents, including the GAC samples, were calculated as follows:

$$Adsorption\ Amount(mg/g) = \frac{C_0 - C_t}{m} \times V \quad (1)$$

$$Adsorption\ Rate(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where $C_0$ and $C_t$ are the TBP concentrations (mg/L) of the testing solution before and after adsorption, respectively; m is the mass of the sample (g); and V is the volume of the testing solution (L).

## 2.4. Economic efficiency

The economic effectiveness of commercial sorbents used for organic wastewater treatment was evaluated by considering sorbent disposal requirements, duty cycles, production costs (including transportation conditions), and utility factors based on expected effluent characteristics [7]. The economic effectiveness index, expressed in US dollars, can be estimated using the following equation:

$$Economic\ Effectiveness\ Index = \frac{Duty\ Cycle \times Utility\ Factor}{Sorbent\ Demand \times \mathrm{Cos}\,ts} \tag{3}$$

## 3. Results and Discussion

### 3.1. Adsorbent characteristics

The physical characteristics of the three granular activated carbons (GACs) are summarised in Table 1. The lignite-derived carbonaceous GAC (GAC-1) exhibited a specific surface area of 968 m²/g and a total pore volume of 0.66 cm³/g, with an ash content of 12.4%. The walnut-shell GAC (GAC-2) showed similar values (920 m²/g, 0.58 cm³/g, 4.8% ash), while commercial coconut-shell GAC (GAC-3) had the highest surface area (1190 m²/g) and pore volume (0.71 cm³/g) but the lowest ash content (3.5%).

Table 1. Physical Characteristics of three samples

| Raws | Packing density g/cm³ | Average grain size mm | Specific surface area m²/g | Porosity cm³/g | Ash content % | Functional groups |
|---|---|---|---|---|---|---|
| Carbonaceous | 0.45 | 0.9~2.5 | 968 | 0.66 | 12.4 | C=C,<br>C-O-C |
| Phloem-shell | 0.48 | 0.4~2.0 | 920 | 0.58 | 4.8 | O-H, C=C,<br>C-O-C |
| Coconut shell | 0.50 | 0.4~2.0 | 1190 | 0.71 | 3.5 | O-H, C=C,<br>C-O-C |

The specific surface area of GAC-1 is moderate compared to high-performance carbon materials (2000–3000 m²/g) reported for TBP adsorption [28]. However, the mesopore fraction of GAC-1 is notably high (approximately 65% of total pore volume, with pore radii centred at 1.8 nm and 20 nm). This mesopore-dominant structure is advantageous for adsorbing relatively large organic molecules like TBP (molecular weight 266.3 g/mol, molecular diameter ≈1.1 nm), as it facilitates rapid intraparticle diffusion. As demonstrated by Kolyvakis [27] for organic micropollutants, a high mesopore fraction significantly accelerates intraparticle mass transport by reducing steric hindrance and shortening diffusion path lengths. By contrast, commercial coconut-shell GAC, despite its higher surface area, is primarily microporous (typically >60% micropores), which may impose diffusion limitations for molecules of TBP size. FTIR analysis confirmed the presence of O–H, C=C, and C–O–C functional groups on all three GACs. The presence of C–O–C groups on GAC-1 likely promotes specific interactions with the phosphate group of TBP molecules [12], partially compensating for its lower specific surface area.

### 3.2. TBP adsorption performance

The TBP concentration calibration curve for stock solutions ranging from 100 ppm to 400 ppm is presented in Figure 1. The relative standard deviation was ±2% at 200–400 ppm and ±5% at 100 ppm. Concentrations below 100 ppm were determined by extrapolation based on spectrophotometric colorimetry using ammonium molybdate [4].

