



# Article A Prominent Streptomyces sp. Biomass-Based Biosorption of Zinc (II) and Lead (II) from Aqueous Solutions: Isotherm and Kinetic

Sheetal Kumari <sup>1</sup><sup>(b)</sup>, Nitin Kumar Agrawal <sup>2</sup>, Animesh Agarwal <sup>2</sup>, Anil Kumar <sup>3</sup>, Neeraj Malik <sup>4</sup>, Dinesh Goyal <sup>5</sup>, Vishnu D. Rajput <sup>6</sup><sup>(b)</sup>, Tatiana Minkina <sup>6</sup><sup>(b)</sup>, Pinki Sharma <sup>7</sup><sup>(b)</sup> and Manoj Chandra Garg <sup>1,5,\*</sup><sup>(b)</sup>

- <sup>1</sup> Amity Institute of Environmental Science (AIES), Amity University Uttar Pradesh, Sector-125, Noida 201313, India
- <sup>2</sup> Department of Applied Sciences and Humanities, Moradabad Institute of Technology, Moradabad 244001, India
- <sup>3</sup> Department of Zoology, Kisan (P.G) College, Hapur, C. C. S. University, Simbhaoli, Meerut 245207, India
- <sup>4</sup> Department of Zoology, S.M. College Chandausi, Shambal, M. J. P. Rohilkhand University, Bareilly 243632, India
- <sup>5</sup> Department of Biotechnology, Thapar Institute of Engineering & Technology, Patiala 147004, India
- <sup>6</sup> Academy of Biology and Biotechnology, Southern Federal University, 344090 Rostov-on-Don, Russia
- <sup>7</sup> Department of Hydrology, Indian Institute of Technology Roorkee, Roorkee 247667, India
- \* Correspondence: manoj28280@gmail.com

Abstract: Traditional freshwater sources have been over-abstracted in the worldwide crisis of water scarcity. Effluents have extremely high amounts of Zn<sup>2+</sup> and Pb<sup>2+</sup>, according to an investigation of wastewater samples taken from several industrial zones. However, these heavy metals are among the most harmful to both humans and wildlife that are currently known. Streptomyces sp. is utilized in this study as a biosorbent to biosorb  $Zn^{2+}$  and  $Pb^{2+}$  from single and binary aqueous solutions. Several factors, such as biomass concentration (0.25-4 g), metal solution concentration  $(5-50 \text{ mg L}^{-1})$ , solution pH (2-5), and contact time were standardized. Streptomyces sp. biomass was able to extract 93% Pb<sup>2+</sup> and 91% Zn<sup>2+</sup> from a single and 95% Pb<sup>2+</sup> and 97% Zn<sup>2+</sup> from a binary metal aqueous solution containing 25 mg  $L^{-1}$  and pH 4. The highest adsorption capacity in both single and binary sorption experiments was determined to be shared by Zn2+ and Pb2+. The biosorbent's metal adsorption increased from 0.48 to 4.56 mg g<sup>-1</sup> for Pb<sup>2+</sup> and from 0.21 mg g<sup>-1</sup> to 4.65 mg g<sup>-1</sup> for Zn<sup>2+</sup> when the metals were present singly, and from 0.44 to 4.18 mg  $g^{-1}$  for Pb<sup>2+</sup> and from 0.41 mg  $g^{-1}$  to 5.67 mg  $g^{-1}$ for  $Zn^{2+}$  when the metals were present in binary form. The amount of metal ions was raised from 5 to 50 mg L<sup>-1</sup>. Correlation coefficient ( $R^2$ ) values indicate that the adsorption pattern for  $Zn^{2+}$  and  $Pb^{2+}$ followed Freundlich isotherm  $R^2 > 0.9543$  for single and 0.9582 for binary sorption system. In order to remove  $Zn^{2+}$  and  $Pb^{2+}$  from an aqueous solution, *Streptomyces* sp. is a potential and different source of adsorbents.

Keywords: biosorption; Freundlich isotherm; heavy metal

# 1. Introduction

Heavy metal pollution of water is a global issue that is becoming worse. Many metals have been found to be highly toxic. Heavy metals can accumulate through the food chain even in low amounts, posing major risks to people, animals, and the environment [1]. The potential health risk presented by environmental heavy metals is receiving more and more attention. However, as a result of various human activities like mining and industrial processes, natural biogeochemical cycles are disturbed, leading to an increase in the deposition of heavy metals in terrestrial and aquatic environments [2]. Many sectors discharge heavy metals like lead and zinc in wastewater, particularly plating, battery, pigment, and ammunition production [3]. The need for innovative metal removal methods



Citation: Kumari, S.; Agrawal, N.K.; Agarwal, A.; Kumar, A.; Malik, N.; Goyal, D.; Rajput, V.D.; Minkina, T.; Sharma, P.; Garg, M.C. A Prominent *Streptomyces* sp. Biomass-Based Biosorption of Zinc (II) and Lead (II) from Aqueous Solutions: Isotherm and Kinetic. *Separations* **2023**, *10*, 393. https://doi.org/10.3390/ separations10070393

Academic Editors: Eduardo Díez and Araceli Rodríguez

Received: 17 May 2023 Revised: 23 June 2023 Accepted: 28 June 2023 Published: 4 July 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). is growing as a result of strict environmental legislation and the authority granted to the institutions set up to implement these laws. For more than ten years, experts have been searching for less expensive and more efficient ways to clean up heavy metal-contaminated streams and lessen the rising risk to the public's health [4]. The most widely used methods for removing metal ions from wastewater are electrodialysis, chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction, and ultrafiltration [5,6]. The biosorption approach has become a popular and affordable replacement for traditional water and wastewater treatment over the past 20 years [7].

