HUNGARIAN JOURNAL OF
INDUSTRY AND CHEMISTRY
Vol. 53(2) pp. 55–59 (2025)
hjic.mk.uni-pannon.hu
DOI: 10.33927/hjic-2025-18

VALORIZATION OF BIOMASS-DERIVED LOW-COST ADSORBENTS FOR SUSTAINABLE PESTICIDE REMEDIATION FROM AQUEOUS SOLUTIONS: A COMPARATIVE STUDY

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Escalating pesticide usage over recent decades has severely compromised global water resources, necessitating cost-effective remediation. Adsorption employing affordable sorbents has emerged as a promising solution. This research evaluates two low-cost adsorbents, derived from wheat straw and ground branches, to remove the pesticides atrazine, imidacloprid, metolachlor and tebuconazole from aqueous solutions. Surface modification with NaOH and citric acid enhances the specific surface area and functionality of adsorbents. A batch adsorption experiment was quantified using a UPLC-MS/MS measurement method. Citric acid-modified wheat straw demonstrated superior removal efficiencies for atrazine (76.03%), imidacloprid (59.32%) and metolachlor (70.34%) compared to the other sorbents investigated due to enhanced functional groups on its surface (–COOH, –OH). However, untreated wheat straw and ground branches exhibited suboptimal pesticide removal, with a singular exception for ground branches, which showed a notable 75.08% removal efficiency for tebuconazole. Generally, these economical adsorbents are suitable for the remediation of low-concentration pesticides from aqueous solutions.

Keywords: low-cost adsorbent, pesticides, surface modification, wheat straw, ground branches

1. Introduction

The exponentially growing global population necessitates a substantial increase in food and fiber production, leading to widespread pesticide use in intensive agricultural systems. This practice is crucial for controlling pests, diseases and weeds, thereby boosting the yield per hectare as well as ensuring food security for a population projected to reach nearly 11 billion by 2100 [1]. The use of pesticides significantly improves agricultural output by mitigating pest damage, which accounts for an approximate 45% annual loss in agricultural production, and preventing numerous diseases [2],[3]. The agricultural advantages of pesticides, particularly their role in enhancing crop yields, have led to their application worldwide. Consequently, global pesticide use has grown by over 1.5 times over the past three decades [4].

Pesticides are chemical compounds utilized in the agricultural sector to kill/repel/control pests, including fungi, rodents, insects and weeds. Pesticides generally encompass insecticides, herbicides, fungicides, rodenticides and nematicides [5]. Furthermore, pesticides are broadly categorized into several classes - including organophosphates, carbamates, pyrethroids, organochlorines and neonicotinoids - with insecticides being a major group. Globally, over 3.5 million tons of pesticides are applied annually, 47.5, 29.5, 17.5 and 5.5% of which are herbicides, insecticides, fungicides and other types of chemicals, respectively [1]. In addition, the major classes of pesticides include phosphonates, chlorophenoxy herbicides and dipyridyl herbicides, alongside fungicides such as thiocarbamates, triazoles and strobilurins. Organophosphates, which are derivatives of phosphoric or phosphoramidic acid, are now the most prevalent in agriculture due to their higher efficacy and lower environmental persistence compared to organochlorines and carbamates, representing over 36% of the global market. The top ten pesticide-consuming nations are China, the USA, Argentina, Thailand, Brazil, Italy, France, Canada, Japan and India [6].

Despite their agricultural benefits, the widespread use of pesticides has become a significant environmental and human health problem. Pesticides infiltrate the environment through various pathways, predominantly via their agricultural application, where excess and residual amounts come into contact with soil in the form of rainfall, irrigation and diffusion. They contaminate groundwater through leaching and enter bodies of surface water via agricultural runoff, especially flood-like rain, as well as other pathways. These often mobile and

