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TULTECH

Investigation of Phenol Adsorption Process Utilizing Wood Sawdust

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Abstract

This study serves as an attempt to utilize wood waste in Albania for environmental protection purposes. The use of wood sawdust is been explored as an alternative for treating water with phenol content. The sawdust used is obtained from the local furniture manufacturing industry. Based on the prevalence of tree species in Albania, five types of sawdust are selected: beech, pine, oak, fir, and maple. Meanwhile, the used water sample was a synthetic phenolic solution. The periodic adsorption process is studied to evaluate the kinetics of adsorption and the adsorption capacity of the untreated samples of interest. The experimental results indicate that the adsorption occurs according to the pseudo-first-order model, suggesting that the process relies on both the solution concentration and the availability of adsorption sites. The optimal time to reach adsorption equilibrium is 3 hours. The adsorption isotherm that best describes the process is the Freundlich isotherm, with constants K_f and n 0.27 and 2.85 respectively, indicating for a multilayer adsorption on heterogeneous sites. The type of sawdust turned out to be crucial in the amount of phenol removal. Among the sawdust types studied, oak sawdust exhibits the highest phenol adsorption capacity, followed by fir, maple, pine, and beech.

Keywords: *Phenol, synthetic wastewaters, adsorption, sawdust*

INTRODUCTION

Due to industrial advancement, Albania encounters significant challenges concerning the pollution of natural water sources, attributed to phenolic compounds among others [1]. Phenol, an organic pollutant originating from various industrial processes such as petroleum refining, petrochemicals, pharmaceuticals, and manufacturing, poses a significant threat to water quality due to its toxicity and recalcitrance to conventional treatment methods.

The discharge of phenol-containing effluents into the environment, especially into rivers and streams, leads to severe ecological disturbances and poses health hazards to aquatic life and human beings. This situation necessitates the urgent need for effective strategies to mitigate the impact of phenol on the environment and human health [2].

The treatment of phenol-contaminated wastewaters has prompted research into various methodologies like photo-catalysis [3], extraction [4], distillation [5], chemical oxidation, electrochemical oxidation [6], membrane filtration [7], biological treatment etc. [8]. Among these, adsorption has gained prominence as an efficient, cost-effective, and environmentally friendly technique [9].

Phenol adsorption typically occurs through several mechanisms like physical adsorption – which involves non-specific interactions such as Van der Waals forces, electrostatic forces, and London dispersion forces between the phenol molecules and the surface of the adsorbent. It does not involve any chemical bonding but relies on the physical attraction between the adsorbate (phenol) and the adsorbent surface [10]; chemical adsorption (chemisorption) - which involves stronger interactions and chemical bonding between the phenol molecules and the surface functional groups of the adsorbent (such as C=O and N–H2). This bonding might include covalent bonds or hydrogen bonding, leading to a more stable and irreversible attachment of phenol to the adsorbent surface; ion exchange - Some adsorbents possess ion

exchange sites on their surface. Phenol molecules, being weakly acidic, can interact with these exchange sites, replacing other ions that were previously adsorbed onto the surface [11]; micropore diffusion - Phenol molecules can diffuse into the micropores or internal structures of the adsorbent, allowing further interaction between the adsorbate and the adsorbent's interior surface area. The specific mechanisms involved in phenol adsorption can vary based on the characteristics of the adsorbent material, the properties of the phenol molecules, and the environmental conditions during the adsorption process [12].

Choosing the most suitable adsorbent for industrial purposes necessitates considering various aspects: adsorption capability, cost-effectiveness, regeneration potential, reusability, and environmentally safe disposal of used adsorbent [13]. Within this framework, employing waste (wood sawdust) from the wood processing industry for wastewater treatment emerges as an intriguing alternative.

Albania, with its diverse timber resources and wood industry, offers a unique opportunity to investigate the adsorption capabilities of locally sourced sawdust. Understanding the adsorption behaviour of phenol onto wood sawdust can provide valuable insights into utilizing this readily available and renewable material for wastewater treatment processes.

This article presents a comprehensive investigation of the phenol adsorption process employing oak, pine, fir, maple, and beech sawdust varieties commonly found in the Albanian market. The research delves into the kinetics, isotherms, and comparative adsorption capacities of these sawdust types, shedding light on their potential as eco-friendly adsorbents for phenol removal from contaminated waters.

MATERIALS AND METHODS

Sawdust sampling and pre-treatment: The research utilizes sawdust sourced from the Albanian furniture industry. Out of the diverse timber varieties in Albania, five specific types of sawdust are selected: oak, pine, maple, fir, and beech. Preceding its use, the sawdust underwent a series of boiling water washing to eliminate colorants and easily soluble compounds. Subsequently, it is dried at 90°C until constant weight. Only the fraction with particle sizes smaller than 1mm is employed for the study.