Currently, a large number of studies published in various journals have enriched the biosorption field. When heavy metal pollutants are present in large amounts of solution in trace quantities, these approaches become ineffective. One of the few options for such a situation is adsorption.

Several microorganisms, including bacteria, algae, fungi, and yeast cells, are capable of removing heavy metals from aqueous solutions [8]. In fact, metal ions in solution interact with bacteria. Numerous studies examining the interactions between metals and bacteria have, for instance, suggested using bacterial biomass to treat effluents for metal removal. Heavy metal removal via microbial biomass, also known as biosorption, has received a lot of interest recently. Streptomyces species have advantages including minimal investment costs and good treatment efficiency because they are stable and do not require harsh treatments. The most prevalent microscopic filamentous bacteria in the environment are strains of *Streptomyces*. This strain is frequently employed to research complex processes, such as the biosorption or adsorption of heavy metals. A filamentous form of the Gram-positive bacterial genus *Streptomyces rimosus* has been suggested by numerous studies examining the interactions between bacteria and metals. It can grow in a variety of settings. Marine algae, bacteria, yeasts, fungi, and waste mycelia from the food and fermentation industries are some examples of biosorbents [9]. Some types of biomass waste from industrial fermentation make excellent metal absorbers. *Streptomyces* species have advantages including minimal investment costs and good treatment efficiency because they are stable and do not require harsh treatments. It is important to understand that some waste biomass—which can be collected as waste products from fermentation industries—is actually a commodity, not garbage. Waste could be one of the most accessible and affordable sources for the removal of heavy metals. Even though many different kinds of bacteria have been extracted, research utilizing metal-tolerant bacteria from industrial effluent has demonstrated that collecting and identifying native bacteria is crucial since they are ecologically responsible and maintain the ecosystem in their area [10]. The use of industrial waste biomass as a biosorbent would increase the economic viability of a microbial-based system because the biomass is cheap, easy to recover after fermentation, and produced in vast quantities. Adsorbents made of nanocomposites were used to remove heavy metals from aqueous solutions [7]. Ion-imprinted polymers have been utilized to remove heavy metal ions from complex matrices at low concentrations.

Table 1 provides a comprehensive comparison of different treatment approaches for the removal of heavy metals, specifically focusing on biosorption as compared to other methods. Biosorption, which involves the adsorption of heavy metals onto biosorbents such as biomass, algae, or microorganisms, offers several advantages. It exhibits high removal efficiency for specific metals, making it suitable for a wide range of applications. Biosorption can be highly selective for targeted metals, allowing for effective metal removal while minimizing the impact on other components in the water. Additionally, biosorption is often cost-effective, requiring minimal energy and generating minimal waste. In contrast, the other treatment approaches listed in the table offer alternative strategies for heavy metal removal. Chemical precipitation involves the formation of insoluble precipitates with heavy metals, while ion exchange uses solid resin materials to selectively exchange metal ions [11]. Electrocoagulation utilizes electrochemical processes to induce coagulation and removal of heavy metal ions, and membrane filtration relies on the passage of water through semi-permeable membranes to separate heavy metals [12]. Activated carbon adsorption is another effective method, utilizing the high affinity of activated carbon for heavy metals. Each method has its own unique advantages and limitations [13]. Factors such as removal efficiency, selectivity to different metals and conditions, cost, and environmental impact vary among the different treatment approaches. For example, chemical precipitation and ion exchange are relatively cost-effective, while membrane filtration and activated carbon adsorption offer high selectivity [12,14,15]. However, they may also have limitations, such as the generation of sludge, membrane fouling, or the need for regeneration. Understanding the characteristics and differences of these treatment approaches is crucial in selecting the most suitable method for a specific heavy metal removal application. The table serves as

Table 1. Comparison of heavy metal treatment approaches: biosorption vs. other methods.

a valuable reference, providing an overview of the key features and considerations when