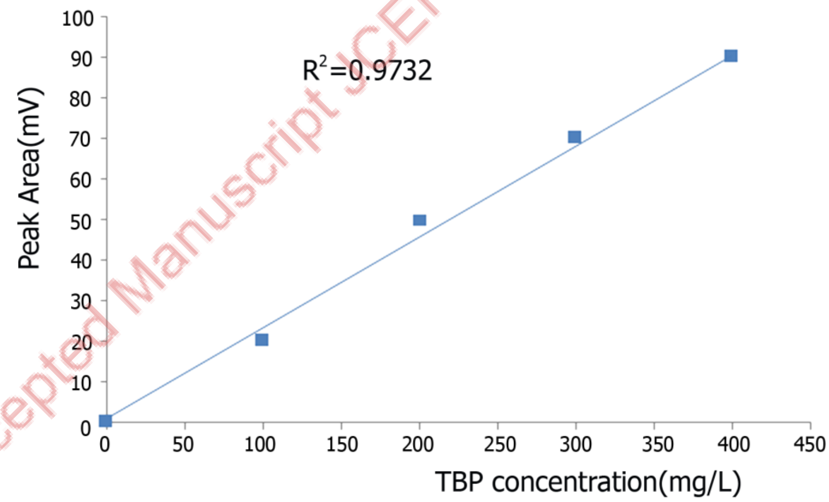

Figure 1. TBP concentration calibration curve diluted with distilled water.

Figure 2 presents the TBP adsorption behaviour of the three GACs at different solid-liquid ratios (SLRs: 1:10, 1:50, and 1:100) in a 400 ppm TBP stock solution. As the SLR increased, the residual TBP concentration decreased for all adsorbents, while both the adsorption amount (mg/g) and removal rate (%) increased. At an SLR of 1:100, the adsorption amounts ranged from 38.7 mg/g (GAC-1) to 39.7 mg/g

(GAC-2), with GAC-3 showing 39.8 mg/g. The corresponding removal rates were 96.2% (GAC-1), 99.6% (GAC-2), and 99.5% (GAC-3).

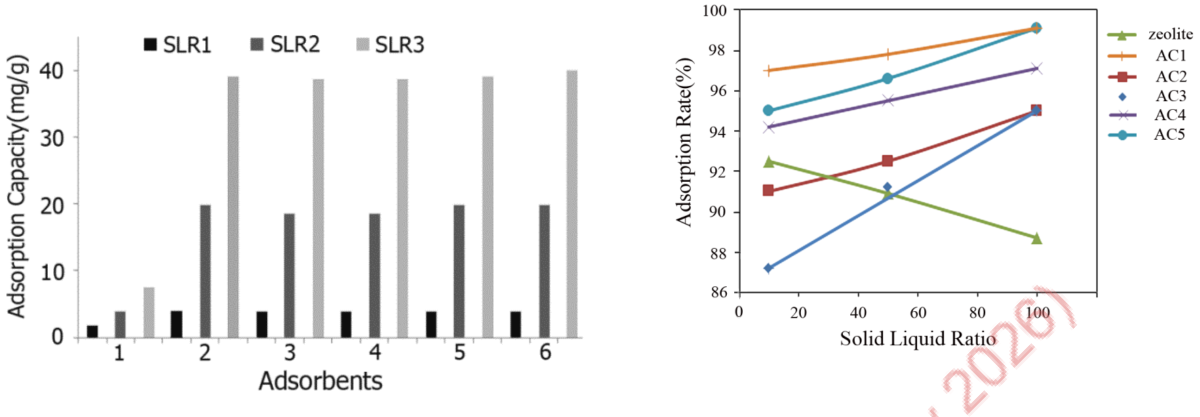

Figure 2. Variations in the adsorption amounts and rates of several sorbents with SLRs.

These adsorption capacities (38.7–39.8 mg/g at 400 ppm initial concentration) are comparable to those reported for other carbon-based adsorbents. Bakhiia et al. [28] reported that high-surface-area carbon materials (2000–3000 m²/g) exhibit excellent TBP uptake in aqueous nitric acid solutions. Given that GAC-1 has a specific surface area approximately one-third to one-half of those materials, its adsorption capacity of 38.7 mg/g is remarkably competitive. This finding suggests that factors other than specific surface area – particularly the mesopore volume fraction and surface functional group chemistry – play crucial roles in determining TBP adsorption performance. Notably, GAC-2 achieved the highest removal rate (99.6%) despite having the lowest specific surface area (920 m²/g) among the three GACs, further supporting this hypothesis. The high removal rates (>99% for GAC-2 and GAC-3) meet the stringent discharge standard of below 3 ppm organic content required by the National Environmental Protection Standard (2021) [1,2], indicating that both domestically produced GACs are technically viable for practical wastewater treatment applications.

