Research Article

Adsorption of 3-Chloroaniline on Potato Skin in Aqueous Solution

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The adsorption behaviour of aromatic amine 3-chloroaniline (3-CA) from aqueous solution on fresh potato skin was investigated. A series of batch experiments were conducted under different experimental conditions of contact time, 3-chloroaniline concentration, weight of potato skin, pH, temperature, and ionic strength using RP-HPLC analysis. Adsorption equilibrium of 3-chloroaniline at concentration of 10 μg/mL on 1 g weight of chopped potato skin was achieved in 24 hours. Using different varieties of potato skin showed that the adsorption of 3-CA on Nicola variety is higher compared to Sante and Maris Peer varieties. Adsorption on potato skin was found to be generally higher compared to cortex and pith tissues. Analysis of adsorption isotherm shows that equilibrium data was fitted to Freundlich model ($R^2 = 0.977$). Maximum adsorption capacities of 3-chloroaniline were found in the pH range from 3 to 9, whereas low adsorption quantities were found in high acidic and high basic solutions (pH 2 and pH 13, resp.). Adsorption capacity increased with an increase in temperature from 4°C to 30°C but decreased with further increase of temperature to 40°C. Testing the ionic strength showed that increasing the concentration of electrolyte reduces the adsorption efficiency. This study indicated that the fresh potato skin (without any treatment) is possible to use as a new adsorbent for removal of 3-chloroaniline from industrial waste water.

1. Introduction

The concentration of chlorinated aniline in the environmental samples is continuously increased due to the degradation of various pesticides and frequent use in a variety of industries in several processes as reagents or intermediates in the manufacture of pigments, pharmaceuticals, dyes, rubber, cosmetics, and medicines [1–5]. These aromatic amines compounds may be hazardous to plant, animals, and human for long duration even at very low concentration (μg/L) and are suspected to be carcinogenic and highly toxic to human beings and aquatic life [6]. Due to this anxiety, the US Environmental Protection Agency (EPA) included most of these substances in list of priority pollutants [7].

Nowadays, the awareness of increasing water pollution and the use of removal of chlorinated amines from wastewater are so important. Adsorption is one process applied to wastewater treatment due to high efficiency, environmental friendliness, low cost, insensitivity to toxic substances, and the possibility of recycling the materials [8].

3-Chloroaniline is one of the chlorinated aromatic amines, and it is not only distributed through the industrial production but also formed as a product of thermal and microbial degradation of application potato sprout inhibitor chlorpropham (CIPC) in potato stores [9–13]. In reviewing the literature, adsorption studies of 3-chloroaniline have been investigated in aqueous solutions on various adsorbents such as soil [14], chelating resin [2], and clays [3, 6, 15, 16].

Potato peel is disposed as a waste that lags about 80–100 grams from every 1 kg of potato crop. Activated carbons prepared from potato peels can be used as adsorbent to remove most of contaminants from aqueous solutions and wastewaters such as heavy metals [17–19], dyes [20–22], and phenolic compounds [23, 24].

The novelty of the present research is to examine the adsorption efficiency of 3-CA on fresh potato skin
as adsorbent (without any treatment and modifying with chemicals). This study accords with our earlier observations that showed difficult extraction of 3-CA from potato peel [25]. In reviewing the literature, several investigations have been reported on the fate of chloroaniline compounds in the plants indicating bound or nonextractable residues of these compounds [26–28].

In this study, high performance liquid chromatography (HPLC) was used, which is one of the most common techniques for the separation and determination of chlorinated aniline in environmental samples [3, 7].

2. Materials and Methods

2.1. Standards. Analytical grade reagent of 3-chloroaniline (99%) was purchased from Sigma-Aldrich Chemie GmbH (Germany). The concentration of stock solution of 3-CA was chosen to be below its solubility’s (5400 μg/mL at 20°C) in water. For the preparation of stock aqueous solution of 5000 μg/mL of 3-CA in water, an accurate weight of 0.5 g was weighted and dissolved in water in a 100 mL volumetric flask. The solution was noticed after a few minutes of mixing on the magnetic stirrer to be completely dissolved. However, to ensure complete dissolution of 3-CA solution, it was stirred for 24 hours using a magnetic stirrer in an incubator (LMS LTD Cooled Incubator, model number 303) at 20°C temperature. Detailed examination of solubility of 3-CA in aqueous solution showed no significant difference between preparation of 3-CA in water and its preparation in methanol [25].