Treatment Approach	Principle	Efficiency	Selectivity	Cost	Environmental Impact	References
Biosorption	Adsorption of heavy metals onto biosorbents such as biomass, algae, or microorganisms	High removal efficiency for specific metals	Can be highly selective for specific metals	Generally cost-effective	Low energy requirements and minimal waste generation	[13]
Chemical Precipitation	Formation of insoluble precipitates with heavy metals	Varies depending on the specific metals and conditions	Limited selectivity based on solubility and pH	Relatively cost-effective	Generation of sludge or precipitates as byproducts	[14]
Ion Exchange	Exchange of heavy metal ions with ions on solid resin	High removal efficiency for specific metals and conditions	Selective based on resin properties and operating	Relatively cost-effective	Generation of brine or regenerant solution	[15]
Electrocoagulation	Electrochemical coagulation and floc formation	Varies depending on the operating parameters	Moderate selectivity based on the membrane pore size	Relatively cost-effective	Generation of sludge or byproducts	[12]
Membrane Filtration	Passage of water through a semi-permeable membrane	Varies depending on the membrane properties	Varies depending on the surface properties	Varies depending on the specific application	Energy requirements depend on the membrane type	[11]
Activated Carbon Adsorption	Adsorption of heavy metals onto activated carbon	High affinity for heavy metals	High selectivity based on metals and chemical species	Varies depending on the	Generation of spent carbon as a byproduct	[13]
Chemical Oxida- tion/Reduction	Chemical conversion of heavy metals to less soluble or less toxic forms	Varies depending on the chemical reaction and conditions	Selective based on the target metals and the chosen oxidizing or	Varies depending on the specific application specific application	Generation of byproducts or residual chemicals	[16]
Membrane Processes	Selective removal of heavy metals through ion-exchange membranes	Varies depending on the membrane properties and operating conditions	Selective based on the membrane properties and ion exchange capacity	Varies depending on the membrane and system setup	Low energy requirements and minimal waste generation	[11]

comparing biosorption with other treatment methods.

The objective of the current study was to evaluate the efficacy of *Streptomyces* sp. biomass for the adsorption-based removal of  $Zn^{2+}$  and  $Pb^{2+}$ . To ascertain *Streptomyces* sp.'s adsorption capability, batch isotherm and kinetic investigations were carried out in the laboratory. The impact of pH, biomass volume, and beginning metal concentration on removal was investigated. People around the site suffered severe health problems from both contaminants, so Pb (II) and Zn (II) metal ions will be the focus of the research [17].

# 2. Materials and Methods

# 2.1. Preparation of Adsorbent

*Streptomyces* sp. biomass, a by-product of the fermentative procedures used in pharmaceutical fermentation, was gathered from Ranbaxy Paonta Sahib in Himachal Pradesh, India. Biomass was dried in an oven at 80 °C for two days, blended into a smooth paste, and sieved to obtain uniform particle size (2 mm) before being used as an adsorbent to extract heavy metals from an aqueous solution.

## 2.2. Preparation of Adsorbate

One liter of water was used to dissolve 4.397 g of zinc sulphate (Zn(SO<sub>4</sub>)) and 1.83 grammes of lead acetate (Pb( $C_2H_3O_2$ )<sup>2</sup>) to create a single and binary metal stock solution containing 1000 mg L<sup>-1</sup> of Zn<sup>2+</sup> and Pb<sup>2+</sup>. The stock solution (1000 mg/L) was diluted with distilled water to produce a working solution (5 to 50 mg L<sup>-1</sup>). The pH was then raised from 2 to 5 by adding 1N NaOH and 1N HCl to the solution.

#### 3. Biosorption Studies

Streptomyces sp.'s ability to biosorb heavy metals was assessed in batch mode using a single and binary metal sorption tool. The batch experiment was carried out in a 250 mL Erlenmeyer flask with various adsorbent dosages (0.25–2%) while maintaining a constant heavy metal concentration (25 mg/L) and shaking it for 24 h at room temperature and 120 rpm on an open rotary shaker. Similar to this, batch tests at various pH ranges (2 to 5) and metal concentrations (5 to 50 mg L<sup>-1</sup>) were carried out. Samples were extracted at intervals ranging from 0.08 to 24 h.

#### 3.1. Determination of Total Residual Metal

An atomic absorption spectrophotometer (GBC 932AA, Artarmon, Australia) was used to measure the total residual concentration of metal in the filtrate. The standard was a working standard solution of  $Zn^{2+}$  and  $Pb^{2+}$  made from 1000 mg of  $L^{-1}$  stock purchased from Acros Organic Ltd. in Morris Plains, New Jersey, USA. The calculation of residual concentration R (%) is given as [18].

$$R(\%) = \frac{C_i - C_f}{C_i} 100$$
 (1)

where the initial and final metal concentrations,  $C_i$  and  $C_f$ , are measured in mg L<sup>-1</sup>.

#### 3.2. Metal Uptake by Biomass

The following formula was used to compute specific metal uptake  $(q_e)$ :

$$q_e = \frac{C_i - C_f}{m} V \tag{2}$$

where *V* is the volume of the metal solution in mL,  $C_i$  and  $C_f$  are the initial and final metal concentrations at a given time in mg L<sup>-1</sup>, respectively, and *m* is the mass of the biomass in g.

# 4. Adsorption Isotherm

It is essential to analyze the isotherm data in order to create an equation that accurately captures the outcomes and can be applied to design. To evaluate the viability and effectiveness of biosorption in wastewater treatment, it is critical to determine the performance of the sorption [19]. The surface characteristics, the affinity of *Streptomyces* sp. cells' binding sites, and the uptake mechanism are all shown using the isotherm model. Therefore, it is essential to create suitable biosorption mathematical models. In order to evaluate the experimental data, the adsorptive isothermal model and the Freundlich equation were applied.

