Research Centre for Biochemical, Environmental and Chemical Engineering

School of Chemical Engineering and Material Sciences

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Ph.D. THESES

REMOVAL OF PHARMACEUTICAL RESIDUE FROM WATER AND REAL WASTEWATER USING ACTIVATED CARBON DERIVED FROM AGRO-INDUSTRIAL WASTES

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1. INTRODUCTION

The provision of safe and uncontaminated water has become an increasingly complex global challenge, driven by factors such as population growth, urbanization, industrial expansion, agricultural activities, and environmental changes. The escalation of water pollution, exacerbated by the presence of hazardous substances including micro-contaminants, endocrine-disrupting compounds, and pesticides poses significant threats to both human health and ecological stability. To address water pollution, various treatment technologies have been developed. Adsorption using activated carbon (AC) is a well-established and cost-effective method due to its high surface area and diverse functional groups, which enable the selective removal of toxic pollutants. However, the high production costs and regeneration challenges limit its widespread industrial adoption. Utilizing agro-industrial wastes as a precursor for AC synthesis presents a sustainable solution to these challenges.

This thesis is dedicated to developing sustainable, cost-effective, and environmentally friendly adsorbents derived from agro-industrial wastes for the removal of pharmaceutical compounds from Milli-Q water, wastewater, and lake water. Additionally, it evaluates the recyclability performance of the developed adsorbents and compares their costs with commercial AC prices.

2. METHODS

This work consists of three different methods used to convert agro-industrial wastes (olive stone waste (OSW), banana peel

(BP), and pinewood (PW)) into activated carbons using KOH, H_3PO_4, NH_4NO_3, and NaOH.

1-A biosorbent derived from OSW was utilized for diclofenac and ciprofloxacin removal from water (Figure 1) after converting it to activated carbon. The OSW underwent a multi-step preparation process, including thorough cleaning, sun-drying, and oven-drying at 105 °C. It was then pulverized to a particle size of 0.7–1.0 mm and washed again. Carbonization was performed in a nitrogen-purged stainless-steel reactor at 450 °C. The resulting material was impregnated with KOH at different weight ratios (1:1, 1:2, 1:3), followed by activation at 550–750 °C. The final OSACs were washed, neutralized, dried, and stored for adsorption experiments.

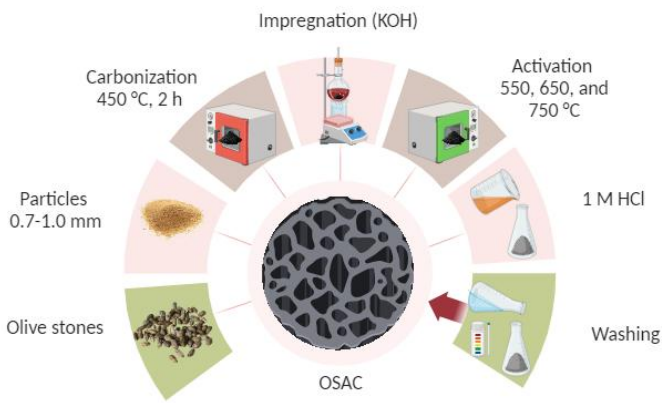

Figure 1 Olive stones activated carbon (OSAC) preparation.

2-Banana peels (BP) were converted into activated carbon (BPAC) for amoxicillin and carbamazepine removal (Figure 2) from different wasters. Initially, BP was cut, washed, and oven-dried at 100°C for 24 hours before being ground and sieved to particles <0.150 mm. The dried BP was impregnated with phosphoric acid (H_3PO_4) and heated at 80°C for 4 hours, followed by oven-drying at 110°C. Carbonization was performed at 350°C, 450°C, and 550°C in a stainless-steel reactor. The resulting BPAC was washed to neutral pH, oven-dried at 105°C, and stored for further research.