Received: 16 June 2025; Revised: 25 June 2025;
Accepted: 27 June 2025
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persistent pollutants accumulate in ecosystems, degrading food quality and fostering pest resistance. Ultimately, this accumulation in the environment facilitates their entry into the food chain, exposing humans to risks via their consumption and inhalation as well as dermal contact [2]. Water contamination by pesticides is particularly pressing, threatening aquatic life, compromising drinking water as well as leading to bioaccumulation and biomagnification [7]. The ubiquitous presence of these chemicals and their metabolites across various environmental compartments, originating from both point and nonpoint sources [8] poses a grave threat to both human well-being and the environment. Chronic exposure to pesticide residues has been linked to numerous serious health issues, including various cancers, reproductive impairments, neurological damage and endocrine disruption [8]. These critical issues highlight an urgent need for effective strategies to remove agrochemicals from water systems. Consequently, the development of low-cost, efficient and environmentally-friendly innovative methods is crucial to prevent pesticide pollution.

Various methods exist for pesticide remediation, including photocatalytic decomposition, chemical oxidation, advanced oxidation processes, membrane technologies, electrochemical decomposition, coagulation, flocculation, biological remediation and hybrid approaches [4],[9]. However, many of these techniques are often expensive, complex and produce a substantial amount of sludge. Adsorption stands out as a preferred alternative due to its simplicity, economic viability, ease of operation, versatility and high removal efficiency [10]. Furthermore, low-cost adsorbents derived from agricultural byproducts such as barley straw, rice straw, wheat straw, sugarcane bagasse, sawdust, banana peel and orange peel offer numerous advantages, including being environmentally sound, easy to use, abundant and sustainable [11].

The utilization of agricultural wastes as adsorbents for pesticide removal presents a viable and advantageous alternative as it adds value to these waste materials while leveraging an abundant, low-cost raw resource. These waste materials are primarily composed of cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, water and hydrocarbons, containing various functional groups that offer potential sorption capacity for a diverse range of pollutants [12]. Agricultural byproducts can be used in their natural form, typically involving washing, grinding and sieving to achieve a desired particle size for adsorption tests. Alternatively, they can be used in a modified form, undergoing pre-treatment through established modification techniques to enhance their performance.

This study investigates the removal of the pesticides atrazine, imidacloprid, metolachlor and tebuconazole from water using low-cost adsorbents derived from agricultural waste, specifically wheat straw and ground branches. To address the inherent variability of agricultural waste as a raw material for adsorption, chemical modifications were employed to create a functionalized adsorption surface and increase pore volume, which in turn improves their removal capacities. The research specifically assessed the effectiveness of these adsorbents having been modified by NaOH and citric acid in order to compare their pesticide removal efficiencies against those of native (unmodified) adsorbents, namely wheat straw and ground branches.

2. Experimental

2.1. Materials

Unmodified wheat straw and ground branches are agricultural byproducts that serve as adsorbents. Furthermore, the raw wheat straw and ground branches were modified with NaOH and citric acid to enhance their surface functionalities [13] as well as improve pesticide removal as shown in *Figure 1*. These unmodified and modified adsorbents were obtained from the Geographical Institute, HUN-REN Research Centre for Astronomy and Earth Sciences. Pesticide standards (atrazine, imidacloprid, tebuconazole and metolachlor), citric acid and NaOH were obtained from Sigma-Aldrich. Ultrapure water was used to wash the adsorbents and for other adsorption process activities.

2.2. Methods

Initially, the adsorbents were washed with ultrapure water. Subsequently, batch adsorption experiments were conducted using an adsorbent dosage of 0.1 g, an initial concentration (*Ci*) of 10 μg/L, a pH of 7.5 and a contact time of 24 hours at 20 °C in 3 mL of solvent. The adsorbents were separated from the treated water by centrifugation (3000 rpm for 20 mins, Ohaus FC5816R) and syringe filtration (GF/PET, 0.45 μm,

Figure 1: Samples of straw washed with ultrapure water (A), modified with NaOH (B), modified with citric acid (C), ground branches (D), modified with NaOH (E) and modified with citric acid (F)