#### 4.1. Freundlich Model

The heterogeneous distribution of the sorbent's active sites in the monolayer sorption scenario is also taken into consideration by this isotherm [20].

$$q_e = K_f C_e^{1/n} \tag{3}$$

where  $K_f$  denotes adsorption intensity and n, adsorption capacity. Logarithmic form of Equation (5)

$$\log_e q_e = \log_e \left( K_f C_e^{1/n} \right) \tag{4}$$

$$= \log_e K_f + \log_e C_e^{1/n} \tag{5}$$

$$\log_e q_e = \log_e K_f + \frac{1}{n} \log_e C_e \tag{6}$$

The linear plot of log ( $q_e$ ) vs. loge ( $C_e$ ) can be used to calculate  $K_f$  and 1/n. The parameters were calculated using experimental values from experiments on adsorption capacity.

#### 4.2. Langmuir Model

Langmuir isotherm: The Langmuir isotherm assumes a homogeneous adsorbent surface and a monolayer adsorption process, where adsorption occurs at specific sites on the surface. It suggests that once a site is occupied, no further adsorption can occur at that site.

$$q = (q_{\max} b C_e) / (1 + b C_e)$$
(7)

where q is the amount of adsorbate per unit mass of adsorbent (mg/g), qmax is the maximum adsorption capacity (mg/g), b is the Langmuir constant related to the energy of adsorption (L/mg), and  $C_e$  is the equilibrium concentration of the adsorbate in the solution (mg/L).

## 5. Kinetic Study

Kinetic modelling is a valuable approach for process equipment design, as it replaces the need for laborious and resource-intensive experiments. The acquired kinetic information is highly practical and applicable in various technological fields. In this study, different kinetic models were employed to establish a correlation between the kinetics of metal ions adsorbed in *Streptomyces* sp. biomass. The researchers focused on assessing the biosorption kinetics by studying the removal of heavy metals, namely zinc ( $Zn^{2+}$ ) and lead ( $Pb^{2+}$ ), using *Streptomyces* sp. at different temperatures. The investigation considered a two-kinetics model that encompasses the pseudo-first order and pseudo-second order reactions. To explore the kinetics further, the researchers conducted experiments with varying exposure times ranging from 5 to 90 min.

#### Mechanism of Biosorption

The initial step in the interaction between metals and cell walls involves the biosorption of metal ions, which typically occurs on microorganisms' outer surfaces. At the outer surfaces of bacterial cells, metal ions can be physically held in place by electrostatic or van der Waals forces. Subsequently, through chemical interactions, the adsorbed metal ions can bind to the chemical functional groups of biomolecules present on the cell surface and even within the cellular structure [7]. Physical adsorption, characterized by a weak van der Waals attraction between the adsorbate and the surface, is an exothermic process that occurs spontaneously according to thermodynamics. The mechanism of the adsorption process involves four sequential processes:

(1) Transportation of metal ions from the surrounding bulk liquid to the liquid film or boundary layer.

(2) Surface diffusion, where metal ions migrate from the boundary film to the external surface of the adsorbent.

(3) Pore diffusion, where metal ions move from the surface towards the intraparticle active sites within the adsorbent.

(4) Sorption-based metal ion uptake at the active locations. The mechanism of the contacts during the adsorption process is broken down into four parts that follow one another.

# 6. Results

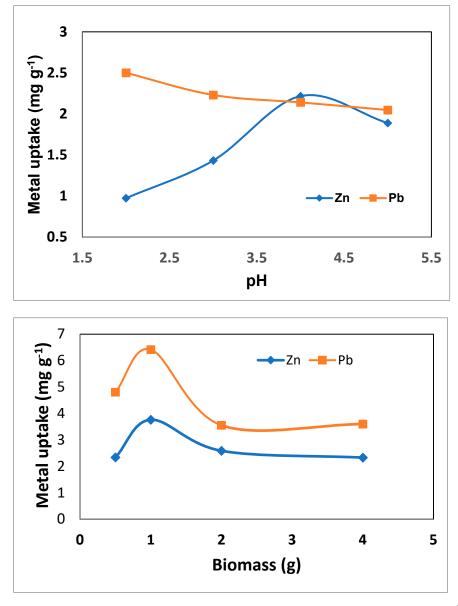
Investigations on the biosorption of Zn<sup>2+</sup> and Pb<sup>2+</sup> from solutions of single and binary metals were conducted at various pH levels, biomass amounts, and metal concentrations during various contact times.

