The Use of Exoskeletons and Molts of Farmed Mealworm (Tenebrio molitor) for the Removal of Reactive Dyes from Aqueous Solutions

Tomasz Jóźwiak 1, Urszula Filipkowska 1,* and Tadeusz Bakula 2

1 Department of Environmental Engineering, University of Warmia and Mazury in Olsztyn, Warszawska St. 117a, 10-957 Olsztyn, Poland; tomasz.jozwiak@uwm.edu.pl
2 Department of Veterinary Prevention and Feed Hygiene, University of Warmia and Mazury in Olsztyn, Oczapowskiego 13 St., 10-718 Olsztyn, Poland; baka@uwm.edu.pl
* Correspondence: urszula.filipkowska@uwm.edu.pl

Abstract: The study aim was to test the applicability of exoskeletons and molts from mealworm (Tenebrio molitor) cultures as sorbents for anionic dyes: Reactive Black 5 (RB5) and Reactive Yellow (RY84). Factors investigated included: characteristics of sorbents (FTIR, pHZC), the influence of pH on sorption efficiency, sorption kinetics (pseudo-first, pseudo-second-order, intraparticle diffusion models), and determination of the maximum sorption capacity (Langmuir 1, Langmuir 2, Freundlich, and Dubinin–Radushkevich models). The sorption efficiency of anionic dyes on the tested sorbents was the highest at pH 2. The time needed to reach the sorption equilibrium for both dyes was 120–150 min. The sorption kinetics of the dyes were best described by the pseudo-second-order model. Maximum sorption capacity data showed the best fit to Langmuir 2 isotherm, suggesting that at least two types of sorption centers played an important role in dye sorption. Presumably, for both of the tested sorbents, the active sites in question were protonated amine (-NH3+), acetamide (NHCOCH3), and hydroxyl groups (-OH3+) of chitin and protein. The maximum RB5 and RY84 sorption capacity of the tested sorbents was 78.70 mg/g and 60.49 mg/g, respectively, for mealworm exoskeletons, as well as 55.72 mg/g and 44.25 mg/g, respectively, for mealworm molts.

Keywords: mealworm; exoskeletons; molts; sorption; reactive dyes

1. Introduction

Dyes are heavily used in industry to color fibers, textiles, leather, paper, and other products. Reactive dyes are the most popular choice due to their long shelf-life and considerable versatility [1]. However, up to 50% of the dyes can be left in the effluent due to processing limitations [2]. Colored wastewater can exert a number of adverse environmental effects if discharged untreated into natural water bodies [3]. Dyes can significantly reduce the transparency of water, even at concentrations as low as a few mg/L. The resultant blockage of sunlight affects aquatic plants and can inhibit the primary production process [4]. Colorants also limit the diffusion of atmospheric oxygen in water, which, combined with the inhibition of photosynthesis, may lead to the deoxygenation of water bodies. Moreover, dyes tend to be toxic to aquatic organisms [5]. Further exacerbating the problem, colorants are hard to biodegrade because of their often complicated chemical structure, which means that water contamination with colorants can persist for extended periods of time [6]. These potential environmental effects mean that the decolorization of wastewater requires the most effective methods available.

The sorption process is deemed to be one of the most attractive options for treating colored effluent [7]. During sorption, pollutants are adsorbed onto the surface of a sorbent. The exact cost and efficiency of the process depend mainly on the type of sorption.
materials used [8]. Activated carbon is currently the most popular choice of sorbent for removing dyes [9]. Its large surface area, which can exceed 3000 m²/g, bestows activated carbon with a very high sorption capacity [10,11]. The drawback is that the substance is expensive to produce and regenerate, which is why cheaper and/or more efficient alternatives are being sought.

Chitin has been gaining popularity as a sorption material in recent years. This polysaccharide is the main building block of arthropod exoskeletons, as well as a major component of the cell walls of fungi, some algae, and bacteria [12]. Industrial volumes can be harvested from shells of shrimps and crabs, i.e., waste products of seafood processing [13]. Chitin-based sorption materials can prove very useful in the treatment of colored wastewater [14]. Compared with commercial activated carbons, chitin can boast higher sorption capacity towards anionic reactive dyes, which are the major component of colored wastewater [15]. These considerable sorptive properties of chitin are due to the high concentrations of acetamide and amine functional groups, which act as key sorption centers [16]. Unfortunately, raw materials for chitin production are scarce in countries where marine crustaceans are not fished. Furthermore, chitin availability is limited by pharmaceutical companies, which purchase high volumes of biopolymer to produce drugs and dietary supplements.

As an alternative, chitin may be harvested from exoskeletons and molts of insect larvae farmed for food and feed [17]. The mealworm (Tenebrio molitor) is one example of an insect farmed on a large scale for human consumption in many countries [18] and classified by the European Food Safety Authority as a “novel food” in June 2021. The chitin from mealworm molts—a waste product of mealworm farming—has very similar sorptive properties to commercial chitin from snow crab shells [15].