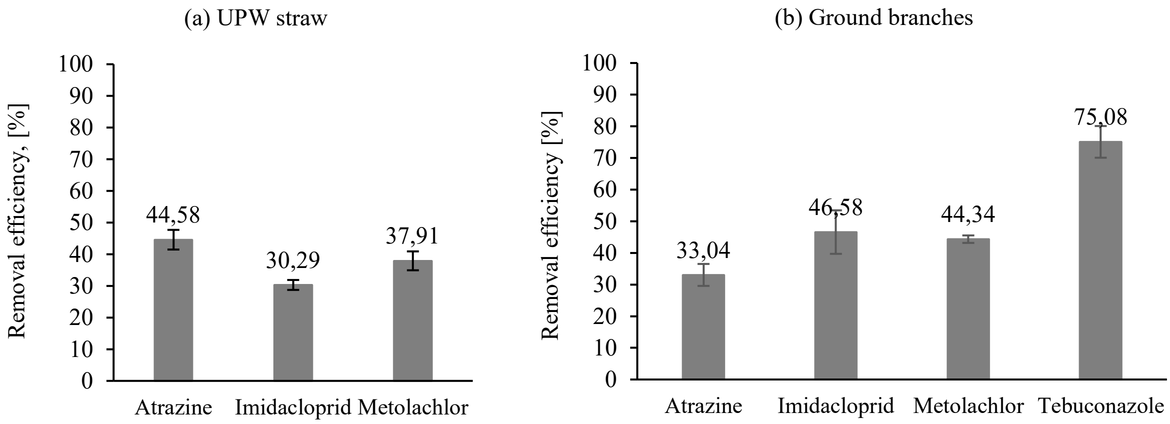

Figure 2: Removal efficiency of (a) wheat straw washed with ultrapure water (UPW) and (b) ground branches

CHROMAFIL). Pesticide quantification was performed using an ACQUITY UPLC H-Class System coupled with an Xevo TQ-S Micro mass spectrometer (Waters). Target analytes were separated in an XBridge Premier BEH C18 Column (2.5 µm, 2.1 i.d., 100 mm, Waters) at 60 °C. Multiple Reaction Monitoring (MRM) transitions for quantification were as follows: 216→174 (atrazine), 256→209 (imidacloprid), 284→252 (metolachlor) and 308→70 (tebuconazole). The adsorption removal efficiency was calculated using the following equation:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1),$$

where C_0 denotes the initial concentration of the pollutant in the solution (before adsorption) in mg/L and C_e represents the equilibrium concentration of the pollutant in the solution (after adsorption had reached its equilibrium) in mg/L.

3. Results and discussion

3.1. Removal efficiency of unmodified adsorbents

The removal efficiencies of unmodified native adsorbents, namely wheat straw and ground branches, to remove the pesticides atrazine, imidacloprid, metolachlor and tebuconazole from aqueous solutions are presented in *Figure 2*.

The results revealed that unmodified wheat straw and ground branches exhibit suboptimal pesticide removal efficiencies with the notable exception of tebuconazole. Specifically, the unmodified adsorbent ground branches achieved a 75.08% removal efficiency for tebuconazole, potentially attributable to their elevated lignin content, which appears to exhibit a selective affinity for this particular pesticide.

3.2. Removal efficiency of modified adsorbents

Compared to their unmodified counterparts washed with ultrapure water (UPW) and modified by NaOH, wheat straw as an adsorbent modified by citric acid exhibited significantly enhanced pesticide removal capacities, as is shown in *Figure 3*. Specifically, citric acid-modified wheat straw achieved superior removal efficiencies, reaching 76.03, 59.32 and 70.34% for atrazine, imidacloprid and metolachlor, respectively. This enhanced performance of citric acid-modified wheat straw is attributed to the introduction of carboxyl (–COOH) and hydroxyl (–OH) functional groups onto the adsorbent surface, thereby creating additional adsorption sites and augmenting the removal of specific target pesticide compounds [14]. Conversely, NaOH-modified wheat straw exhibited comparatively lower removal efficiencies, specifically for atrazine, imidacloprid and metolachlor that achieved 53.02, 25.45 and 34.16%, respectively. This is likely because a high activation temperature is required to break hydrogen bonds between cellulose fibers of wheat straw, thereby increasing the surface area of the adsorbent, in conjunction with its modification by NaOH to enhance its adsorption efficiency.