# 6.1. Effect of pH

The biosorption process is significantly regulated by pH. The variation of equilibrium uptake with the initial pH of the  $Zn^{2+}$  and  $Pb^{2+}$  solution is shown in Figure 1.  $Zn^{2+}$ biosorption was significantly increased when the pH was elevated to 2 to 4 and dropped when the pH was between 4 and 5.  $Zn^{2+}$  biosorption increased from 0.974 mg g<sup>-1</sup> to 2.217 mg g<sup>-1</sup>. The pH range of 2 to 5 resulted in a Pb<sup>2+</sup> biosorption (2.5 mg g<sup>-1</sup> to 2.04 mg  $g^{-1}$ ) (Figure 1). The greatest pH (pH 4) at which both heavy metals were still dissolved but not precipitated was used in this study to identify the appropriate pH (Figure 1). Numerous studies show that pH significantly affects how well heavy metals are absorbed from aqueous solutions [21]. The primary variable that affects the initial capacity and rate of metal ion biosorption by biosorbents is the pH of the sorption medium. As the stability of the metal ionic species in the solution reduces, it is generally accepted that the sorption of metal cations like Cd<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, and Co<sup>2+</sup> increases with pH [22]. As seen in Figure 1, when the pH declined (2-4), the surface charge of the cells increased overall, but this caused an electrostatic interaction between positively charged binding sites and negatively charged metal complex ions. As a result, metal absorption increased significantly at pH 4 (from 0.974 mg  $g^{-1}$  to 2.217 mg  $g^{-1}$ ). However, the biosorption decreased (from 2.5 mg  $g^{-1}$  to 2.04 mg  $g^{-1}$ ) and the overall surface charge on the cells turned negative as the pH increased from 4 to 5. The increase in biosorption that is observed with increasing pH (2 to 4) values could be brought on by changes to the sorbent surface, which alters how metal complex ions interact with cells primarily through electrostatic forces, complex formation or electron sharing in nature, or changes to membrane transport. However, as pH increases, H+ ions that are directly connected to the adsorbent or that are a part of surface functional groups like OH, COOH, etc. are replaced by Pb(II) and Zn(II) ions, which reduces the amount of competition. Another possibility is that the metal ion will adsorb as a result of the  $Pb(OH)^+$  and  $Zn(OH)^2$  ions bonding to the adsorbent surface [23,24].

# 6.2. Effect of Biomass Amount

Figure 1 shows the influence of initial biomass amount on *Streptomyces* sp.'s equilibrium metal uptake of both  $Zn^{2+}$  and  $Pb^{2+}$  metal solution. For both  $Zn^{2+}$  (3.76 mg g<sup>-1</sup>) and  $Pb^{2+}$  (6.41 mg g<sup>-1</sup>) at pH 4 and 25 mg L<sup>-1</sup> metal concentration, the greatest equilibrium uptakes were seen at 1 g biomass. Higher densities of binding sites may interfere with one another, which could explain this. The higher metal-to-biosorbent ratio at 1 g of *Streptomyces* sp. biomass may be the cause of the higher metal sorption, which decreases when the biomass amount is raised [25].



**Figure 1.** The effect of pH and amount of biomass (g) on the equilibrium uptake of  $Zn^{2+}$  and  $Pb^{2+}$  by *Streptomyces* sp. (room temperature; agitation rate = 120 rpm,  $C_i = 25 \text{ mg } \text{L}^{-1}$ ).

For the biosorption of Cd (II) (Tamilselvan et al. 2012) and Ni (II) [26], a comparable trend of metal removal (%) with increases in biosorbent dose was observed. Even if there was a failure of proportionality in the biosorption at larger biomass doses, the higher metal removal percentage at such doses is simply a result of the higher availability of metal-binding sites. Cell agglomeration under high biosorbent dose results in a decrease in the intercellular distance, which protects metal ion binding sites by reducing their exposure [27].

# 6.3. Effect of Metal Ion Concentration

The relationship between the initial  $Zn^{2+}$  and  $Pb^{2+}$  concentrations and the equilibrium metal absorption of *Streptomyces* sp. for both single and binary metal biosorption systems was investigated. The amount of *Streptomyces* sp. used in this study was 0.25–4 g. Similar outcomes for Cd (II) removal were reported by [28], employing cuttlebone and the alga Anabaena sphaerica, respectively. The biosorption process is facilitated by the higher thrusting force caused by the increasing variations in metal concentration between the cell surface and the bulk solution [29].

The percentage removal of  $Zn^{2+}$  ions from aqueous solutions through biosorption by *Streptomyces* sp. was found to be higher than that of Pb<sup>2+</sup> ions in single metal biosorption at a concentration of 10 mg L<sup>-1</sup>. However, as the concentrations increased (from 10 to 50 mg/L), the percentage removal of  $Zn^{2+}$  ions decreased (Table 2). Conversely, the percentage removal of  $Zn^{2+}$  ions was lower than that of Pb<sup>2+</sup> ions in binary metal biosorption at all concentrations ranging from 5 to 50 mg L<sup>-1</sup>.

**Table 2.** Percentage removal of  $Zn^{2+}$  and  $Pb^{2+}$  from single and binary metal aqueous solution by *Streptomyces* sp.

		% Re	moval		
Concentration (mg L <sup>-1</sup> ) –	Single Sorption System		Binary Sorption System		
(ling L =)	Zn <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Pb <sup>2+</sup>	
5	86.86	73.05	92.13	98.43	
10	86.53	87.35	95.23	96.57	
15	77.08	90.63	94.75	95.9	
25	90.76	93.04	97.04	94.96	
50	90.41	92.52	97.82	97.26	

This observation suggests that  $Pb^{2+}$  ions tend to occupy a significant number of available binding sites, which hinders the adsorption of  $Zn^{2+}$  ions. Consequently, the biosorption capacity for  $Zn^{2+}$  ions is relatively poor in both single and binary metal sorption systems compared to  $Pb^{2+}$  ions.

These findings highlight the competitive nature of metal ions for binding sites on the biosorbent. The higher affinity of the biosorbent for  $Pb^{2+}$  ions and its preference for binding sites can lead to reduced  $Zn^{2+}$  ion adsorption, especially at higher metal concentrations.

