Removal of sodium salicylate from aqueous solution using spruce wood sawdust as an eco-friendly adsorbent

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Abstract: This study reports the application of Spruce wood sawdust as a low-cost and eco-friendly adsorbent for the removal of sodium salicylate from aqueous solutions. The effects of physicochemical parameters on the sodium salicylate adsorption process such as initial pH, temperature, solid/liquid ratio, initial concentration, contact time, and ionic strength were investigated. The optimum adsorption conditions were found as: equilibrium time = 3h, adsorbent dosage = 0.5 g/L, pH = 6.5, initial sodium salicylate concentration = 10 mg/L and temperature = 25°C. The kinetic study shows that the pseudo-second-order model is suitable to describe the adsorption process. The adsorption isotherm models (Langmuir, Freundlich, Temkin and generalized) were tested to understand the adsorption mechanism of sodium salicylate onto wood sawdust surface. The adsorption of sodium salicylate follows the Langmuir isotherm model. The maximum monolayer uptake capacity was found to be 99.01 mg/g. In addition, the temperature seems to have no noticeable effect on the adsorption of sodium salicylate. Finally, the thermodynamic parameters indicate that the adsorption is spontaneous (ΔG°<0) and exothermic (ΔH°=-5.081 kJ/mol) in nature. Overall, Spruce wood sawdust can be used as a cost-effective and eco-friendly adsorbent for wastewater treatment applications.

Keywords: Adsorption; Eco-friendly adsorbent; Wastewater; Spruce wood sawdust; Sodium salicylate.

1. Introduction

The pollution of the aquatic ecosystems is a major environmental problem and can cause severe damages to humans and biodiversity. It is well known that the industrial sectors are the major origin of water contamination. The toxicity and stability are the most common proprieties of the industrial contaminants (i.e. pharmaceuticals, heavy metals, dyes, pesticides, etc.). Recently, the pharmaceutical residues have attracted great attention as emerging pollutants in water pollution studies because of their detrimental effects at such low concentrations in aquatic environments. It is important to note that several pharmaceutical compounds like estrogens, antibiotics and anticancer have been detected in urban wastewaters. These pharmaceutical contaminants originated from human and/or veterinary medicine. The pharmaceutical industries are the first source of this pollution in the environment. The sodium salicylate is a drug derivative used as analgesic and antipyretic as well as for the treatment of the rheumatic effects. It was qualified as a typical contaminant in wastewaters and presented high toxicity and the ability to accumulate in the ecosystem. Therefore, it is highly recommended to treat industrial effluents before its discharge to the environment using eco-friendly wastewater treatment strategies.

Various wastewater decontamination technologies such as photocatalytic degradation, reduction, electrocoagulation, and adsorption. Among these techniques, the adsorption was considered as one of the most promising methods for the removal of pollutants from aqueous solutions because of its flexibility, low-cost, high efficiency and operational simplicity. In this context, the raw agricultural by-products have been widely studied as abundant, renewable, inexpensive, biodegradable and eco-friendly materials because of their adsorption ability for removal of organic and inorganic pollutants from contaminated effluents. Great interest has been paid for the application of these lingo-cellulosic biomaterials (including wood sawdust, leaves, seeds, shell, peels, husks and straws) as alternative economic adsorbents to replace the conventional activated carbons.
Wood sawdust by-products have been proposed as an excellent candidate for cleaning up the contaminated waters because of their molecular structure containing a large amount of surface functional groups (especially hydroxyl functions)\textsuperscript{21}. The main polysaccharides constituents of the wood sawdust are cellulose, hemicellulose and lignin\textsuperscript{19}. This structure chemistry makes it a potential adsorbent material with a stronger affinity for various kinds of pollutants.

To the best of our knowledge, no investigation on the removal of pharmaceutical contaminants (especially sodium salicylate as a model pollutant) from aqueous solution using Spruce wood sawdust has been published so far in the available literature. Therefore, the current research work was carried out as the first study with aims to present a detailed investigation on the adsorption of sodium salicylate onto Spruce wood sawdust. The effects of various operating parameters on the adsorption process such as pH, temperature, contact time, adsorbent dose, salt effect and initial concentration were systematically evaluated. The kinetic and isotherm models were employed to describe the mass transfer mechanism at the solid-solution interface during the adsorption phenomenon. Moreover, the thermodynamic parameters were calculated to investigate the thermodynamic behavior of the sodium salicylate adsorption process.