Batch experiments for the study of phenol adsorption on sawdust: All sawdust-synthetic wastewater treatment experiments are realized after the same protocol. In a sequence of chemical flasks, 100ml of phenol solutions (synthetic wastewater), of certain concentrations, are treated with 1g sawdust, under mechanical stirring. After a certain contact time, they are subjected to filtration and the filtrate is analysed for phenol content.

The determination of phenol concentration in aqueous solutions is performed using the spectrophotometric method (APHA, 510C), involving the treatment of 100ml sample with 1 ml of 4AAP (4-aminoantipyrine) in the presence of 2.5ml NH_4OH, 2ml buffer, 1ml K_3FeCN_6 and the measurement of the absorbance at 500nm wavelength (using UV1200 spectrophotometer) after 25 minutes of settling.

Data analysis for adsorption kinetic model evaluation: Two adsorption kinetic models have been considered: pseudo first-order model and pseudo second-order model. Nonlinear regression is applied for both cases and the analyses have been made based on the regression coefficient (R^2).

The pseudo first-order model:

$$q_t = q_e(1 - e^{K_1 t}) \quad (1)$$

The pseudo second-order model:

$$q_t = \frac{q_e^2 * K_2 * t}{1 + K_2 * q_e * t} \quad (2)$$

Where: t is the time of adsorption (hour); q_t is the amount of phenol adsorbed at time t (mg/g sawdust); qe is the amount of phenol adsorbed until equilibrium time is reached (mg/g sawdust); K_1 is the pseudo first-order model constant (min^{-1}); K_2 is the pseudo second-order model constant (min^{-1}).

Evaluation of q_t and q_e is done according to equations:

$$q_t = \frac{(C_0 - C)V}{M}; \; q_e = \frac{(C_0 - C_e)V}{M} \tag{3}$$

Two adsorption isotherms have been considered for this purpose: Langmuir isotherm and Freundlich isotherm; as two of the most used ones in the literature. Non-linear regression has been considered for Freundlich model and linear regression for the Langmuir one.

Linear Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{1}{a}C_e \tag{4}$$

Nonlinear Freundlich isotherm:

$$q_e = K_F C_e^{1/n} \tag{5}$$

Where: C_e is the concentration of phenol in solution at adsorption equilibrium time (mg/l); a and b are the Langmuir constants; K_f and n are the Freundlich constants.

EXPERIMENTAL RESULTS

Adsorption Kinetics Study

The aim of this set of experiments is to understand the rate and mechanism of the phenol adsorption process onto wood sawdust. For this purpose, a series of 100 ml synthetic phenol samples with an initial concentration of 100 ppm were treated with 1g of oak sawdust for contact times ranging from 1 to 24 hours. To comprehend the adsorption mechanism, two kinetic models have been considered: the pseudo first-order and pseudo second-order models. Nonlinear regression methodology is used. The experimental results are presented in Figure 1.

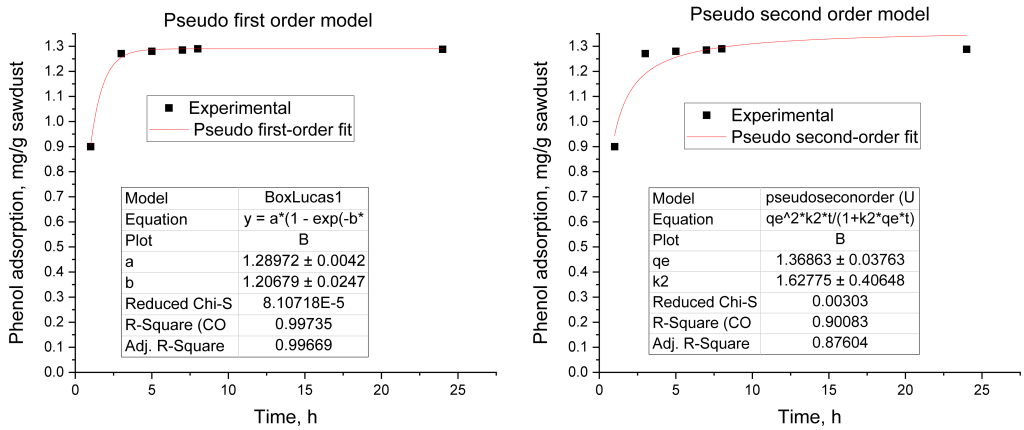

Figure 1. The kinetic models for the adsorption of phenol in oak sawdust.