Figure 3 illustrates the effect of stirring time on TBP adsorption. The TBP concentration in the sample solutions decreased rapidly during the first 60 minutes of contact, then gradually stabilised, reaching equilibrium after approximately 120 minutes for all three GACs. This indicates that adsorption and desorption processes reached saturation equilibrium within 120 minutes.

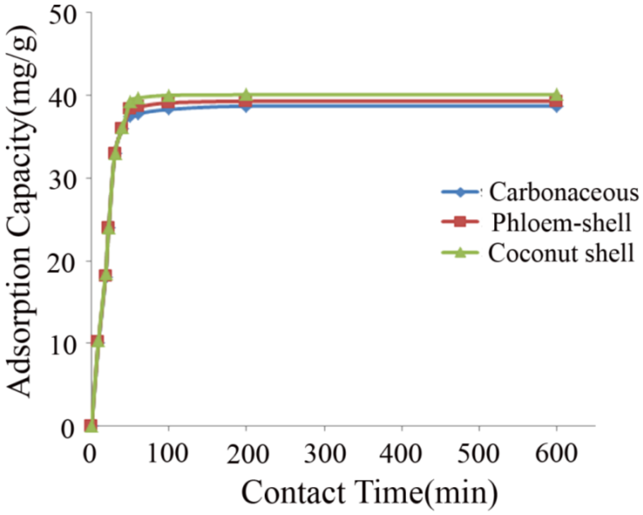

Figure 3. Effect of stirring time on TBP adsorption.

The equilibrium time of approximately 120 minutes observed in this study is shorter than the 150–180 minutes typically reported for TBP adsorption onto conventional activated carbons in the literature. The faster equilibrium achieved in our study is attributed to the well-developed mesopore structure of GAC-1 and GAC-2 (Table 1). As shown, both domestically produced GACs contain a high proportion of mesopores (GAC-1: 65% mesopores, 20% micropores; GAC-2: similar distribution), whereas commercial coconut-shell GAC is predominantly microporous. Kolyvakis [27] demonstrated that for organic micropollutants, a high mesopore fraction significantly accelerates intraparticle mass transport by reducing diffusion path lengths and eliminating steric hindrance at pore entrances. TBP has a molecular diameter of approximately 1.0–1.2 nm, which is comparable to the width of micropores (<2 nm). In a microporous adsorbent, TBP molecules may experience restricted diffusion or pore blocking, prolonging the time required to reach equilibrium. In contrast, the mesopore-rich structure of GAC-1 and GAC-2 allows TBP molecules to rapidly access internal adsorption sites without being constrained by narrow pore entrances, thereby achieving equilibrium more quickly. This equilibrium time also agrees with Causse and Faure [6], who studied TBP droplet interactions on metal surfaces and reported that steady-state conditions were typically attained within 1–2 hours.

No previous study has systematically compared lignite-derived, walnut-shell-derived, and coconut-shell-derived GACs for TBP removal from Zr alloy production wastewater. The present results demonstrate that domestically produced GACs, particularly walnut-shell GAC, achieve TBP removal performance indistinguishable from that of imported commercial coconut-shell GAC.

### 3.3. Pore structure and adsorption mechanism

Pore size distribution analysis revealed that the lignite-derived carbonaceous GAC (GAC-1) exhibits a bimodal pore radius distribution with peaks at 1.8 nm (small mesopore) and 20 nm (large mesopore). The micropore content is relatively low (approximately 20%), while mesopores constitute about 65% of the total pore volume. This pore structure differs from that reported by Zhang [15] for lignite-based activated carbons used for coking wastewater treatment, where micropores dominated (approximately 50–60%). The difference likely arises from the specific steam activation conditions employed in our study, which were optimised to generate mesopores suitable for liquid-phase adsorption of relatively large organic molecules.