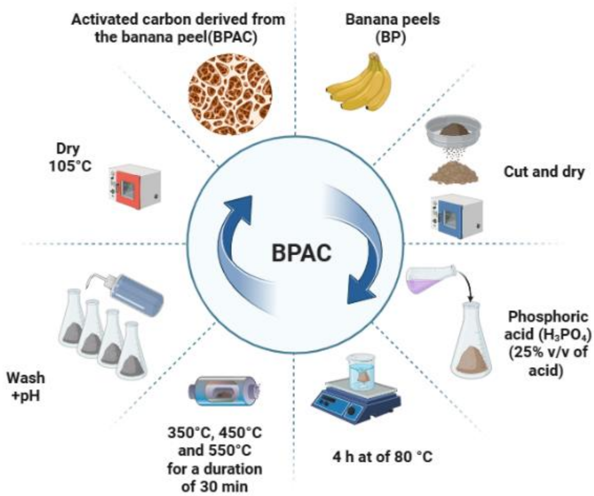

Figure 2 Banana peels activated carbon (BPAC) preparation.

3-Pinewood (PW) was processed into activated carbon (FPWAC) through a two-stage activation process (Figure 3) to remove both diclofenac and ciprofloxacin from different wasters. Initially, PW pieces were washed, dried at 105°C, and impregnated with ammonium nitrate (NH_4NO_3) at varying ratios (1-4 wt.%), followed by pyrolysis at 300–600°C for 1.5–3 hours under nitrogen flow. Adsorption tests determined the optimal NH_4NO_3/PW ratio, after which the selected sample underwent NaOH activation (3:1 ratio) with stirring, drying, and further heating at 500°C for 2 hours. The resulting FPWAC was washed, filtered, dried, and stored.

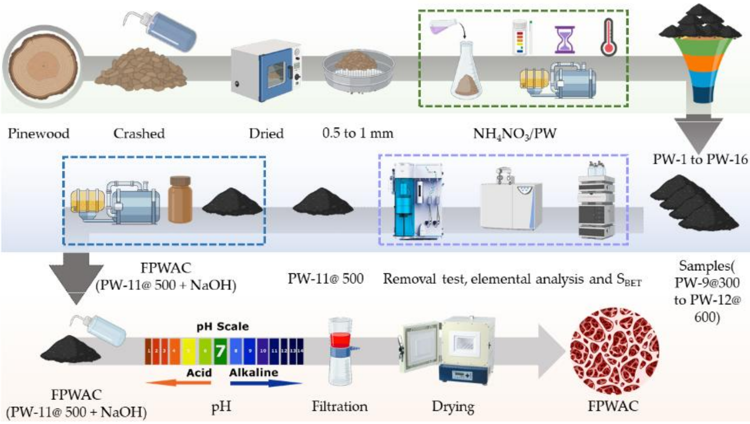

Figure 3 Two stages of FPWAC activation

Characterization methods

1. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDS): SEM was used to examine surface morphology, while EDS provided elemental mapping at an accelerating voltage of 3–5 kV.
2. Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectra evaluated surface functional groups before and after adsorption, with measurements taken in the range of 400–4000 cm^{-1}.
3. Point of Zero Charge (pH_{pzc}): The pH at which the adsorbent surface charge is neutral was determined by measuring pH changes in NaCl solutions.
4. Boehm Titration: This method quantified functional groups in raw and activated carbons by titration with various reagents.
5. X-ray Diffraction (XRD): XRD assessed the crystallinity of samples.
6. Thermogravimetric Analysis (TGA): TGA analyzed thermal stability, with heating from 50°C to 700°C.
7. Proximate and Ultimate Analysis: These analyses followed ASTM standards to measure ash content, moisture, volatile matter, and elemental composition.

8. Specific Surface Area (S_{BET}): Surface area was measured using the BET method, employing nitrogen adsorption at 77 K after outgassing the samples.

Other experiments

The work also investigated the adsorption, desorption, and isotherms, kinetics of pharmaceutical pollutants removal using OSAC, BPAC, and FPWAC. The adsorption experiments were conducted under various conditions such as pH, dosage, temperature, and pollutant concentration, with High-Performance Liquid Chromatography used for analysis. Isotherm models, including Langmuir and Freundlich, were applied to understand adsorption behavior, with Langmuir assuming uniform adsorption sites and Freundlich describing non-ideal conditions. Kinetic studies were performed using pseudo-first-order and pseudo-second-order models to investigate the rate of adsorption, highlighting the significance of chemisorption in some cases. Additionally, desorption tests were performed to evaluate the reusability of the adsorbents, with solvents like ethanol, hydrochloric acid, and nitric acid used to recover pollutants from the adsorbents, assessing their effectiveness for multiple cycles of use.