2. Experimental

2.1. Reagents

Sawdust prepared from Spruce wood was obtained from a local company. Then, the wood sawdust was washed several times with distilled water to remove the soluble organic matter and then, was dried in an oven at 105°C for 24 h. The dried sample was then powdered using an electric grinder (SM 100 Restsch, Germany). Sieving of wood sawdust was done using a vibrating screen. The particle sizes between 250 and 500 μm were recovered for further use in adsorption experiments. The adsorbate stock solution of 1000 mg/L was prepared by dissolving an appropriate amount of sodium salicylate (C\textsubscript{6}H\textsubscript{5}NaO\textsubscript{3}) in distilled water. The solutions used in adsorption tests were obtained by successive dilution to obtain the desired concentrations.

2.2. Adsorption experiments

The adsorption experiments were conducted in 150 mL Erlenmeyer flasks containing 50 mL of adsorbate solution with a constant agitation speed of 150 rpm. The adsorption tests of sodium salicylate on the wood sawdust were performed at different experimental conditions such as initial pH (2–12), solid/liquid contact time (0–300 min), adsorbent dosage (0.1–1.5 g/L), temperature (25–50°C) and initial concentration (10–200 mg/L). The initial solution pH was adjusted to the desired values by the addition of HCl (0.1 M) or NaOH (0.1 M) solutions. The samples analysis was carried out before and after adsorption using UV-visible spectrophotometer 2300UV at the maximum absorption wavelength of 295 nm. The following equations calculate adsorption efficiency and the adsorbed amount:

**Adsorption efficiency:**

\[
R(\%) = \left(\frac{C_0 - C_e}{C_0}\right)\times 100
\]  

(1)

**Adsorbed amount (mg/g):**

\[
Q_e = \left(\frac{C_0 - C_e}{m}\right)\times V
\]  

(2)

where \(C_0\) (mg/L) is the initial concentration of the solution, \(C_e\) (mg/L) is the equilibrium concentration, \(m\) (g) and \(V\) (L) is the mass of the adsorbent and volume of the solution, respectively.

3. Results and Discussion

3.1. Adsorption kinetic study

The adsorbate/adsorbent contact time is an important factor in the adsorption process; because it determines the equilibrium adsorption capacity and the optimum contact time. The results obtained from the adsorption experiments are presented in Figure 1.

![Figure 1](image-url)  

**Figure 1.** Effect of contact time on the adsorption of sodium salicylate onto wood sawdust. (Conditions: \(R = 0.5\) g/L, \(C_0 = 10\) mg/L, pH = 6.5 and \(T = 25^\circ\text{C}\))
The experimental data show that the adsorption of sodium salicylate on the wood sawdust increases rapidly at the beginning of the adsorption to an optimum contact time of 180 min. This adsorption behavior can be explained by the presence of a large number of vacant active sites on the wood sawdust surface at the beginning of adsorption process. After 180 min, there is a plateau corresponding to the equilibrium adsorption of sodium salicylate on the wood sawdust. Finally, a contact time of 180 min was selected for investigation of other operating parameters which affects the adsorption process.

The experimental data of the adsorption of sodium salicylate onto wood sawdust were analyzed by applying the linearized forms of the following kinetic models:

The pseudo-first-order model the equation gives 24

\[ \ln (Q_e - Q_t) = \ln Q_e - k_1 t \]  \hspace{1cm} (3)

The pseudo-second-order model 24 is expressed by the equation (4):

\[ \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \]  \hspace{1cm} (4)

The intraparticle diffusion model 25 is represented by the equation (5):

\[ Q_t = k_3 t^{1/2} + C \]  \hspace{1cm} (5)

where \( Q_t \) and \( Q_e \) are the adsorbed amounts (mg/g) at time \( t \) and equilibrium, respectively; and \( k_1 \) (1/min), \( k_2 \) (mg/g/min), and \( k_3 \) (mg/g/min\(1/2\)) are the rate constants of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, respectively.

![Figure 2. Linear plots of (a) pseudo-first-order, (b) pseudo-second-order and (c) intraparticle diffusion models for sodium salicylate adsorption onto wood sawdust](image)

The values of different kinetic parameters have been generated graphically from Figure 2 and are given in Table 1. The correlation coefficient \( R^2 \) value was higher for the pseudo-second-order kinetic model than that of the pseudo-first-order kinetic model. This suggests that the kinetic data were best fitted to the pseudo-second-order model. Moreover, the experimental and calculated \( Q_e \) values agree very well, which further indicates that the adsorption of sodium salicylate on the wood sawdust follows the pseudo-second-order model. This indicates that the pseudo-second-order kinetic model provides a better description of the adsorption of sodium salicylate on the wood sawdust.