However, just as with crab and shrimp shells, the production of chitin from mealworm exoskeletons and molts is time-consuming and expensive. Other constituents of the exoskeletons/molts, such as protein and minerals (up to 90% of the raw material by weight), are irrecoverably wasted in the process [17,19–20]. Theoretically, these components could be capable of adsorbing dyes. It can therefore be hypothesized that “the total sorption capacity of mealworm exoskeletons and molts against dyes is greater than the sorption capacity of pure chitin extracted from the same quantity of raw material”. If confirmed, it would imply that harvesting pure chitin for sorbents from insect exoskeletons and molts is not commercially reasonable. The present work aims to verify the aforementioned hypothesis. To the best of the authors’ knowledge, fragments of insect shells have not been investigated as sorbents so far.

Our study investigated the performance of exoskeletons and molts of mealworms as sorption materials for the removal of popular industrial dyes: Reactive Black 5 and Reactive Yellow 84, from aqueous solutions.

2. Materials and Methods

2.1. Sorbents

The molts and exoskeletons used in the study came from mealworm (Tenebrio molitor) grown for animal feed by the Department of Veterinary Prevention and Feed Hygiene, University of Warmia and Mazury in Olsztyn, Poland. The insects were fed oatmeal and carrots. No instances of cannibalism were observed, indicating that the mealworm was provided sufficient protein. Chitin fractions in dry matter were 8.4–9.6% for the exoskeletons and 17.0–18.0% for the molts [17,19].

2.2. Sorbates (Dyes)

The Reactive Black 5 and Reactive Yellow 84 were purchased from the “BORUTA S.A.” dye and pigment production plant in Zgierz (Łódzkie Province, Poland).

Reactive Black 5 (RB5) is an anionic, reactive azo dye popular in the textile industry. Its anionic (acidic) nature is attributable to the sulfone groups present in its structure
(Figure 1). It has two characteristic vinyl-sulfone groups, which provide it with the capacity to undergo chemisorption and permanently bind to the material being dyed. Its molar mass is 991.8 g/mol, and the maximum absorbance peak is at $\lambda_{\text{max}} = 600$ nm. The material is used to dye cellulose, viscose, cotton, and polyamide fiber and is sold under the popular trade names Begazol Black B and Remazol Black B.

![Figure 1](image)

**Figure 1.** Structural formulas of Reactive Black 5 and Reactive Yellow 84.

Similar to Reactive Black 5, Reactive Yellow 84 (RY84) is an anionic, reactive azo dye popular in the textile industry. Just like RB5, RY84 is acidic due to its sulfone functional groups (Figure 1). Its reactivity is attributable to chlorotriazine functional groups, which allow it to permanently bind to the material via a condensation reaction. Its molar mass is relatively high at 1628.2 g/mol, and its maximum absorbance peak is at $\lambda_{\text{max}} = 356$ nm. It is generally used to dye cotton, viscose, and polyester fibers. Alternative trade names include Active Yellow HE-4R and Lamafix Yellow HER.

### 2.3. Chemical Reagents

The following chemical reagents were used in the study:

- Hydrochloric acid (HCl) — 37% — (solution pH correction);
- Sodium hydroxide (NaOH) > 99.9%-micropellets — (solution pH correction);
- Petroleum ether (40–60 °C) — dewaxing of molts and exoskeletons.

All chemical reagents used were purchased from POCH S.A., Gliwice, Poland, and were of p.a. (analytical purity) grade or higher.

### 2.4. Laboratory Equipment

The following laboratory equipment was used for the study:

- HI 110 pH meter (HANNA Instruments, Olsztyn, Poland) — for measurement and correction of solution pH;
- An 11 basic laboratory grinder (IKA, Willmington, NC, USA) — for grinding exoskeletons and molts biomass;
- SK-71 laboratory shaker (JEIO TECH, Daejeon, Republic of Korea) — for the sorption process;
- MS-53M multi-channel stirrer (JEIO TECH, Daejeon, Republic of Korea) — for the sorption process;
- UV-3100 PC spectrophotometer (VWR Spectrophotometers, Mississauga, ON, Canada) — for quantifying dye in solutions;
- FT/IR-4700LE FT-IR Spectrometer with single reflection ATR attachment (JASCO International, Tokyo, Japan) — for determining the FTIR spectra of the sorbents;
• Gemini VI (Micromeritics, Norcross, GA, USA)—for the measurements of porosity and surface area of the sorbent.