3. THESES

The new scientific findings of this PhD dissertation were the development of sustainable, cost-effective, and environmentally friendly adsorbents from agro-industrial waste to remove a mixture of pharmaceutical compounds from water, wastewater, and lake water. The effectiveness of all activated carbons in removing diclofenac, ciprofloxacin, amoxicillin, and carbamazepine was further examined by testing their recyclability performance. The primary factors affecting their capacity to absorb contaminants were analyzed. Additionally, the production costs for all activated carbons were calculated. The new scientific findings in this thesis can be summarized as follows:

1. I have successfully converted olive stone waste (OSW) **into activated carbon** (OSAC) **using KOH to remove a mixture of diclofenac and ciprofloxacin from** MQ water, **lake water, and wastewater.** I synthesized OSAC at 750 °C using KOH (1:3), which exhibited a high surface area (946 m^2/g) compared to OSW (265 m^2/g). I found that diclofenac and ciprofloxacin were effectively removed from various water matrices within 75 minutes under optimal conditions (25 °C, pH 7, 50 mg/L initial concentration, and 1 g/L dosage). Additionally, I observed that the **adsorption process was endothermic**, maintaining stable efficiency across a pH range of 2–8, with only a slight decline at pH 9–11, while temperature increases beyond 30 °C had no significant impact. Through Boehm titration, I confirmed a 98% increase in basicity, which was supported by EDS mapping that also detected the presence of potassium. OSAC maintained consistent adsorption performance across seven cycles in MQ water, lake water, and wastewater. I concluded that the adsorption followed the Langmuir model ($R^2 = 0.971$ for diclofenac, 0.943 for ciprofloxacin), indicating monolayer adsorption, while the pseudo-first-order kinetic model demonstrated that the adsorption rate is primarily governed by the concentration gradient between the liquid and solid phases.

The results of this work were published in *Chemosphere Journal*: Al-Sareji, Osamah J., Ruqayah Ali Grmasha, Mónika Meiczinger, Raed A. Al-Juboori, Viola Somogyi, Csilla Stenger-Kovács, and Khalid S. Hashim. "A sustainable and highly efficient fossil-free carbon from olive stones for emerging contaminant removal from different water matrices." Chemosphere 351 (2024): 141189. (D1, IF = 8.8)

2- I have effectively transformed banana peel waste (BP) **into activated carbon** (BPAC) **using H_3PO_4 to remove a mixture of amoxicillin and carbamazepine from** MQ water**, lake water, and wastewater.** I found that the developed activated carbon showed a significant increase in surface area, from 0.650 m^2/g (BP) to 912 m^2/g (BPAC) after the activation process. I determined that the optimal conditions for adsorption were 25 °C, a dosage of 1.2 g/L, a saturation time of 120 minutes, a pollutant concentration of 25 mg/L, and pH 5, although pH sensitivity could limit its practical application. Additionally, I successfully removed amoxicillin and carbamazepine using BPAC over seven cycles, achieving over 90% removal efficiency in MQ water. However, efficiency declined by 6% in lake water and 9% in wastewater due to matrix effects. Post-adsorption SEM analysis indicated partial pore filling, while Boehm titration revealed a 2.5-fold increase in total acidic groups and a 1.36-fold increase in basicity. Proximate and ultimate analyses showed an increase in fixed carbon content from 0.67% to 74% and in carbon content from 42% to 74%, along with reductions in hydrogen and oxygen content, confirming effective carbonization. Adsorption followed the Langmuir isotherm model, while kinetics were best described by the pseudo-second-order model, with pollutant removal driven by hydrophobic interactions, π–π interactions, and intra-particle diffusion.