The low micropore fraction and high mesopore fraction of GAC-1 have two important consequences for TBP adsorption. First, mesopores provide accessible pathways for TBP molecules to diffuse into the interior of the carbon particles, minimising the risk of pore blocking at the entrance of narrow micropores. This explains the relatively fast equilibrium time (120 min) observed for GAC-1 despite its moderate specific surface area. Second, the high mesopore volume increases the availability of adsorption sites on pore walls for TBP molecules, compensating for the lower micropore area that would otherwise contribute to the total specific surface area.

Frederick et al. [22] and Gorham et al. [23] have shown that organic adsorbates with molecular dimensions exceeding 0.8 nm often exhibit reduced accessibility to micropores (<2 nm) due to size exclusion effects. TBP, with a molecular weight of 266.3 g/mol and a molecular diameter of approximately 1.1 nm, likely experiences such size exclusion in highly microporous carbons. Therefore, the mesopore-dominant structure of GAC-1 is not a disadvantage but rather a design feature that enhances TBP accessibility and adsorption kinetics.

### 3.4. Economic effectiveness and practical applicability

Table 2 presents the economic effectiveness index calculated for the three GACs based on production cost, transport cost, durability, recyclability, and disposal requirements. The effective factor was 0.046 for lignite-derived carbonaceous GAC (GAC-1), 0.06 for walnut-shell GAC (GAC-2), and 0.0148 for commercial coconut-shell GAC (GAC-3). Under the calculation method used (Equation 3), a lower effective factor indicates better overall economic performance.

Table 2. Economic efficiency of commercial sorbents

| Sorbents | Demands | Durability | Costs | | Recycle % | Effective Factor |
|---|---|---|---|---|---|---|
| | | | Production | Transport | | |
| Carbonaceous | 1.1 | 150 | 890 | - | <30 | 0.046 |
| walnut-shell | 1 | 150 | 1000 | - | <40 | 0.06 |
| Coconut shell | 1 | 150 | 1050 | 3000 | <40 | 0.0148 |

GAC-1 shows superior economic effectiveness (effective factor 0.046, the lowest among the three) primarily due to its production cost, which is less than one-fifth that of imported coconut-shell GAC (Table 2). Transport costs for GAC-1 and GAC-2 are negligible because they are produced domestically, whereas imported coconut-shell GAC incurs substantial transport expenses (estimated at 3000 USD per unit). Durability and recyclability are similar for all three GACs (recycle rates <30–40%), indicating that the cost advantage of domestically produced GACs is not offset by inferior mechanical properties.

This finding is particularly significant given that most commercially available GACs for wastewater treatment are imported, making them expensive and logistically challenging to procure in resource-limited settings. As noted by Kolyvakis [27], the practical applicability of an adsorbent depends not only on its adsorption performance but also on its material cost, regeneration potential, and local availability. While Bakhiia et al. [28] developed an effective purification scheme for sorbent regeneration, the high initial cost of high-surface-area carbon materials (2000–3000 $m^2/g$) may limit their widespread adoption in large-scale industrial applications. Gauden et al. [24] and Cannon et al. [25,26] have extensively studied the long-term operation and thermal regeneration of GACs in filter beds, demonstrating that pore structure evolution during repeated use can affect economic feasibility. Although our study did not evaluate multi-cycle regeneration performance, the low production cost of GAC-1 suggests that even single-use or limited-cycle applications would be economically viable, especially when compared to imported alternatives. Furthermore, the domestic availability of lignite as a raw material ensures a stable supply chain, unlike imported coconut-shell GAC which is subject to international market fluctuations.

## 4. Conclusions

This study evaluated the feasibility of using domestically produced lignite-derived carbonaceous granular activated carbon (GAC) and walnut-shell-derived GAC as cost-effective alternatives to imported commercial coconut-shell GAC for the removal of tributyl phosphate (TBP) from wastewater generated during Zr alloy production.