2.5. Sorbent Preparation

The mealworm exoskeletons and molts were subjected to the same pre-sorption procedure. The material was ground in a laboratory mill and passed through laboratory sieves with mesh diameters of 3 mm and 2 mm. The 2–3 mm biomass fraction was washed with deionized water, then poured into a beaker with petroleum ether, and left for 24 h (25 °C) to dewax. The biomass was then filtered and rinsed with deionized water to remove the petroleum ether. Once dried in a laboratory desiccator (105 °C), the sorbent composed of crushed and cleaned mealworm exoskeletons (MES) and mealworm molts (MMS) was ready for analysis.

2.6. Determination of pH Effect on Dye Sorption Efficiency

A total of 0.20 g portions of either the exoskeleton-based (MES) or molt-based (MMS) sorbent was weighed into a series of Erlenmeyer flasks (500 mL). Then, 200 mL of either the RB5 or RY84 solution (50 mg/L, pH 2–11) was added to each flask. The flasks were placed on a laboratory shaker (150 RPM, vibration amplitude 30 mm) for 120 min. Afterward, 10 mL samples were collected into a polypropylene test tube to quantify the dye remaining in the solution. The solutions were also pH-tested after the sampling.

2.7. Determination of Dye Sorption Kinetics

A total of 1.00 g portions of the tested sorption material (either MES or MMS) were distributed into a series of narrow laboratory beakers (1000 mL). Then, 1000 mL of a dye solution (either RB5 or BR46, 50 mg/L or 250 mg/L) was added into the beakers while ensuring optimal sorption pH (determined based on the tests in Section 2.6). The beakers were placed on a multi-station magnetic stirrer (150 RPM). Standard 40 × 8 mm Teflon-coated cylindrical magnetic stirrers were used to mix the solution with the sorbent. At specific time intervals (0, 10, 20, 30, 45, 60, 90, 120, 150, 180, 240, and 300 min), an automatic pipette collected 2 mL solution samples into the prepared test tubes.

2.8. Determination of pH Effect on Dye Sorption Efficiency

A total of 0.20 g portions of a sorbent (either MES or MMS) were transferred into 500 mL Erlenmeyer flasks, then diluted in the same flasks in 200 mL of a dye solution (RB5 or RY84) with a concentration of 10–500 mg/L and optimal pH (determined based on the tests in Section 2.6). The flasks were placed on a laboratory shaker (150 RPM, vibration amplitude 30 mm). Once the established time to sorption equilibrium had passed (individually set for each dye and sorbent according to the tests in Section 2.7), samples were collected from the flasks into test tubes.

All experimental procedures described in Sections 2.6–2.8 were performed in triplicate at a constant 25 °C. The stirring rate was set to ensure thorough mixing of the sorbent with the entire volume of the solution. The concentration of dye in the samples was spectrophotometrically determined using 10 mm quartz cuvettes. Dye curves were plotted for concentrations of 0.0–50.0 mg/L at wavelengths of 600 nm (RB5) and 356 nm (RY84). Solutions of >50 mg/L were diluted in deionized water.

2.9. Computation Methods

The amount of dye adsorbed onto MES/MMS was computed from Formula (1).

\[ Q_s = (C_0 - C_s) \times \frac{V}{m} \]  

(1)

\(Q_s\)—the mass of sorbed dye [mg/g];

\(C_0\)—the initial concentration of the dye [mg/L];
C₅—concentration of the dye after sorption [mg/L];
V—the volume of the solution [L];
m—sorbent mass [g].

The data on dye sorption onto the tested sorbents were modeled using the pseudo-first-order model (2), pseudo-second-order model (3), and the intraparticle diffusion model (4).

\[
Q = q_e \times (1 - e^{-k_1 \times t})
\]  
(2)

\[
Q = \frac{(k_2 \times q_e^2 \times t)}{(1 + k_2 \times q_e \times t)}
\]  
(3)

\[
Q = k_{id} \times t^{0.5}
\]  
(4)

Q—the instantaneous value of sorbed dye [mg/g];
qₑ—the amount of dye sorbed at equilibrium state [mg/g];
t—time of sorption [min];
k₁—pseudo-first-order adsorption rate constant [1/min];
k₂—pseudo-second-order adsorption rate constant [g/(mg·min)];
kₐd—intraparticle diffusion model adsorption rate constant [mg/(g·min⁰.⁵)].

Maximum sorption capacity data were modeled using three sorption isotherms: Langmuir 1 (5), Langmuir 2 (Langmuir double isotherm) (6), Freundlich (7), and Dubinin–Radushkevich (8).

\[
Q = \frac{(Q_{max} \times K_c \times C)}{(1 + K_c \times C)}
\]  
(5)

\[
Q = \frac{(b_1 \times K_i \times C)}{(1 + K_i \times C)} + \frac{(b_2 \times K_i \times C)}{(1 + K_i \times C)}
\]  
(6)

\[
Q = K \times C^{\frac{1}{n}}
\]  
(7)

\[
Q = Q_{max} \times \exp \left( -B \times \left( R \times T \times \ln \left( 1 + \frac{1}{C} \right)^2 \right) \right)
\]  
(8)