Working solutions were prepared from the stock solution and stored in the fridge at 4°C. The water used for preparation of the standards and the mobile phase was supplied from an ELGA PURELAB Option deionizer model LA613.

2.2. HPLC Analysis. The HPLC system used comprised a Gilson® 234 autosampler, Cecil 1100 Series pump, Phenomenex® Security Guard™ (part number KJO-4282) guard column with analytical column Phenomenex (ODS-2 250 mm × 4.6 mm 5 μm SphereClone), and a Thermo Separation Spectra Series UV100 detector coupled with Dionex PeakNet software. A column oven (LaChrom, Merck L-7350) was connected with a cooling system (Techné, Tecam® R 4-2) to control the column at 20°C temperature. An isocratic method was employed using mobile phase prepared from methanol (HPLC grade from Fisher Scientific, UK) and water (55:45 v/v%). The water used for preparation of the mobile phase was filtered through a Supor® 200 47 mm, 0.2 μm membrane filter. The mobile phase was degassed for at least 20 minutes using an ultrasonic bath (Camlab CamSonix C425). HPLC analysis was performed at a detection wavelength of 210 nm, pump flow rate of 1.5 mL/min with an injection volume of 20 μL, and chromatographic run for 10 minutes.

2.3. Batch Adsorption Experiments. Batch adsorption studies of 3-CA were performed by spiking of triplicates of chopped potato skin (0.5 × 0.5 cm) with aqueous solution of 3-CA solution in a 100 mL screw jar. The spiked skin was agitated for contact time using an orbital incubator (Gallenkamp orbital incubator cooled) which is set up at 20°C and 100 rev/min. Sample from the solution was transferred into HPLC vial using 2 mL syringe and filter disk syringe (17 mm) and the remaining concentration of 3-CA in the aqueous solution was determined by injecting 20 μL into HPLC. The remaining concentration of 3-CA in the sample solution is expressed on the concentration in the solution at equilibrium state (C_e). The amount adsorbed (Q) in μg of 3-chloroaniline per g of potato skin and the adsorption efficiency (%) were calculated according to the following equations:

\[
\text{adsorption capacity (Q)} = \frac{V}{m} (C_i - C_e),
\]

\[
\text{adsorption efficiency (%) } = \frac{(C_i - C_e)}{C_i} \times 100,
\]

where \(V\) is the volume (mL) of 3-chloroaniline solution used, \(m\) is the weight of the potato skin (g), and \(C_i\) and \(C_e\) are the initial and equilibrium concentrations of 3-chloroaniline solution (μg/mL), respectively. \(Q\) values were then plotted against their corresponding \(C_e\) values to construct the adsorption isotherms [29]. Different parameters including the contact time, adsorption isotherm, adsorbent skin amount, pH, temperature, and ionic strength were investigated.

3. Results and Discussion

3.1. Different Potato Varieties. Adsorption of 3-CA onto different potato skin varieties was investigated. In terms of decreasing the initial concentration of 3-CA as a function with contact time, Figure 1 shows high adsorption of 3-CA on Nicola variety compared to Sante and Maris Peer varieties. Complete adsorption of 3-CA onto potato skin was shown after 24 hours with all three potato varieties. The adsorption process is likely to involve many of the attraction
forces that lead to high adsorption capacity of 3-CA. The mechanisms of adsorption processes may involve Van der Waals forces, electrostatic interaction, hydrogen and covalent bonding, ligand exchange, and hydrophobic bonding or partitioning which are the most important types of the interactive forces between adsorbent and adsorbed material [30]. The occurrence of these mechanisms depends on the nature of the functional group of both adsorbed material and adsorbate surface; however, not all these mechanisms may occur simultaneously. The difference in the adsorption extent onto these three different potato skin varieties at the first 8 hours can be explained by the fact that potato varieties have different characteristics including moisture, texture, nutrient contents, and skins composition [31, 32].