It is observed that the adsorption of phenol in sawdust corresponds better to the pseudo first-order model, with a correlation coefficient, R^2, of 0.997, suggesting that the adsorption process is characterized by a rate that is proportional to the number of unoccupied sites on the adsorbent surface. Thus, the process depends on both the solution concentration and the number of available adsorption sites. This is common for systems operating at high initial

concentration values [14]. The adsorption rate is a time variable. It diminishes during time, ultimately approaching the equilibrium state. During the early time intervals, the amount of phenol adsorbed by the sawdust increases rapidly, reaching its maximum value of 1.288mg phenol/g sawdust after more than 3 hours. Following this duration, the adsorption capacity stabilizes, signifying complete occupation of all available adsorptive sites. Consequently, the sawdust requires a minimum of 3 hours to exhibit its maximum adsorption capacity (adsorption equilibrium time). All subsequent experiments are conducted under this specific contact time.

Adsorption Model Investigation

Sorption models play a crucial role in assessing the adsorption capacity of a specific adsorbent and the mathematical approach that represents the process. Therefore, the investigation focused on examining how the initial concentration of the phenol aqueous solution affects the adsorption capacity of sawdust. The experimental series involved treating 100ml of synthetic phenol solution, varying in initial concentrations from 10 to 200mg/l, with 1g of oak sawdust for a contact period of 3 hours. Subsequently, the solution underwent filtration, and the filtrate was subjected to phenol content analysis. The experimental outcomes displaying the relationship between the phenol adsorbed (measured in mg/g sawdust and %) and the initial concentration are illustrated in Figure 2 and 3.

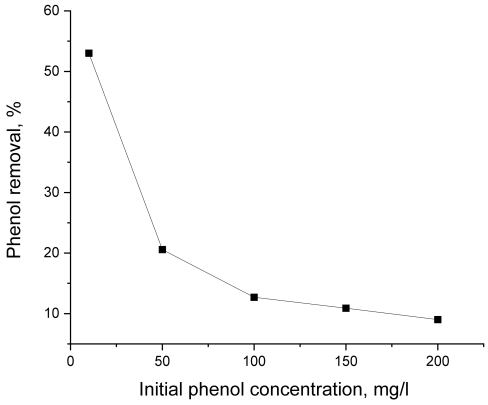

Figure 2. Experimental results of phenol adsorption efficiency vs initial concentration.

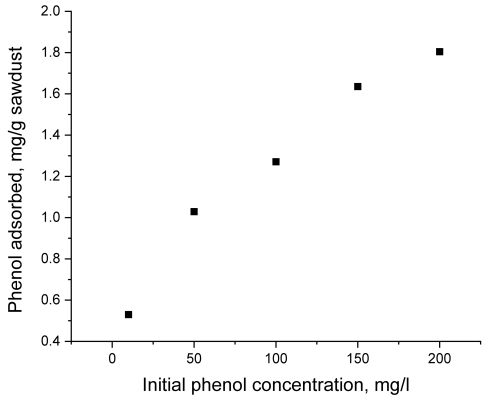

Figure 3. Experimental results of phenol adsorption capacity in mg/g oak sawdust vs initial concentration.

As can be observed, with an increase in the initial solution concentration, there is a noticeable reduction in the absorbed phenol quantity. This decrease suggests a substantial competition among phenol molecules in the solution to occupy active sites on the adsorbent surface. This competitive interaction limits the potential increase in efficiency.

To evaluate the adsorption isotherm, the dependence of the adsorbed phenol amount against the equilibrium concentration of the solution is graphed, Figure 4. Langmuir and Freundlich isotherms are taken into consideration, Figure 5 and 6. Nonlinear regression has been applied for the Freundlich model. While for the Langmuir model linear regression has been considered (only for visual purposes). Analysis are been made upon R^2 correlation coefficient. It is noticed that adsorption follows the Freundlich isotherm, with R^2 0.986, with K_f and n constants 0.27 and 2.85 respectively, suggesting for a multilayer adsorption on heterogeneous sites.

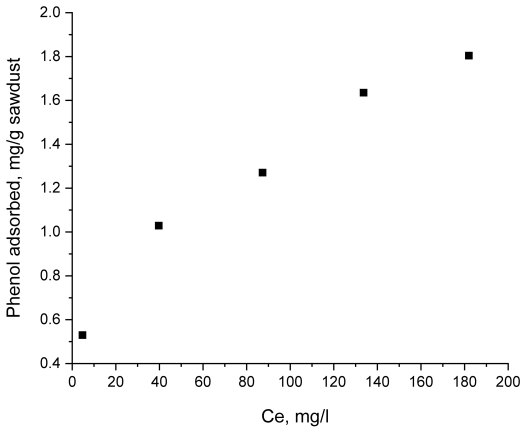

Figure 4. Experimental results of adsorption isotherm of phenol in sawdust.