Q—the mass of sorbed dye [mg/g];
C—concentration of the dye left in the solution [mg/L];
Qₘₐₓ—maximum sorption capacity from the Langmuir equation [mg/g];
b₁—maximum sorption capacity of the sorbent (type I active sites) [mg/g];
b₂—maximum sorption capacity of the sorbent (type II active sites) [mg/g];
K_c—constant from the Langmuir equation [L/mg];
K_i and K₂—constants from the Langmuir 2 equation [L/mg];
K—the sorption equilibrium constant in the Freundlich model;
n—constant in the Freundlich model;
B—constant in the Dubinin–Radushkevich model [mol²/J²];
R—universal gas constant—8.314 [J/mol·K];
T—absolute temperature (K).

3. Results and Discussion
3.1. Characteristics of Tested Sorbents (FTIR, Surface)

The FTIR spectra of the sorbents from mealworm exoskeletons and mealworm molts are very similar to each other, suggesting their similar chemical composition. Both materials show absorption bands characteristic of chitin, proteins, and lipids (Figure 2).
The saccharide-specific peaks at 1068 cm\(^{-1}\) and 1025 cm\(^{-1}\) indicate the presence of chitin and suggest C-O stretching for the C3 and C6 of the pyranose ring [21]. The peaks at 1155 cm\(^{-1}\) (symmetrical C-O-C stretching) and 1114 cm\(^{-1}\) (asymmetrical C-O stretching) are also typical of saccharides [21]. The small peak of 2961 cm\(^{-1}\) suggests a methylene group in the saccharide ring of chitin [22].

The distinct peak at 1626 cm\(^{-1}\) (amide I region) is indicative of a hydrogen bond between a carbonyl and hydroxyl group of the same polysaccharide chitin chain. The peak at 1540 cm\(^{-1}\) (amide II region) is attributable to N-H bending—a feature of the chitin acetamide group [22,23] (Figure 2). The presence of acetamide groups in the MES and MMS structure is also indicated by the typical peaks at 3290 cm\(^{-1}\) and 2870 cm\(^{-1}\), corresponding to N-H (Amide A) and C=O bonds [24]. The peak at 1233 cm\(^{-1}\), visible in the amide III region, is also indicative of a C=O bond [25].

The peaks at 1450 cm\(^{-1}\) and 1374 cm\(^{-1}\) correspond to the CH\(_2\) and CH\(_3\) stretching vibrations typical of lipids. Finally, 2917 cm\(^{-1}\) and 2850 cm\(^{-1}\) peaks are due to symmetrical and asymmetrical stretching of CH\(_2\)/CH\(_3\), lipid chains, and terminal protein groups [26].

Using a Gemini VI apparatus, the porous structure and pore distribution were measured for the tested sorbents using the low-temperature nitrogen sorption method. The BET area determined for both MES and MMS is 0.13 ± 0.02 m\(^2\)/g and 0.24 ± 0.03 m\(^2\)/g, respectively, whereas the total pore volume was 0.00115 cm\(^3\)/g and 0.00166 cm\(^3\)/g, respectively.
3.2. Influence of pH on the Dye Sorption Efficiency on MES and MMS

RB5 and RY84 sorption efficiency on MES and MMS peaks at pH 2 and deteriorates as the pH increases, with the worst performance noted at pH 11. The highest drop in dye adsorption is observed between pH 2 and 4. In the RB5 groups, a slight increase in sorption intensity is noted at pH 9. Dye sorption of RB5 and RY84 to MES and MMS is the lowest at pH 11 (Figure 3a,b).

![Graphs showing the influence of pH on dye sorption efficiency](image1)

Figure 3. The effect of pH on the sorption effectiveness of (a) RB5 and (b) RY84 onto MES and MMS (mean + range). The effect of MES and MMS on solution pH during dye sorption: (c) RB5 and (d) RY84. (e,f) Determination of pH_{ZPC} for MES and MMS with the drift method.
The high efficiency of anionic dye sorption at low pH resulted from a strong positive charge acquired by the sorbent. The hydronium ions of the acidic solution caused some functional groups (e.g., amine acetamide, hydroxyl) to protonate.

\[ -\text{NHCOCH}_3 + \text{H}_2\text{O}^+ \rightarrow -\text{NH}_2\text{COCH}_3^+ + \text{H}_2\text{O} \]

\[ -\text{NH}_2 + \text{H}_2\text{O}^+ \rightarrow -\text{NH}_2^+ + \text{H}_2\text{O} \]

\[ -\text{OH} + \text{H}_2\text{O}^+ \rightarrow -\text{OH}_2^+ + \text{H}_2\text{O} \]