## Equilibrium Modeling

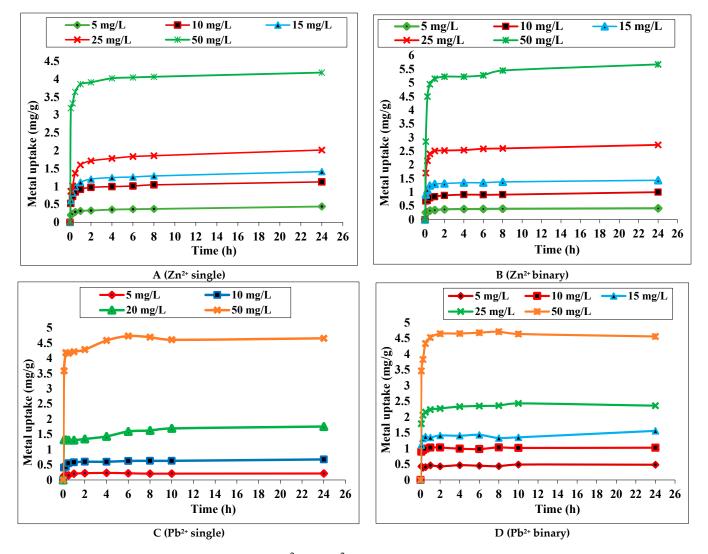
For both biosorption systems, *Streptomyces* sp. found that the equilibrium sorption capacity of biomass increased with an increase in the initial  $Zn^{2+}$  and  $Pb^{2+}$  concentration up to 50 mg L<sup>-1</sup>, as indicated in Table 3.

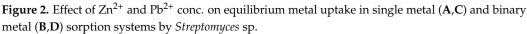
Conc.		) for a Single ption System	q <sub>max</sub> (mg g <sup>-1</sup> ) for Binary Metal Biosorption System		
(mg $L^{-1}$ )	q <sub>pb</sub>	q <sub>zn</sub>	q <sub>pb</sub>	$q_{zn}$	Total q ( $q_{pb} + q_{zn}$ )
5	0.21	0.48	0.41	0.44	0.85
10	0.67	1.02	1.00	1.13	2.13
15	1.75	1.56	1.43	1.42	2.85
25	2.58	2.36	2.72	2.02	4.74
50	4.65	4.56	5.67	4.18	9.85

Table 3. Streptomyces sp. equilibrium metal uptake for a single and binary aqueous solution.

The loading capabilities of biosorbents for a singular metal exhibited an increment from 0.48 to 4.56 mg g<sup>-1</sup> and from 0.21 mg g<sup>-1</sup> to 4.65 mg g<sup>-1</sup> correspondingly, as the initial concentrations of Zn<sup>2+</sup> and Pb<sup>2+</sup> metals were augmented from 5 to 50 mg L<sup>-1</sup>. Similarly, within the binary biosorption system, the loading capacities of the biosorbents witnessed an escalation from 0.44 to 4.18 mg g<sup>-1</sup> for Zn<sup>2+</sup> and from 0.41 mg g<sup>-1</sup> to 5.67 mg g<sup>-1</sup> for Pb<sup>2+.</sup> The heightened loading capacity of the biosorbents with the augmentation of Zn<sup>2+</sup> concentration may be attributed to an augmented likelihood of collisions occurring between the ions and the biosorbents. To evaluate the adsorption yields, experimental data encompassing diverse initial Zn<sup>2+</sup> and Pb<sup>2+</sup> concentrations were utilized (Table 1).

The equilibrium uptakes for  $Zn^{2+}$  biosorption from an aqueous solution by *Streptomyces* sp. was higher than Pb<sup>2+</sup> biosorption for both single and binary metals at low concentrations (5 to 10 mg L<sup>-1</sup>), whereas it was decreased at higher concentrations (15 to 50 mg L<sup>-1</sup>) (Table 3 and Figure 2). This indicates that, at greater metal concentrations (15 to 50 mg L<sup>-1</sup>), Pb<sup>2+</sup> appears to have occupied its binding sites, where  $Zn^{2+}$  adsorption occurred relatively poorly in both single and binary metal sorption systems.





# 7. Isotherm Study

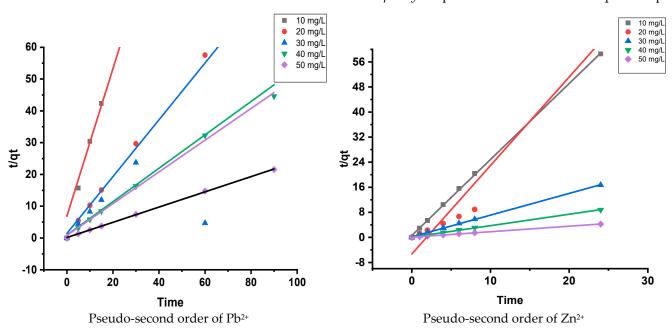
The sorption performance of *Streptomyces* sp. biomass was comprehensively assessed through the determination of sorption isotherms involving the heavy metals  $Zn^{2+}$  and  $Pb^{2+}$  (as presented in Table 4). It is discernible that, within both single and binary metal sorption systems, the adsorption capacity of *Streptomyces* sp. exhibited a consistent trend. According to the findings, the Freundlich isotherm may be more relevant to explain the nature of heavy metals adsorption on the prepared *Streptomyces* sp. biomass than the Langmuir isotherm. Notably, the adsorption capacity for  $Zn^{2+}$  (ranging between 1.5 and 3.28) consistently surpassed that for Pb<sup>2+</sup> (ranging between 0.8769 and 2.4).