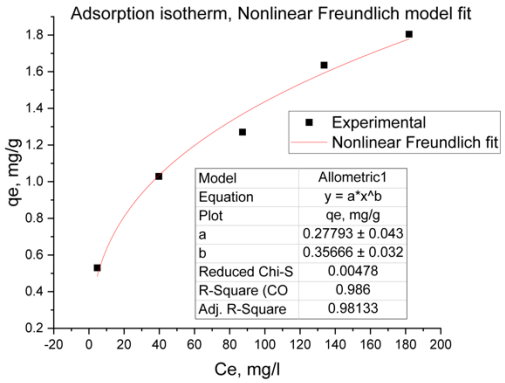

Figure 5. Non-linearized Freundlich isotherm for the adsorption of phenol on oak sawdust.

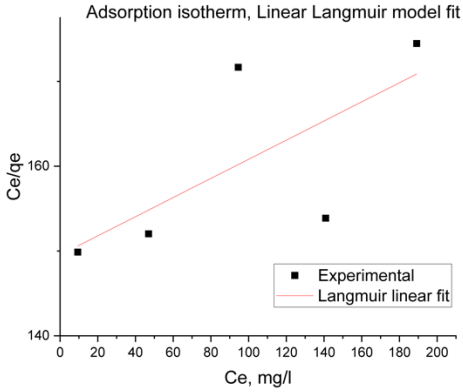

Figure 6. Linearized Langmuir isotherm for the adsorption of aqueous phenol on oak sawdust.

The Impact of Sawdust Varieties on Adsorption

The objective of these experiments is to assess and compare the adsorption efficiency of various types of sawdust for aqueous phenol. Five types of sawdust were examined: oak, fir, maple, pine, and beech. The experiments entailed treating 100ml of synthetic phenol solution, with an initial concentration of 100mg/l, using 1g of sawdust for a duration of 3 hours. The findings obtained from these experiments are showcased in Figure 7.

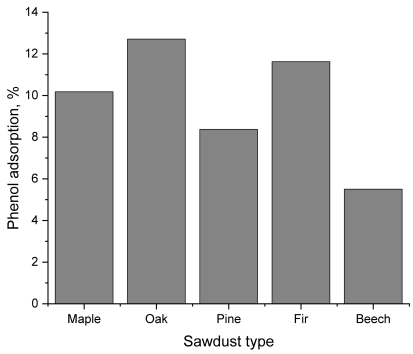

Figure 7. Phenol adsorption efficiency for various types of sawdust.

In general, while the assessed sawdust shows comparatively lower phenol adsorption capacity against other studied adsorbents like activated carbon or polymeric adsorbents, it retains a favourable standing in contrast to certain others, such as kaolinite or bentonite [15]. Relatively to each other, oak sawdust demonstrates the best adsorption capacity for phenol at 12.7%, followed by fir at 11.6%, maple at 10.18%, pine at 8.37%, and beech at 5.5%. Although this requires a deeper study, it is believed that the reason lies in the chemical composition of the adsorbent. The chemical components present in sawdust, such as lignin and cellulose can form hydrogen bonds or other interactions with phenol molecules, aiding in adsorption. Lignin is especially important in this direction as it is composed of various functional groups, including alcohol hydroxyl group, phenolic hydroxyl group, carbonyl group, carboxyl group, methoxyl, and sulfonic acid, which directly determine their chemical reactivity [16]. While the presence and hemicellulose can positively affect the porosity and surface area available for adsorption [17]. Extractives also could influence the interactions and affinity for phenol adsorption. These are compounds found in different amounts across wood species. Oak typically has a higher lignin content [18], which might contribute to its higher adsorption capabilities compared to fir, pine, maple and beech.

CONCLUSIONS

The primary objective of this series of experiments was to gain insights into the rate and mechanism of the phenol adsorption process onto wood sawdust. The utilization of oak sawdust in the experiments served to elucidate the adsorption mechanisms, considering the pseudo first-order and pseudo second-order kinetic models, observing a closer fit with the pseudo first-order model. This indicated that phenol adsorption correlates with unoccupied sites on the adsorbent surface, influenced by solution concentration and site availability.

Moreover, experiments revealed reduced phenol absorption with increasing initial solution concentrations, implying heightened competition among phenol molecules for adsorption sites. The adsorption isotherm analysis showed adherence to the Freundlich model, suggesting multilayer adsorption on heterogeneous sites.

Comparing different sawdust types, oak demonstrated the highest phenol adsorption capacity, followed by fir, maple, pine, and beech. This superiority might be attributed to varying chemical constituents in the sawdust, such as lignin, cellulose, hemicellulose, and extractives, influencing the adsorption process.

While oak's higher lignin content could contribute to its superior adsorption capabilities, further exploration into the chemical composition's role in phenol adsorption is warranted. These findings indicate the potential of utilizing oak sawdust, and possibly other wood types, as effective adsorbents for phenol removal in wastewater treatment.

CONFLICT OF INTERESTS

The authors would like to confirm that there is no conflict of interests associated with this publication and there is no financial fund for this work that can affect the research outcomes.

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