The positively charged functional groups of the sorbents (-\text{NH}_2^+, -\text{OH}_2^+) electrostatically interact with the negatively charged groups of the dyes (-\text{SO}_3^-), greatly promoting sorption. As the pH increases, there are fewer and fewer hydronium ions in the system, limiting the protonation of functional groups. The lower number of positively charged functional groups translates to lower sorption efficiency of the anionic dyes. At pH > 4, the dye binding rate became relatively low, as only the primary amine groups (fairly sparse on the MES and MMS surface) are still being protonated. This explains the significant decrease in RB5 and RY84 sorption on the tested sorbents at pH 2–4. At high pH (pH > 9), dye sorption may have been further impeded by the negative charge attained by the sorbent, potentially caused by the deprotonation of certain (e.g., hydroxyl or carboxylic) functional groups upon interaction with the dissolved hydroxyl ions.

\[ -\text{COOH} + \text{OH}^- \rightarrow -\text{COO}^- + \text{H}_2\text{O} \]

\[ -\text{OH} + \text{OH}^- \rightarrow -\text{O}^+ + \text{H}_2\text{O} \]

The negatively charged functional groups electrostatically repulse the anionic dyes, suppressing sorption. RB5 and RY84 removal at high pH may have also been inhibited by competition with OH^- ions for sorption centers.

The positive effect of low pH on anionic dye sorption efficiency has been corroborated by studies on RB5 sorption onto purified chitin [27], feathers [28], and activated carbon [29], as well as RY84 sorption onto cotton fiber [30] and sunflower hulls [31].

The slight increase in RB5 sorption efficiency observed at pH 9 (Figure 3a) is caused by the primary amine groups in the dye structure. At pH 9, MES and MMS already possessed a total negative charge, while a significant amount of the amine groups of RB5 have been ionized (-\text{NH}_2^+). Despite the generally anionic nature of the RB5, its protonated amine functional group generates a local positive electric charge, which may have electrostatically interacted with the negatively charged sorbent’s surface, driving RB5 sorption.

The positive effect of pH 9 on RB5 sorption has also been reported in studies investigating its sorption on eggshell membranes [32] and cotton fiber [30]. However, the same positive effect is not noted for the RY84 group due to the lack of primary amine groups in the dye.

Sorbents based on mealworm exoskeletons and molts affect solution pH during sorption (Figure 3c,d). With starting pH of 4–10, the solution pH after sorption is 6.88–7.49 for MES and 6.77–7.40 for MMS. The type of dye has little effect on pH trends in the system. The pH-modifying capacity of the sorbents results from their high content of readily-ionized functional groups, such as amine or carboxyl groups. At low pH, protons from hydronium cations are bound to basic functional groups (-\text{NH}_2 + \text{H}_2\text{O} \rightarrow -\text{NH}_2^+ + \text{H}_2\text{O}). The solution pH is inversely proportional to the levels of hydronium ions. In contrast, at high pH, acidic functional groups release their protons, resulting in the neutralization of the hydroxide anions (-\text{COOH} + \text{OH}^- \rightarrow -\text{COO}^- + \text{H}_2\text{O}) and lower pH. The sorbents always tend towards a system pH close to the pH_{ZC} for the given sorbent (PZC—point of zero charges), i.e., the pH at which the number of positively charged sites on the tested sorbent is the same as the number of negatively charged ones. The point of zero charges determined for MES and MMS using Boehm titration is pH_{ZC} = 7.26 and pH_{ZC} = 7.02, respectively (Figure 3e,f). The higher pH_{ZC} determined for MES compared with MMS may be due to a higher number of basic functional groups (e.g., -\text{NH}_2 or -\text{NHCOCH}_3).
Subsequent stages of the study, as described in Sections 3.3 and 3.4, were carried out at optimal sorption pH for RB5 and RY84—pH 2.

3.3. Kinetics of Dye Sorption on MES and MMS

The time needed to reach the sorption equilibrium is within the 120–150 min range for both dyes (RB5 and RY84) and sorbents (MES and MMS) (Figure 4). Similar sorption times have also been reported in studies investigating RB5 sorption on carbonized carob tree biomass (120 min) [33] and loquat seed shells (150 min) [34], as well as RY84 sorption on wool [35] (180 min).

![Figure 4](image)

*Figure 4.* Trends in dye levels throughout the sorption process: (a) RB5 on MES, (b) RY84 on MES, (c) RB5 on MMS, and (d) RY84 on MMS. Pseudo-first-order model and pseudo-second-order model.

The rate of dye sorption on MES and MMS was the fastest at the start of the process. After just 10 min, the fraction of dyes sorbed is 54% to 61% of \( q_e \) for MES and 46% to 51% for MMS \( q_e \) (\( q_e \) — the amount of dye sorbed at equilibrium state).

The faster sorption at higher initial concentrations of RB5/RY84 probably resulted from the higher likelihood of dye molecules colliding with sorbent active sites, resulting in faster saturation of the sorption centers and termination of the process.
In each experimental group, the pseudo-second-order model shows the greatest fit to the data (higher values of $R^2$ and smaller values of Chi-square—$\chi^2$) (Table 1, Figure 4), which is typical of organic dye sorption on biosorbents [36–38].