Firstly, both domestically produced GACs exhibited excellent TBP adsorption performance. At a solid-liquid ratio of 1:100 and an initial TBP concentration of 400 ppm, the adsorption amounts were 38.7 mg/g (lignite-derived GAC) and 39.7 mg/g (walnut-shell GAC), corresponding to removal rates of 96.2% and 99.6%, respectively. The adsorption equilibrium was reached within 120 minutes for all tested adsorbents, confirming that both domestic GACs are highly effective for TBP removal from aqueous solutions.

Secondly, when compared to imported commercial coconut-shell GAC (39.8 mg/g, 99.5% removal), the two domestically produced GACs showed comparable performance. Notably, the equilibrium time for TBP adsorption on lignite-derived GAC (120 min) was shorter than that reported for many conventional activated carbons (150–180 min). This kinetic advantage is attributed to the well-developed mesopore structure (65% mesopores) of the lignite-derived GAC, which facilitates rapid intraparticle diffusion – a structural feature that distinguishes it from the predominantly microporous coconut-shell GAC.

Thirdly, regarding economic effectiveness, the integrated index (considering production cost, transport cost, durability, recyclability, and disposal requirements) clearly favoured the domestically produced GACs. The lignite-derived carbonaceous GAC showed the best overall cost-effectiveness, primarily because its production cost is less than one-fifth that of imported coconut-shell GAC. Domestic production also eliminates transport expenses, further enhancing its economic advantage. To the best of our knowledge, this study provides the first quantitative economic comparison of TBP adsorbents.

Fourthly, importantly, lignite-derived carbonaceous GAC – originally developed and used almost exclusively for gas purification – has been successfully validated as a low-cost, high-performance alternative for treating TBP-contaminated wastewater from Zr alloy production. This represents a novel extension of its application field, with no prior example of its use for TBP removal from liquid-phase industrial wastewater.

This study advances the field in three significant ways. First, it demonstrates that a mesopore-dominant pore structure (65% mesopores) can be more advantageous for TBP adsorption than a high specific surface area alone, challenging the conventional assumption that higher surface area always yields better adsorption performance. Second, it provides the first comprehensive comparison of lignite-derived, walnut-shell-derived, and coconut-shell-derived GACs for TBP removal, establishing a benchmark for future adsorbent selection. Third, it proves that domestically produced GACs – particularly lignite-derived GAC – are not merely cheaper substitutes but can achieve superior overall cost-effectiveness compared to imported commercial products.

Taken together, the findings of this study strongly support the conclusion that domestically produced lignite-derived carbonaceous GAC and walnut-shell-derived GAC are effective, low-cost alternatives to imported coconut-shell GAC for the removal of TBP from Zr alloy production wastewater. The lignite-derived GAC, in particular, combines competitive adsorption performance with superior economic viability, making it a promising candidate for large-scale industrial applications where cost and local availability are critical constraints.

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## CRediT Author Statement

Author Contributions: *Guk Chol Kim* : Conceptualization, Methodology, experiment, Validation; *Jong Hyok Kim* : experiment, Formal Analysis, Data

Curation, Writting Draft Preparation; *Yong A Choe* : Material Analysis; *Jin Song O* : Review and Editing.

All authors have read and agreed to the published version of the manuscript.

## References

[1] Satyabrata, M.S., Ganesh, P., Velavendan, N.K., Pandey, C., Mallika U., Kamachi, M.R. (2015). Effects of temperature, concentration of acid and metal ions on the solubility of tri-n-butyl phosphate in aqueous phase. J. Radioanal. Nucl. Chem., 303, 335-339. DOI:10.1007/s10967-014-3351-3.

[2] Burger, L. L., Forsman, R. C. (1951). The solubility of tributyl phosphate in aqueous solutions (Report No. HW-20936). Hanford Works. Richland, Washington, United States.

[3] Kenji, S., Kiwao, K. (1995). Determination of organophosphoric acid triesters in aquatic environmental samples by GC/MS. Journal of Environmental Chemistry. 5, 4, 821-827. DOI:10.5985/jec.5.821.