According to the intraparticle diffusion model, the diffusion is the rate-limiting step in the adsorption process if the \( (Q_t \text{ vs. } t^{1/2}) \) plot passes through the origin. From Figure 2c, it was observed that the intraparticle diffusion plot did not pass through the origin, indicating that the intraparticle diffusion mechanism was not the sole rate-limiting
mechanism. Therefore, the adsorption process of sodium salicylate on the wood sawdust involves some other mass transfer mechanism like boundary layer diffusion simultaneously. A similar suggestion was reported for adsorption of phthalate esters onto zeolite/Fe$_3$O$_4$.

Table 1. Kinetic constants for adsorption of sodium salicylate on the wood sawdust.

| Kinetic models         | Constants  |
|------------------------|------------|
|                        | $R^2$      | 0.952 |
|                        | $Q_e$ (mg/g) | 11.356 |
|                        | $k_1$ (min$^{-1}$) | 0.020 |
| Pseudo-second-order    | $R^2$      | 0.995 |
|                        | $Q_e$ (mg/g) | 16.129 |
|                        | $k_2$ (g/mg.min) | 0.002 |
| Intraparticle diffusion | $R^2$ | 0.928 |
|                        | $k_p$ (mg/g.min$^{1/2}$) | 0.813 |
|                        | $C$       | 1.884 |

3.2. Effect of adsorbent dosage

The adsorbent dose was varied from 0.1 to 2.0 g/L for 3 hours and an initial concentration of 10 mg/L. Figure 3 illustrated the effect of the adsorbent dosage on the adsorbed amount and adsorption efficiency. By increasing the adsorbent dosage, a reduction in the uptake capacity was observed. This reduction of the adsorbed amount could be due to the adsorbent characteristics like the density of adsorbent. In addition, the sodium salicylate adsorption efficiency increased with increasing the wood sawdust amount. This can be attributed to an increase of solid/solution contact surface and the number of adsorption sites. The adsorption efficiency almost remains unchanged after adsorbent dosage 0.5 g/L. This suggests that the additional fraction of wood sawdust (beyond 0.5 g/L) remains uncovered due to the aggregation of the adsorbent particles at higher adsorbent dosages. Beatriz et al. reported similar adsorption behavior for Acid Red 18 removal from aqueous solutions using magnetite nanoparticles and magnetite nanoparticles modified by sodium alginate.

![Figure 3](image-url)

**Figure 3.** Effect of the adsorbent dose on the adsorption of sodium salicylate on the wood sawdust. (Conditions: Contact time = 3 h, $C_0$ = 10 mg/L, pH = 6.5 and T = 25°C)

3.3. Effect of pH

The adsorption processes can be affected by the initial pH values of the solution, due to interactions of adsorbate functional groups with adsorption sites. The adsorption experiments were carried out to evaluate the influence of initial pH (in the pH range of 2–12) on the removal of sodium salicylate. Figure 4 represents the experimental results. The observed adsorption behavior can be explained as follows:
At acidic conditions, the adsorption of sodium salicylate on the wood sawdust was favorable. This could be explained by the electrostatic attractions between deprotonated functional groups of the adsorbate (hydroxyl and carboxyl functions) and protonated functions (positively charged) on the wood sawdust surface. The sodium salicylate was deprotonated according to the following scheme:

At alkaline medium, the decrease of the adsorption of sodium salicylate on the wood sawdust may be related to the competition between hydroxide ions and adsorbate molecules for active sites on the adsorbent surface. Similar results were obtained for adsorption of organic pollutants on the polymeric adsorbents. Overall, pH = 6.5 was chosen as the optimal pH for the subsequent adsorption experiments.

Figure 4. Effect of pH on the adsorption of sodium salicylate onto wood sawdust. (Conditions: contact time = 3 h, R = 0.5 g/L, C_{0} = 10 mg/L and T = 25°C)

3.4. Effect of ionic strength
The ionic strength is one of the important factors influencing the aqueous phase equilibrium. The adsorption of organic compounds can be sensitive to changes in the ionic strength of the solution. For this reason, it is important to study the ionic strength effect on the adsorption process. To investigate the impact of this parameter on the removal of sodium salicylate by wood sawdust, we introduce different masses of NaNO_{3} to mixtures of 50 mL of sodium salicylate solution with an initial concentration of 10 mg/L and 0.5 g/L of the wood sawdust at pH 6.5 and 25°C. The masses of interfering ions (NaNO_{3}) used in this study are 0.5, 1.0, 1.5, 2.0 and 3.0 mg. The obtained experimental results indicate that the adsorption efficiency of sodium salicylate decreases with increasing ionic strength (concentration of NaNO_{3}). This suggests that the nitrate ions compete with sodium salicylate.