**Table 1.** Kinetic parameters of sorption of anionic dyes onto MES and MMS, determined from the pseudo-first order and pseudo-second order models (based on the average of three measurements).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Dye</th>
<th>Concentration [mg/L]</th>
<th>First-Order Model</th>
<th>Second-Order Model</th>
<th>Exp. Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ [1/min]</td>
<td>$q_{e,cal.}$ [mg/g]</td>
<td>$R^2$</td>
<td>$\chi^2$</td>
</tr>
<tr>
<td>MES</td>
<td>RB5</td>
<td>50</td>
<td>0.0829</td>
<td>20.78</td>
<td>0.9717</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>0.0743</td>
<td>58.84</td>
<td>0.9581</td>
</tr>
<tr>
<td></td>
<td>RY84</td>
<td>50</td>
<td>0.0742</td>
<td>20.16</td>
<td>0.9758</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>0.0606</td>
<td>51.08</td>
<td>0.9499</td>
</tr>
<tr>
<td>MMS</td>
<td>RB5</td>
<td>50</td>
<td>0.0847</td>
<td>19.92</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>0.0706</td>
<td>43.72</td>
<td>0.9800</td>
</tr>
<tr>
<td></td>
<td>RY84</td>
<td>50</td>
<td>0.0675</td>
<td>16.00</td>
<td>0.9944</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>0.0553</td>
<td>34.92</td>
<td>0.9690</td>
</tr>
</tbody>
</table>

Initial dye levels have a significant effect on the $k$ and $q_e$ values derived from the pseudo-second-order model (Table 1). This may suggest that RB5 and RY84 have relatively low affinity to the sorbent active sites and that the sorbent efficiency is high only at high dye concentrations. The similar $k$ values for experimental groups with the same initial dye levels (Table 1) suggest that RB5 and RY84 follow similar sorption mechanisms on MES and MMS.

The data on dye sorption kinetics are also modeled using the intraparticle diffusion model (Table 2, Figure 5). The analysis of the resultant constants shows that the process unfolded in two primary sorption phases, characterized by different sorption rates and durations.

**Table 2.** Dye diffusion rate constants determined from the intraparticle diffusion model. * [mg/(g·min$^{0.5}$)].

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Dye</th>
<th>Concentration [mg/L]</th>
<th>Phase 1</th>
<th>Phase 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$</td>
<td>$q_{e,cal.}$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>MES</td>
<td>RB5</td>
<td>50</td>
<td>3.807</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>11.993</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>RY84</td>
<td>50</td>
<td>3.592</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>9.687</td>
<td>10</td>
</tr>
<tr>
<td>MMS</td>
<td>RB5</td>
<td>50</td>
<td>3.443</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>7.647</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>RY84</td>
<td>50</td>
<td>2.626</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>5.545</td>
<td>20</td>
</tr>
</tbody>
</table>

In the first phase, the dye molecules most likely diffused from the solution onto the surface of the sorbent and bound to the most accessible active sites. This phase is characterized by high sorption rates in a short amount of time. Once most of the sorbent active sites are saturated, the second phase commences, in which the dyes mainly occupy hard-to-reach sorption sites in the deeper layers of the sorbent. Due to the lower accessibility to remaining sorption sites and the increased competition between dyes, phase 2 is longer than the first, with lower sorption intensity (Table 2, Figure 5).

As already mentioned, the shorter length of phase 1 in the experimental groups with higher initial dye concentrations is due to the faster saturation of the active sites and, thus, the faster transition of the process to phase 2 (Table 2).

The MMS groups feature generally lower values of $k_a$ and a longer phase 1, suggesting that the sorbent surface had fewer sorption centers than MES (Table 2). The higher $k_a$ values determined for MES may also point to a higher sorption efficiency compared with MMS.
3.4. Maximum Sorption Capacity of MES and MMS

Maximum sorption capacity data for MES and MMS are modeled using three isotherms: Langmuir 1, Langmuir 2, Freundlich, and Dubinin–Radushkevich (Table 3, Figure 6). Judging by the $R^2$ coefficient of determination and the Chi-squared test ($\chi^2$), the Langmuir 2 model shows the greatest fit to data in all experimental groups. This indicates that at least two types of sorption centers play an important role in RB5/RY84 sorption on MES/MMS. Presumably, for both of the tested sorbents, the active sites in question are protonated amine (-NH$_3^+$), acetamide (-NH$_2$COCH$_3^+$), and hydroxyl groups (-OH$_2^+$) of chitin and protein.