The results of this work were published in *Materials Journal*: Al-sareji, Osamah J., Ruqayah Ali Grmasha, Mónika Meiczinger, Raed A. Al-Juboori, Viola Somogyi, and Khalid S. Hashim. "A Sustainable Banana Peel Activated Carbon for Removing Pharmaceutical Pollutants from Different Waters: Production, Characterization, and Application." Materials 17, no. 5 (2024): 1032. (Q2, IF=3.1)

3- I developed a novel activated carbon from pinewood waste (FPWAC) **through a two-stage chemical activation process** using NH_4NO_3 and NaOH **to remove a mixture of diclofenac and ciprofloxacin from MQ water and wastewater.** I found that the FPWAC had a BET surface area of 913 m^2/g. SEM-EDS analysis revealed well-defined honeycomb channels that enhanced pollutant accessibility. The surface morphology after the adsorption process became amorphous with irregular holes, confirming successful adsorption. I determined that the optimal removal conditions were at pH 6, with a 120-minute saturation time, using an FPWAC dosage of 1 g/L, a pollutant concentration of 25 mg/L, and a temperature of 25°C. EDS analysis showed initial carbon and oxygen contents of 78% and 10%, respectively, with post-adsorption changes indicating a 15% decrease in carbon and a 6% increase in oxygen, confirming pharmaceutical molecule attachment. FTIR analysis verified functional group interactions, particularly hydrogen bonding, as evidenced by the diminished hydroxyl band at 3412 cm^{-1}.I successfully tested FPWAC's recyclability, maintaining over 95% removal efficiency for both pollutants in water matrices and 90% in wastewater matrices across six cycles, with ethanol proving to be the most effective regeneration solvent. Adsorption followed multilayer mechanisms, including hydrophobic and π–π interactions and intra-particle diffusion.

The results of this work were published in *Chemosphere Journal*: Al-Sareji, Osamah J., Ruqayah Ali Grmasha, Mónika Meiczinger, Raed A. Al-Juboori, Miklós Jakab, Adrienn Boros, Hasan Sh Majdi, Norbert Miskolczi, and Khalid S. Hashim. "A novel two-stage chemical activation of pinewood waste for removing organic micropollutants from water and wastewater." Chemosphere 363 (2024): 142974. (D1, IF=8.1)

4- I have successfully demonstrated that the produced activated carbons (ACs) are much cheaper than the commercial ones. Therefore, I have proven the economic feasibility of the developed ACs, in addition to their environmental importance. I assessed the commercial viability of large-scale activated carbon production, estimating costs for pilot-scale production using BPAC, OSAC, and FPWAC. The cost evaluation was based on fixed capital investment, total annual operating costs, and vendor quotes for equipment. The estimated capital costs for AC production were $2.1 million for BPAC, $2.3 million for OSAC, and $2.6 million for FPWAC, with annual outputs of 900,000 kg, calculated from a yield of 3,000 kg/day over 300 working days. Production costs were $4.27 per kg for BPAC, $4.53 per kg for FPWAC, and $3.77 per kg for OSAC, with OSAC being the most cost-effective due to its lower chemical input requirements. Commercial AC averages $135 per kg, making the developed ACs significantly more affordable, being 10 to 36 times cheaper. I conclude that the process flow diagram for the chemical activation production of OSAC is the best option among the others (Figure 4). This cost advantage, coupled with superior quality and effectiveness in adsorbing pharmaceutical compounds, suggests that biomass-derived ACs could disrupt the commercial AC market if scaled up, provided they meet broader contaminant efficacy and industry standards.

This point was formulated based on the published literature [1-4].

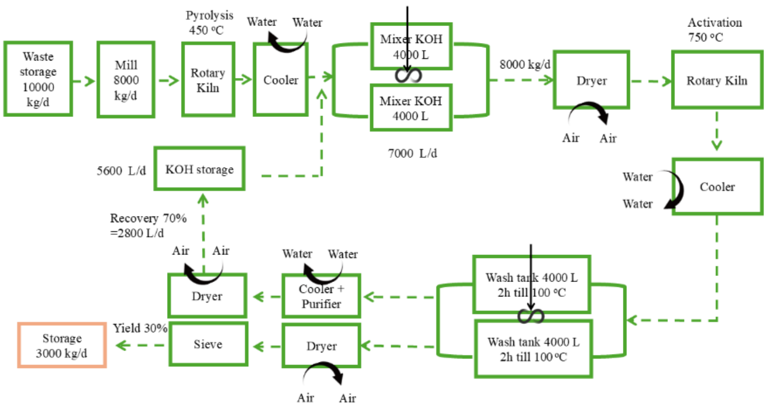

Figure 4 Process flow diagram for the chemical activation production of OSAC

PUBLICATION LIST

Published articles related to thesis research.