[4] Ganesh, S.P., Velavendan, N.K., Pandey, M.K., Ahmed, U., Kamachi M. (2012). Spectrophotometric determination of dissolved tri n-butyl phosphate in aqueous streams of Purex process. J. Radioanal. Nucl. Chem., 293, 529-533. DOI:10.1007/s10967-012-1731-0.

[5] Lamouroux, C., Virelizier, H., Moulin, C., Tabet, J.C., Jankowski, C.K. (2000). Direct determination of dibutyl and monobutyl phosphate in a tributyl phosphate/nitric aqueous-phase system by electrospray mass spectrometry. Analytical Chemistry, 72, 6, 1186-1191. DOI:10.1021/ac990613y.

[6] Causse, J., Faure, S. (2009). Acidic surfactant solutions for tributylphosphate removal in nuclear fuel reprocessing plants: A formulation study. Chemical Engineering Journal, 147, 180-187. DOI:10.1016/j.cej.2008.06.033.

[7] Vikesh, G.L., Prashil, C.W., Virendra, K.R. (2015). Removal of tributyl phosphate from aqueous stream in a pilot scale combined air-lift mixer-settler unit: Process intensification studies. Chemical Engineering and Processing: Process Intensification, 95, 72-79. DOI:10.1016/j.cep.2015.05.004.

[8] Kosari, M., Golmohammadi, M., Towfighi, J., Ahmadi, S.J. (2018). Decomposition of tributhyl phosphate at supercritical water oxidation conditions:

Non-catalytic, catalytic, and kinetic reaction studies. The Journal of Supercritical Fluids, 133, 103-113. DOI:10.1016/j.supflu.2017.09.012.

[9] Misra, S.K., Mahatele, A.K., Tripathi, S.C., Dakshinamoorthy, A. (2009). Studies on the simultaneous removal of dissolved DBP and TBP as well as uranyl ions from aqueous solutions by using Micellar-Enhanced Ultrafiltration Technique. Hydrometallurgy, 96, 1-2, 47-51. DOI:10.1016/j.hydromet.2008.07.013.

[10] Asogan, N.G., Sooboo, S., Sreekantha, B.J. (2018). Simultaneous removal of 2, 4,6-tribromophenol from water and bromate ion minimization by ozonation. Journal of Hazardous Materials, 357, 415-423. DOI:10.1016/j.jhazmat.2018.06.006.

[11] Nahil, M.A., Williams, P.T. (2012). Pore characteristics of activated carbons from the phosphoric acid chemical activation of cotton stalks. Biomass Bioenergy, 37, 142-149. DOI:10.1016/j.biombioe.2011.12.019.

[12] Liu, H., Dai, P., Zhang, J., Zhang, C.L., Bao, N., Cheng, C., Ren, L. (2013). Preparation and evaluation of activated carbons from lotus stalk with trimethyl phosphate and tributyl phosphate activation for lead removal. Chemical Engineering Journal, 228, 425-434. DOI:10.1016/j.cej.2013.04.117.

[13] Yuan, A.Q., Liang, J.Z., Wu, X.D., Ming, X.Q., Li, W.J., Chen, N.X., Huang, Z.W., Zhou, Z.G., Wei, D.P., Ma, S.M. (2019). Purification of waste sulfuric acid from petroleum processing by organic bentonite and activated carbon. Hydrometallurgy of China, 38, 2, 115-122. DOI:10.13355/j.cnki.sfyj.2019.02.009 (in Chinese)

[14] Li, L, Quinlivan, P.A., Knappe, D.R.U. (2002). Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. Carbon, 40, 12, 2085-2100. DOI:10.1016/S0008-6223(02)00069-6.