Table 3. Constants determined from Langmuir 1, Langmuir 2, Freundlich, and Dubinin–Radushkevich models.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Dye</th>
<th>Langmuir 1 Model</th>
<th>Freundlich Model</th>
<th>Dubinin–Radushkevich Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Q_{\text{max}}$</td>
<td>$K_c$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>MES</td>
<td>RB5</td>
<td>71.65</td>
<td>0.084</td>
<td>0.986</td>
</tr>
</tbody>
</table>
Table 4 shows the sorption capacity of the sorbents towards RB5 and RY84. The sorption capacities of the tested mealworm exoskeletons and molts towards RB5 and RY84 are several times higher than those of plant-based sorbents (e.g., seed hulls and shells, fruit peel, and crop stems). MES and MMS have higher sorption capacity than some types of activated carbons (e.g., those derived from walnut wood, palm tree husks, or bamboo) and are exceeded only by commercial activated carbon and pure chitin (Table 4).
### Table 4. Comparison of the sorption capacity of biosorbents and activated carbons against BV10 and BR46.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Sorbent</th>
<th>Sorption capacity [mg/g]</th>
<th>pH of sorption</th>
<th>Time of sorption [min]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>RB5</td>
<td>Coconut shells</td>
<td>0.82</td>
<td>2.0</td>
<td>60</td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>Pumpkin seed husks</td>
<td>1.00</td>
<td>3.0</td>
<td>60</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>Sunflower biomass</td>
<td>1.10</td>
<td>3.0</td>
<td>210</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>Macadamia seed husks</td>
<td>1.21</td>
<td>3.0</td>
<td>510</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>Cotton fibers</td>
<td>2.74</td>
<td>3.0</td>
<td>240</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>Sunflower seed shells</td>
<td>2.89</td>
<td>3.0</td>
<td>210</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>Buckwheat hulls</td>
<td>4.43</td>
<td>3.0</td>
<td>300</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>Hen feathers</td>
<td>5.19</td>
<td>2.0</td>
<td>210</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>Cotton seed husks</td>
<td>12.90</td>
<td>2.0</td>
<td>30</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>The seed scales of <em>Eriobotrya japonica</em></td>
<td>13.76</td>
<td>3.0</td>
<td>150</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>Beech sawdust</td>
<td>13.90</td>
<td>3.0</td>
<td>1440</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>Wheat straw</td>
<td>15.70</td>
<td>7.0</td>
<td>195</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>Wheat straw (other research)</td>
<td>16.72</td>
<td>3.0</td>
<td>210</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>Wood (walnut) activated carbon</td>
<td>19.30</td>
<td>5.0</td>
<td>400</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>Activated carbon from palm shell</td>
<td>25.10</td>
<td>2.0</td>
<td>300</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>Banana peel (powder)</td>
<td>26.90</td>
<td>3.0</td>
<td>60</td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>Rape stalks (waste)</td>
<td>32.80</td>
<td>2.5</td>
<td>30</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>Cotton stems</td>
<td>35.70</td>
<td>1.0</td>
<td>360</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Activated carbon from Carob tree</td>
<td>36.90</td>
<td>2.0</td>
<td>120</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>Activated carbon from bamboo</td>
<td>39.02</td>
<td>2.0</td>
<td>60</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>Molts of mealworm (MMS)</td>
<td>55.72</td>
<td>2.0</td>
<td>150</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Powdered activated carbon</td>
<td>58.82</td>
<td>-</td>
<td>-</td>
<td>[54]</td>
</tr>
<tr>
<td></td>
<td>Chitin flakes from shrimp shells (produced by Sigma-Aldrich)</td>
<td>60.00</td>
<td>6.0</td>
<td>600</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>Modified activated carbon (SPC)</td>
<td>69.90</td>
<td>2.0</td>
<td>&lt;60</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>Mealworm exoskeletons (MES)</td>
<td>78.70</td>
<td>2.0</td>
<td>150</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Chitin from the molts of mealworm (own study) (CH)</td>
<td>121.15</td>
<td>3.0</td>
<td>300</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>Powdered activated carbon</td>
<td>125.79</td>
<td>2.0</td>
<td>240</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>Chitin flakes from snow crab shells (produced by BioLog Heppe)</td>
<td>131.56</td>
<td>3.0</td>
<td>360</td>
<td>[27]</td>
</tr>
<tr>
<td>RY84</td>
<td>Compost</td>
<td>2.20</td>
<td>3.0</td>
<td>180</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>Sunflower seed husks</td>
<td>4.15</td>
<td>2.0</td>
<td>90</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>Wool</td>
<td>11.00</td>
<td>7.0</td>
<td>180</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>Activated carbon from the <em>Borassus flabellifer</em> plant</td>
<td>40.00</td>
<td>No data</td>
<td>No data</td>
<td>[58]</td>
</tr>
<tr>
<td></td>
<td>Cotton fibers</td>
<td>43.34</td>
<td>2.0</td>
<td>240</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>Mealworm exoskeletons (MES)</td>
<td>44.25</td>
<td>2.0</td>
<td>150</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Hydroxyapatite</td>
<td>50.25</td>
<td>5.0</td>
<td>180</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>Molts of mealworm (MMS)</td>
<td>60.49</td>
<td>2.0</td>
<td>150</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Chitin from the molts of mealworms</td>
<td>138.54</td>
<td>3.0</td>
<td>270</td>
<td>[15]</td>
</tr>
</tbody>
</table>