1- **Al-sareji, Osamah J.,** Ruqayah Ali Grmasha, Mónika Meiczinger, Raed A. Al-Juboori, Miklós Jakab, Adrienn Boros, Hasan Sh Majdi, Norbert Miskolczi, and Khalid S. Hashim. "A novel two stages chemical activation of pinewood waste for removing organic micropollutants from water and wastewater." Chemosphere 363 (2024): 142974. **D1, IF=8.1**

2- **Al-sareji, Osamah J.,** Ruqayah Ali Grmasha, Mónika Meiczinger, Raed A. Al-Juboori, Viola Somogyi, Csilla Stenger-Kovács, and Khalid S. Hashim. "A sustainable and highly efficient fossil-free carbon from olive stones for emerging contaminants removal from different water matrices." Chemosphere 351 (2024): 141189**. D1, IF=8.8**

3- **Al-sareji, Osamah J.,** Ruqayah Ali Grmasha, Mónika Meiczinger, Raed A. Al-Juboori, Viola Somogyi, and Khalid S. Hashim. "A Sustainable Banana Peel Activated Carbon for Removing Pharmaceutical Pollutants from Different Waters: Production, Characterization, and Application." Materials 17, no. 5 (2024): 1032. **Q2, IF=3.1**

Conference oral presentation related to thesis research

1-Osamah J. AL-SAREJI, Mónika MEICZINGER, Ruqayah Ali GRMASHA, Viola SOMOGYI, UTILIZING AGRICULTURAL WASTE FOR EFFICIENT REMOVAL OF ORGANIC MICRO-POLLUTANTS FROM WATER AND WASTEWATER, VIIIth Symposium-2024 International Annual Symposium, on “Environmental Health and Biosecurity: Sciences, Engineering and Application” May

09 - 10, 2024, Budapest – Hungary

2-The application of different wastes to remove organic micropollutants. Osamah J. AL-Sareji, Mónika Meiczinger, Viola Somogyi, Ruqayah Ali Grmasha, Raed A. Al-Juboori. 15th ICEEE-2024 Online International Annual Conference November 21 - 22, 2024 Obuda University, Budapest – Hungary Theme: “Global Environmental Development & Sustainability: Research, Engineering & Management”.

Publication used to support thesis point number 4

[1]C. Ng, W. E. Marshall, R. M. Rao, R. R. Bansode, and J. N. Losso, “Activated carbon from pecan shell: process description and economic analysis,” Ind. Crops Prod., vol. 17, no. 3, pp. 209–217, May 2003.
[2]J. Y. Lai and L. H. Ngu, “The production cost analysis of oil palm waste activated carbon: a pilot-scale evaluation,” Greenh. Gases Sci. Technol., vol. 10, no. 5, pp. 999–1026, Oct. 2020.
[3]M. Nowrouzi, H. Younesi, and N. Bahramifar, “High efficient carbon dioxide capture onto as-synthesized activated carbon by chemical activation of Persian Ironwood biomass and the economic pre-feasibility study for scale-up,” J. Clean. Prod., vol. 168, pp. 499–509, Dec. 2017.
[4]I. M. Lima, A. McAloon, and A. A. Boateng, “Activated carbon from broiler litter: Process description and cost of production,” Biomass Bioenergy, vol. 32, no. 6, pp. 568–572, Jun. 2008.

SCIENTOMETRIC DATA

Number of publications which are base of the PhD thesis: **3**
Impact factors are base of the PhD thesis: **20**

Total accumulative impact factor: **132**
H-index (Google scholar): **13**

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