3.5. Adsorption isotherms
Figure 5 shows that the adsorption capacity of wood sawdust for sodium salicylate increased with increasing initial concentration. The increase of adsorbed amount with initial concentration can be due to the increase of driving force for mass transfer from the liquid phase to the solid phase. Therefore, the high initial concentration facilitates the transport of sodium salicylate from aqueous solution to the wood sawdust, which results in a high uptake capacity. In addition, a plateau was observed at a high initial concentration which could be due to the saturation of active sites on the wood sawdust surface. A similar observation was reported for adsorption of Methylene blue and Safranin-O using Fe_{3}O_{4} nanoparticles.

\[ \begin{align*}
\text{OH} & \quad \text{COOH} \quad -\text{H}^{+} \\
\text{OH} & \quad \text{COO}^{-} \quad -\text{H}^{+} \\
\text{OH} & \quad \text{COO}^{-}
\end{align*} \]
Figure 5. Effect of initial concentration on the adsorbed amount of sodium salicylate on the wood sawdust. (time = 3 h, R = 0.5 g/L, T= 25 °C and pH = 6.5)

In order to describe the distribution of adsorbate molecules at solid/liquid interface, the equilibrium adsorption data were analyzed using the adsorption isotherm models. The linear expressions of Langmuir, Freundlich, Temkin and Generalized models are given by the following equations (6)-(9): The following equation 33 expresses the Langmuir isotherm model:

\[ \frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \]  

where \( K_L \) is the Langmuir binding constant, \( C_e \) is the equilibrium concentration (mg/L), \( Q_m \) and \( Q_e \) are the adsorbed amount maximum and at equilibrium in mg/g, respectively. \( r_L \) (dimensionless) is the separation factor defined as: \( r_L = 1/(1+K_L C_0) \).

- For \( r_L > 1 \): Adsorption is unfavorable
- For \( r_L = 0 \): The adsorption is irreversible
- For \( r_L = 1 \): Adsorption is linear
- For \( 0 < r_L < 1 \): Adsorption is favorable

The Freundlich isotherm model is generally expressed as:

\[ \ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e \]  

where \( K_f \) and \( n_f \) are the Freundlich empirical constants.

The Temkin isotherm model is represented by equation:

\[ Q_e = B \ln K_T + B \ln C_e \]  

where \( K_T \) and \( B \) are the Temkin constants.

The generalized isotherm model is expressed as:

\[ \ln \left( \frac{Q_m}{Q_e} - 1 \right) = \ln K - n_b \ln C_e \]  

where \( K \) is the saturation constant, and \( n_b \) is the coordination binding constant.

The results of fitting of Langmuir, Freundlich, Temkin and Generalized equations to adsorption equilibrium data of sodium salicylate (Figure 6) are summarized in Table 2. The analysis of isotherm models for describing the adsorption behavior of sodium salicylate on the wood sawdust was made by comparing the correlation coefficients (R²). Based on these results, the Langmuir isotherm model appears most satisfactory for modeling the adsorption process. This indicates that the adsorption is a homogeneous monolayer coverage. The maximum adsorbed quantity of the sodium salicylate calculated using the Langmuir isotherm model is comparable to that obtained experimentally. The values of separation factor \( r_L \) (0 < \( r_L < 1 \)) indicate that the adsorption of sodium salicylate on the wood sawdust is favorable, which confirm further the validity of the Langmuir model.

The maximum monolayer uptake capacity was found to be 99.01 mg/g. According to the literature, the adsorption ability of Spruce wood sawdust was compared with other materials, as shown in Table 3. It was concluded that the raw Spruce wood sawdust exhibited a functional uptake capacity for removal of sodium salicylate from aqueous solution. Nonetheless, several adsorbents exhibited an adsorption ability superior to that of our adsorbent material, but these materials are very expensive compared to Spruce wood sawdust. Overall, Spruce wood sawdust is an inexpensive, eco-friendly and efficient material for cleaning up wastewaters containing pharmaceutical compounds like sodium salicylate.
Figure 6. Linear plots of (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Generalized isotherms for sodium salicylate adsorption onto wood sawdust

Table 2. Adsorption isotherm constants for the adsorption of sodium salicylate on the sawdust wood.

| Isotherms      | Constants         | Constants | Constants | Constants | Constants | Constants | Constants |
|---------------|-------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Langmuir      | Q<sub>m</sub>     | 99.01     | K<sub>L</sub> (L/mg) | 0.029 | R<sup>2</sup> | 0.987 | r<sub>L</sub> | 0.147 – 0.775 |
| Freundlich    | K<sub>f</sub>     | 6.999     | n<sub>f</sub> | 1.941 | R<sup>2</sup> | 0.963 |
| Temkin        | B                 | 20.664    | K<sub>T</sub> (L/mg) | 0.331 | R<sup>2</sup> | 0.950 |
| Generalized   | K (L/mg)          | 1.004     | n<sub>b</sub> | 1.551 | R<sup>2</sup> | 0.962 |
Table 3. Comparison of the adsorption capacity of Spruce wood sawdust with other adsorbents available in the literature.