The sorption capacity of non-processed mealworm exoskeletons and molts towards RB5 is 35.0% and 54.0% lower than that of pure chitin. Nevertheless, it seems that extracting chitin from mealworm exoskeletons/molts to be used as a sorbent for RB5 and RY84 is not commercially reasonable. Bearing in mind that exoskeletons and molts contain only up to 10% and 18% chitin, respectively, it follows that 1 g of mealworm exoskeletons and 1 g of mealworm molts have at least 549.3% and 155.4% higher sorption capacity, respectively, than chitin extracted from the equivalent amount of biomass (Table 5). This seems to confirm the starting hypothesis assuming that “the total sorption capacity of mealworm exoskeletons and molts against dyes is greater than the sorption capacity of pure chitin extracted from the same quantity of raw material”.
Table 5. Sorption capacity of MES, MMS, and derived chitin towards RB5.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Quantity of Sorbent [g]</th>
<th>Quantity of RB5 Removable by 1 g Sorbent [mg]</th>
<th>Max. Content of Chitin in Sorbent</th>
<th>Quantity of RB5 Removable by Chitin in 1 g of Sorbent [mg]</th>
<th>Ratio of Sorption Capacity to Chitin in the Sorbent [%]</th>
<th>Increase of Sorption Capacity in Relation to Chitin in the Sorbent [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitin from Mealworm Molts (CH)</td>
<td>1</td>
<td>121.15</td>
<td>100%—1.0 g</td>
<td>121.15</td>
<td>100.0</td>
<td>-</td>
</tr>
<tr>
<td>Mealworm Exoskeletons (MES)</td>
<td>1</td>
<td>78.70</td>
<td>10%—0.1 g</td>
<td>12.12</td>
<td>649.3</td>
<td>549.3</td>
</tr>
<tr>
<td>Mealworm Molts (MMS)</td>
<td>1</td>
<td>55.72</td>
<td>18%—0.18 g</td>
<td>21.81</td>
<td>255.4</td>
<td>155.4</td>
</tr>
</tbody>
</table>

4. Conclusions

Mealworm exoskeletons and molts can be successfully used as sorbents to remove dyes from aqueous solutions, providing greater performance than some types of activated carbon. The results confirmed the starting hypothesis assuming that “the total sorption capacity of mealworm exoskeletons and molts against dyes is greater than the sorption capacity of pure chitin extracted from the same quantity of raw material”. This suggests that extracting chitin for dye removal from mealworm exoskeletons/molts is not commercially reasonable.

The sorption pH is the primary factor determining dye sorption onto MES and MMS. RB5 and RY84 sorption efficiency on the tested sorbents peaked at pH 2. Sorbents based on mealworm exoskeletons and molts had a significant effect on solution pH changes during sorption. This is due to the system’s tendency toward a pH close to the pH\text{PZC} for the sorbent. The pH\text{PZC} values for MES and MMS were pH\text{PZC} = 7.26 and pH\text{PZC} = 7.02, respectively. The higher pH\text{PZC} for MES compared with MMS may point to a higher number of basic functional groups (e.g., -NH_2 or -NHCOCH_3) on the sorbent’s surface.

The time needed to reach the sorption equilibrium fell within the 120–150 min range for both dyes (RB5 and RY84) and sorbents (MES and MMS). The constants derived from the intraparticle diffusion model indicate that the dyes were adsorbed onto the tested sorbents in two distinct phases. The first, short-lasting phase (10–20 min) had high removal rates. In contrast, the second phase tended to last longer (100–130 min) and showed relatively lower intensity.

At least two types of sorption centers were shown to play an important role in RB5/RY84 sorption on MES/MMS. Presumably, for both the sorbents, the active sites in question were protonated amine (-NH_3^+), acetamide (-NH_2COCH_3^+), and hydroxyl groups (-OH^+) of chitin and protein.

Author Contributions: Conceptualization, T.J. and T.B.; methodology, T.J.; software, T.J.; formal analysis, U.F.; investigation, T.J.; resources, T.J., U.F., and T.B.; data curation, T.J.; writing—original draft preparation, T.J.; writing—review and editing, U.F.; visualization, T.J.; supervision, T.J.; project administration, U.F.; funding acquisition, T.J. and U.F. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financed under project No. 29.610.023-110 of the University of Warmia and Mazury in Olsztyn, Poland.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.
References


**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.