			Freundlich	n Constant				
Marial	Single Sorption System			Bina	inary Sorption System			
Metal	K <sub>f</sub>	n	<b>R</b> <sup>2</sup>	K <sub>f</sub>	n	<b>R</b> <sup>2</sup>		
Zn <sup>2+</sup>	1.5	2.88	0.9543	3.28	0.835	0.9463		
Pb <sup>2+</sup>	0.8769	0.3649	0.9348	2.4	1.474	0.8857		
			Langmuir	Constant				
Matal	Single Sorption System			Bina	ry Sorption Sy	Sorption System		
Metal	q <sub>max</sub>	b	<b>R</b> <sup>2</sup>	q <sub>max</sub>	b	<b>R</b> <sup>2</sup>		
Zn <sup>2+</sup>	-2.44	-0.27	0.8595	-1.26	-0.74	0.9371		
Pb <sup>2+</sup>	0.38	0.52	0.7750	2.67	2.78	0.8582		

**Table 4.**  $Zn^{2+}$  and  $Pb^{2+}$  biosorption isotherm parameters for single and binary metals by *Streptomyces* sp.

#### 8. Kinetics Study

A quick approach typical of employing non-living biomass was used for the biosorption of zinc and lead onto the *Streptomyces* sp. One of the most crucial aspects of studying biosorption mechanisms and designing adsorption systems is estimating the biosorption rate for a specific system [30]. In the present investigation, the kinetic experimental data were meticulously scrutinized using an array of mathematical models to discern and characterize the distinct biosorption mechanisms operating within each system. The evaluation of the correlation coefficients (R<sup>2</sup>) pertaining to the pseudo-first order kinetic constants revealed their comparative diminution in relation to those obtained from alternative kinetic equations (as depicted in Table 5). The experimental sorption data exhibiting correlation coefficients surpassing the notable threshold of 0.999 demonstrated the most conspicuous alignment with the pseudo-second order kinetic model (Figure 3) [31]. The pseudo-second order equation has an R<sup>2</sup> coefficient of 0.999, which is the best fit for zinc and lead. The results indicate that the pseudo-second order binding mechanism predominates, and the zinc and lead are adsorbed on the *Streptomyces* sp. adsorbent via a chemisorption step.



**Figure 3.** Graphical plot of pseudo-second order for the biosorption of Pb<sup>2+</sup> and Zn<sup>2+</sup>.

Kinetics Model	Parameters	Zinc	Lead
Pseudo-first order	$k_1 (min^{-1})$	0.0054	0.0130
	qe (mg g <sup>-1</sup> ) R <sup>2</sup>	1.1219	1.3447
	$R^2$	0.6413	0.9265
Pseudo-second order	$\begin{array}{c} k_2 \ (min^{-1}) \\ qe \ (mg \ g^{-1}) \\ R^2 \end{array}$	10.121	0.7877
	qe (mg g $^{-1}$ )	0.4122	0.4308
	$R^2$	0.9996	0.9879

Table 5. Kinetic biosorption parameters.

#### 9. Characterization

# 9.1. Scanning Electron Microscopy

A well-known microscopy technique called scanning electron microscopy (SEM) is increasingly employed to study biological samples and other types of microscopic particles. SEM micrographs of *Streptomyces* sp. exposed to heavy metals were taken to identify morphological alterations in its biomass. The results of the SEM study confirmed that adding heavy metals had a detrimental effect on the biomass of *Streptomyces* sp. as shown in Figure 4. An SEM analysis of the biomass surface revealed that it is porous and compatible with good metal uptake capacity [32]. Figure 4B shows the formation of a thick, assembled heavy metal attachment to *Streptomyces* sp. surface, as well as the buildup of heavy metal molecules inside the porosity structure.