[15] Zhang, M. (2010). Experimental Research on Treatment of Coke Plant Wastewater with Lignite Activated Carbon [Master's thesis]. North China Electric Power University (Hebei), Baoding, China. (in Chinese)

[16] Yang, J.F., Kang, S.H., Chen, G.H., Zhang, Y.M., Zhou, Z.Q., Wang, P. (2014). Removal of oil in the extraction raffinate by activated carbon in uranium mine. Uranium Mining and Metallurgy, 33, 3, 151-154. (in Chinese)

[17] Zhang, Z.B., Cao, X.H., Liang, P., Liu, Y.H. (2013). Adsorption of uranium from aqueous solution using biochar produced by hydrothermal carbonization. J. Radioanal. Nucl. Chem., 295, 1201-1208. DOI:10.1007/s10967-012-2017-2.

[18] Liu, Q.F. (2016). Investigation on the removal of the radioactive nuclides from the mine waste water by active carbon adsorption. Uranium Mining and Metallurgy, 35, 3, 219-223. (in Chinese)

[19] Waqas, A., Sajid, M., Muhammad, Q., Sehrish, A., Zulqarnain, H.K., Huang, Y., Chen, D.Y., Avelino, N.D. (2021). Oxidized biochar obtained from rice straw as adsorbent to remove uranium(VI) from aqueous solutions. Journal of Environmental Chemical Engineering, 9, 2, 105104. DOI:10.1016/j.jece.2021.105104.

[20] Piai, L., Dykstra, J.E., Adishakti, M.G., Blokland, M., Langenhoff, A.A.M., & van der Wal, A. (2019). Diffusion of hydrophilic organic micropollutants in granular activated carbon with different pore sizes. Water Research, 162, 518-527. DOI: 10.1016/j.watres.2019.06.012.

[21] Krupa, N.E., & Cannon, F.S. (1996). GAC: pore structure versus dye adsorption. Journal - American Water Works Association, 88, 6, 94-108. DOI: 10.1002/j.1551-8833.1996.tb06574.x.

[22] Frederick, H.T., Cannon, F.S., & Dempsey, B.A. (2001). Calcium loading onto granular activated carbon with salicylate or phthalate. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 177(2-3), 157-168. DOI: 10.1016/S0927-7757(00)00668-3.

[23] Gorham, J.M., Wnuk, J.D., Shin, M., Fairbrother, H. (2007). Adsorption of natural organic matter onto carbonaceous surfaces: Atomic force microscopy study. Environmental Science & Technology, 41(4), 1238-1244. DOI:10.1021/es061793d.

[24] Gauden, P.A., Szmechtig-Gauden, E., Rychlicki, G., Duber, S., Garbacz, J.K., Buczkowski, J.K. (2006). Changes of the porous structure of activated carbons applied in a filter bed pilot operation. Journal of Colloid and Interface Science, 295(2), 327-347. DOI:10.1016/j.jcis.2005.08.039.

[25] Cannon, F.S., Snoeyink, V.L., Lee, R.G., Dagois, G. (1994). Reaction mechanism of calcium-catalyzed thermal regeneration of spent granular activated carbon. Carbon, 32(7), 1285-1301. DOI:10.1016/0008-6223(94)90114-7 ·

[26] Cannon, F.S., Snoeyink, V.L., Lee, R.G., Dagois, G., DeWolfe, J.R. (1993). Effect of calcium in field-spent GACs on pore development during regeneration. Journal - American Water Works Association, 85(3), 76-89.

DOI：10.1002/j.1551-8833.1993.tb05959.x.

[27] Kolyvakis, P. (2022). Adsorbents for the removal of organic and inorganic contaminants from water [PhD thesis], University of Edinburgh. url:http://dx.doi.org/10.7488/era/2059

[28] Bakhiia, T., Sereda, O., Троценко, O. (2024). Carbon materials for effective purification of aqueous solutions from tributyl phosphate. Physical Chemistry Chemical Physics, 26(40), 25977-25985. DOI: 10.1039/d4cp02731k.

## FIGURE CAPTIONS

Figure 1. TBP concentration calibration curve diluted with distilled water

Figure 2. Variations in the adsorption amounts and rates of several sorbents with SLRs

Figure 3. Effect of stirring time on TBP adsorption

## TABLE CAPTIONS

Table 1. Physical Characteristics of three samples

Table 2. Economic efficiency of commercial sorbents