4. Conclusions

The widespread use of pesticides poses a significant threat to both the environment and human health. While various remediation techniques exist, many are hindered by their high costs and complexity. In contrast, low-cost adsorbents derived from abundant and renewable agricultural byproducts offer a promising alternative. The properties and applications of these materials vary based on their source, treatment and functionalization methods. Specifically, both unmodified and chemically modified (with citric acid and NaOH) adsorbents of wheat straw and ground branches were employed to remove pesticides from aqueous solutions in this study. Citric acid-modified wheat straw demonstrated paramount removal efficiencies for atrazine, imidacloprid and metolachlor of 76.03, 59.32 and 70.34%, respectively, compared to others attributed to enhanced surface functionalities (–COOH, –OH). However, untreated and NaOH-modified wheat straw and ground branches exhibited low pesticide removal efficiencies with the exception of untreated ground branches, which resulted in a notable 75.08% removal efficiency for tebuconazole. Generally, although these economical adsorbents demonstrate high removal efficiencies for low concentrations of pesticides from aqueous solutions, further studies are needed to investigate the disposal and regeneration mechanisms of these adsorbents.

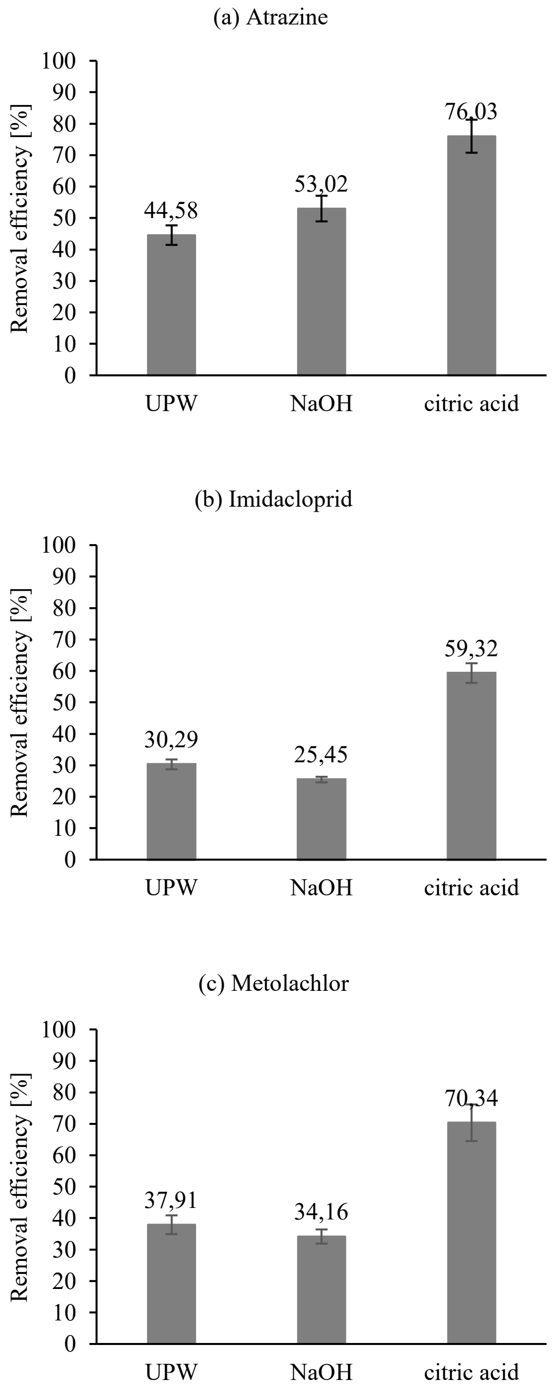

Figure 3: The removal efficiencies of chemically modified adsorbents containing the pesticides (a) atrazine, (b) imidacloprid and (c) metolachlor

Acknowledgements

This research was supported by the National Research, Development and Innovation Office (NKFIH), Hungary within the framework of project identification number 2020-1.1.2-PIACI-KFI-2021-00309.

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