3.2. Different Layers of the Potato Tuber. Potato tubers are composed of distinct tissues: mainly the skin (the coloured and the outer layer of potato tuber), cortex (the area under skin), and pith, which is the more translucent and wetter part in the centre of the potato tuber [33]. Investigation of the adsorption of 3-CA from aqueous solution onto these three layers from potato showed results of higher adsorption on the skin compared to cortex and pith as can be seen in Figure 2. It seems possible that these different adsorption results at the first 8 hours are due to the difference in the composition of these layers within the potato tuber. However, all 3-CA was adsorbed at 24 hours with all layers indicating high adsorption affinity between 3-CA and potato tuber layers.

3.3. Effect of Contact Time on Adsorption of 3-CA on Potato Skin. The effect of contact time was studied at different intervals (0, 0.08, 0.5, 1, 2, 4, 6, 8, 24, and 48 hours) to determine the remaining concentration of 3-CA in the solution until an equilibrium was reached, with no further uptake of adsorption of 3-CA on the skin. The initial concentration of 3-CA was found to decrease with increase in contact time reaching equilibrium after 24 hours (Figure 3). The result can be interpreted that the adsorption of 3-CA onto potato skin occurs rapidly at the beginning of contact times due to the fact that a large number of surface sites are available on the potato skin. Then the adsorption became lower followed by no further adsorption when all these sites are occupied. Based on these results, 24 hours was selected as a base for equilibrium time for further experiments in this study.

3.4. Adsorption Isotherm. The aim of the adsorption isotherm is to reveal the specific relation between the amount adsorbed onto the surface and the equilibrium concentration of the adsorbate in the solution at constant temperature; it should be fitted into suitable isotherm models [29]. The adsorption isotherm of 3-CA on the potato skin was studied at different concentrations (1, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 µg/mL). The general shape of the adsorption isotherm was found as shown in Figure 4. The resulting isotherm indicates that the potato skin has a greater ability to adsorb 3-CA. The isotherm result was analysed using Langmuir and Freundlich isotherms. The result is more in agreement with Freundlich isotherm as...
shown in Figure 5. The Freundlich equation is described by the following linearized form:

\[ \log Q = \log K_f + \left( \frac{1}{n} \right) \log C_e, \]  

(2)

where \( C_e \) is the equilibrium concentration (\( \mu g/mL \)), \( Q \) is the amount adsorbed (\( \mu g \)) per unit weight of adsorbent (g), and \( K_f \) and \( n \) are Freundlich constants, which represent adsorption capacity and adsorption intensity and are calculated from the intercept and slope. The Freundlich isotherm parameters along with \( K_f \) and \( n \) were determined to be 144 \( \mu g/g \) and 3, respectively, with \( R^2 \) of 0.977. Comparative \( K_f \) values for other adsorbents studied are given in Table 1. Generally, a greater value of \( K_f \) refers to a high adsorption capacity, whereas \( n > 1 \) illustrates that the adsorbate is favorably adsorbed on the adsorbent [29, 34]. Freundlich isotherm can be applied for nonideal adsorption on the heterogeneous surfaces when multilayer adsorption is formed [29, 35].

3.5. Effect of the Skin Weight on 3-CA Adsorption. The weight of the adsorbent is important factor for the adsorption efficiency and capacity of 3-chloroaniline. The effect of the weight of the potato skin on adsorption of 3-CA was studied. Five weights were selected (1, 3, 5, 7, and 10 g). The results in Figure 6 show that adsorption efficiency of 3-chloroaniline increases with the increase of potato skin weight, whereas the adsorption capacity decreases with the increase of potato skin. 1g of potato skin was preferred as a best economical adsorbent weight in this study because of high adsorption capacity and adequate adsorption efficiency of 3-CA at this weight.

3.6. Effect of pH. The adsorption of 3-CA in aqueous solution on potato skin was examined by optimizing the effect of pH at a broad range of 2–13 using either acetic acid or sodium hydroxide solutions, while deionized water was used to provide pH 7. Figure 7 shows that the high acidity and alkalinity produce a lower adsorbed quantity of 3-chloroaniline. The adsorption capacities of 3-chloroaniline sharply increase with increasing pH values from 2 to 3 and then remained constant up to 9, followed by decreasing with increasing pH from 9 to 13. The effective pH values that gave high adsorption quantity of 3-chloroaniline were 7 and 9. pH 7 was applied in further studies.