| Adsorbent          | $Q_m$ (mg/g) | Reference |
|--------------------|--------------|-----------|
| Filtrasorb F400    | 351.0        | 39        |
| Sephabeads SP207   | 81.6         | 38        |
| Sephabeads SP206   | 45.2         | 40        |
| Polypyrrole        | 125          | 41        |
| Spent biochar      | 22.70        |           |
| PGDpc_D            | 152.7        |           |
| Spruce wood sawdust| 99.01        | This study|

3.6. Adsorption thermodynamics
The investigation of the temperature influence on the adsorption process was carried out by varying the temperature of the solution from 25 to 50°C using a thermostatic bath, keeping all other parameters constant. Based on the experimental data, thermodynamic parameters including $\Delta H^\circ$, $\Delta S^\circ$, and $\Delta G^\circ$ were calculated to describe thermodynamic behavior of the adsorption of sodium salicylate on wood sawdust. All parameters were calculated using the equations (10) and (11) [42]:

$$\Delta G^\circ = -RT \ln K_d$$  \hspace{1cm} (10)

$$\ln K_d = (\Delta S^\circ/T) - (\Delta H^\circ/RT)$$ \hspace{1cm} (11)

where $R$ is the universal gas constant (8.314 J/mol K), $K_d$ is the distribution constant, and $T$ is solution temperature in °K.

The distribution constant $K_d$ is defined by the equation (12):

$$K_d = Q_e/C_e$$ \hspace{1cm} (12)

The plot of $\ln K_d$ versus $1/T$ is presented in Figure 7. The values of thermodynamic parameters were graphically determined by linear regression analysis and are summarized in Table 4.

![Figure 7. Plot of log $K_d$ vs 1/T for adsorption of sodium salicylate on the wood sawdust](image)

Table 4. Thermodynamic parameters for the adsorption of sodium salicylate on the wood sawdust.

| Adsorbate          | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (J/mol.K) | $\Delta G^\circ$ (kJ/mol) |
|--------------------|---------------------------|---------------------------|--------------------------|
| Sodium salicylate  | -5.081                    | -3.631                    | 298°K, 303°K, 308°K, 313°K, 323°K |
|                    |                           |                           | -3.998, -3.981, -3.963, -3.945, -3.908 |

The negative value of the standard enthalpy $\Delta H^\circ$ shows an exothermic character of the adsorption process. The negative values of the standard Gibbs energy $\Delta G^\circ$ in the studied temperature range allows us to conclude that the adsorption of sodium salicylate on the wood sawdust is spontaneous in nature [43]. In addition, the $\Delta G^\circ$ increased from -3.998 to -3.908 kJ/mol when the temperature was...
increased, indicating a decrease in the feasibility of adsorption at higher temperatures. The values of $\Delta G$ range between -20 and 0 kJ/mol, which means that the adsorption of sodium salicylate onto wood sawdust is a physical adsorption type. The negative value of the entropy ($\Delta S$) suggests a decrease in the randomness at the adsorbent/adsorbate interface during the adsorption process.

4. Conclusion

In the present study, the removal of sodium salicylate from aqueous solution using Spruce wood sawdust as a low-cost and eco-friendly adsorbent was systematically investigated. The effects of physicochemical parameters such as contact time, solution pH, adsorbent dosage, initial concentration and temperature on the adsorption process were evaluated. As a result, the optimal conditions required 180 min of adsorbent/solution contact using 10 mg/l of sodium salicylate and 0.5 g/L of Spruce wood sawdust at pH 6.5 and 25°C. Under these conditions, the adsorbed amount was estimated to be 13.56 milligrams of sodium salicylate per gram of Spruce wood sawdust. The pseudo-second-order model is the most suitable to describe the adsorption kinetic. Experimental data of sodium salicylate were successfully fit to the Langmuir isotherm model with a maximum monolayer uptake capacity of 99.01 mg/g. The values of thermodynamic parameters prove that the adsorption of sodium salicylate on the wood sawdust is an exothermic and spontaneous process. These results indicate that the Spruce wood sawdust is a cost-effective and eco-friendly adsorbent for the removal of sodium salicylate from aqueous solution, and it could be useful in the treatment of wastewaters.

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