The protonation of the functional groups of both adsorbed materials and adsorbents plays important role of pH effect on the adsorption process [36]. Adsorption of \( H^+ \) and \( OH^- \) ions on surface of material changes the surface charge of material (zeta potential value). At low pH, the competition between \( H^+ \) and 3-chloroaniline limits the uptake efficiency. The high concentration of \( H^+ \) in solution
may attack the functional groups of potato skin composition (increases the zeta potential value); consequently, active sites of the potato skin become less available to adsorb 3-chloroaniline. While increasing the pH from 2 to 3, the amine group of 3-CA may become ionized (pK_a = 3.5) which leads to 3-chloroanilinium cation becoming adsorbed on potato skin due to attraction forces between both. Since the adsorption increases with pH and then remains constant in the pH range of 3–9, the active sites on the potato skin bind 3-CA very well perhaps by ion exchange or complexation processes [37]. Another possibility is that 3-CA can be adsorbed as neutral molecule in the pH solution of 3–9 by hydrogen bonding with abundant functional groups on potato skin (e.g., OH and COOH) [30]. Increasing pH values beyond 9 decreased the adsorption capacities due to the fact that the amine group of chloroaniline is less positive [36]. This low adsorption may also be attributed to the competing of the high concentration of OH^- (decreases the zeta potential value) with 3-chloroaniline to form hydrogen bond with water molecule’s presence in potato skin.

3.7. Temperature Effect. Temperature parameter has a critical role in adsorption processes. According to the adsorption theory, adsorption process decreases when the temperature increases. Molecules which were adsorbed earlier on a surface have a tendency to be desorbed from the surface at elevated temperatures [38]. The effect of the temperature on adsorption process was studied. However, a different trend was noticed in case of adsorption of 3-CA on potato skin at various temperatures (4, 10, 15, 20, 30, and 40°C). The adsorption increased from 4°C to 30°C but further increase of temperature to 40°C decreases the adsorption as shown in Figure 8. Increasing the temperature to 30°C indicates an increase in molecular motion and decreases the viscosity permitting 3-CA to penetrate easily into the potato skin surface and interact with active sites leading to more adsorption. The decrease of adsorption above 30°C may be attributed to collapse of hydrogen bond or electrostatic forces of 3-CA on potato skin.

3.8. Ionic Strength. The effect of ionic strength on the adsorption of 3-CA on potato skin was investigated by the presence of electrolyte of NaCl at varying concentrations (0, 0.2, 0.4, 0.6, and 0.8 µg/mL) in 3-CA solutions. The amount adsorbed of 3-CA was found to be decreased with increased NaCl concentration as shown in Figure 9. This decrease in adsorption may be due to the fact that the external electrolyte either decreases the hydrophobic nature of 3-CA molecules in the solution or increases the electrostatic interaction between their ions in the solution and polar molecules of 3-CA. The adsorption is sensitive to changes in the concentration of the supporting electrolyte if the driving force of the adsorption is the electrostatic interaction [39].

4. Conclusion

This work clearly indicates the adsorption of 3-CA to potato skin is a relatively rapid equilibrium process and is strongly dependent on the contact time, initial 3-CA concentration, potato skin weight, pH, temperature, and ionic strength. Contact time of 24 hours is sufficient to adsorb all of 3-CA at concentration of 1 µg/mL on different potato skin varieties and different potato layers. pK_a of 3-chloroaniline is 3.52, indicating that this basic compound will primarily be present as nonionic organic base. It is therefore sensible to hypothesize that specific interactions such as hydrogen bonding or Van der Waals forces may play important role in the adsorption mechanism of neutral molecules and weak base compounds [6, 15]. The adsorption process follows Freundlich isotherm indicating that adsorption of 3-CA on potato skin is favorable. This study revealed that potato skins which are abundantly available as solid waste can be used as new adsorbent to remove toxic chlorinated aniline from industrial effluents.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.
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