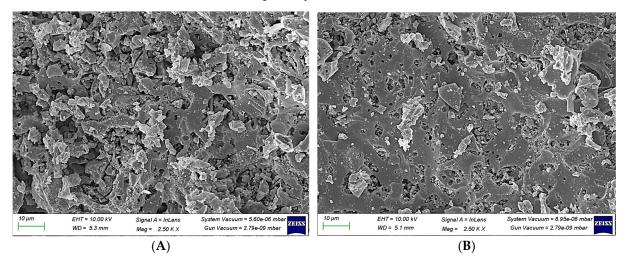
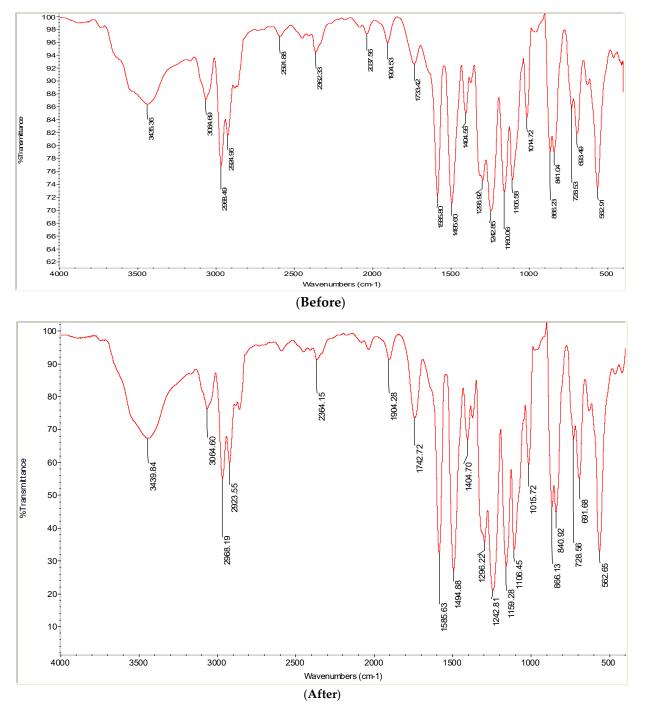


Figure 4. SEM micrograph of the (A) Before & (B) After *Streptomyces* sp. biomass.

#### 9.2. FTIR

An FTIR (Fourier transform infrared) analysis was employed to elucidate the assortment of functional groups existing before and after on the surface of the generated biomass. Spectra within the range of 4000–450 cm<sup>-1</sup> were subjected to examination with a resolution of 4 cm<sup>-1</sup>. As reported by [33], the IR spectra of the compound exhibited distinctive bands at specific wavenumbers: 3435, 3064, 2968, 2924, 2591, 2362, 1904, 1733, 1106, and 562 cm<sup>-1</sup>. These bands were indicative of the presence of primary amine, hydroxyls, alkenes, primary amide, and carbonyl groups (Figure 5). Notably, the surface of *Streptomyces* sp. displayed the presence of carboxyl and carbonyl groups, which could potentially contribute to the binding of heavy metals [34]. Furthermore, the investigation revealed that carboxyl, amino, amide, and hydroxyl groups predominated within the structural composition of *Streptomyces* sp. While an alkane is responsible for a high peak at 3064 cm<sup>-1</sup>, an O-H stretching vibration is responsible for one at 3435 cm<sup>-1</sup>. Figure 5 (after) demonstrates the shift in the position of these bands during heavy metal adsorption, demonstrating the active involvement of the assigned functional groups. The appearance of the primary peaks associated with raw *Streptomyces* sp. at 1733 and 1586 cm<sup>-1</sup> indicates the presence of a large number of aliphatic,

aromatic, and nitro compounds [9]. The peaks are brought on by ring C-C stretching, nitro compound N-O stretching, and aliphatic/aromatic amine C-N stretching [17]. The fact that the characteristic peaks in the FTIR spectra barely moved indicates that *Streptomyces* sp. were successful in absorbing heavy metals. Chemical adsorption between the functional groups of *Streptomyces* sp. and the heavy metals is evident from FTIR measurements.



**Figure 5.** FTIR spectrum of (**Before**) and (**After**) *Streptomyces* sp. biomass for biosorption of heavy metals ( $Zn^{2+}$  and  $Pb^{2+}$ ).

## 10. Conclusions

Heavy metal biosorption is a potential alternative to current methods. In this study, *Streptomyces* sp. was used to show how single and binary heavy metals can be absorbed from the solution. The biosorption equilibrium has been described using a variety of

empirical models for metal absorption by *Streptomyces* sp. The most well-known and frequently utilized model, which accurately captured the behavior of monolayer adsorption, is the Langmuir equation. The findings revealed that the binary sorption system's overall adsorption capacity had increased. When the initial  $Zn^{2+}$  and  $Pb^{2+}$  concentration was increased for *Streptomyces* sp., the loading capacities of the biosorbents were also increased for single and binary metal biosorption. In the examined single and binary metal biosorption systems, it was observed that *Streptomyces* sp. exhibited a higher uptake of  $Zn^{2+}$  compared to Pb<sup>2+</sup> at lower concentrations (5 to 10 mg L<sup>-1</sup>), followed by a decrease in uptake at higher concentrations (15 to 50 mg L<sup>-1</sup>). This trend was consistently observed in both single and binary metal sorption systems, highlighting the superior adsorption capacity of *Streptomyces* sp. for  $Zn^{2+}$  and Pb<sup>2+</sup>. The adsorption properties of the binary component mixture were provided by this result, which is crucial for the design of the adsorption system for wastewater that actually contains a mixture of heavy metals.

**Author Contributions:** Conceptualization, M.C.G.; methodology, M.C.G. and S.K.; software, M.C.G. and S.K.; validation, A.K.; formal analysis, N.K.A. and N.M.; investigation, M.C.G. and P.S.; resources, A.A.; data curation, N.M. and M.C.G.; writing—original draft preparation, M.C.G.; writing—review and editing, S.K.; visualization, S.K. and T.M.; and supervision, D.G. and V.D.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** VDR and TM acknowledge the support from the Ministry of Science and Higher Education of the Russian Federation, agreement no. 075-15-2022-1122.

Data Availability Statement: Not applicable.

Acknowledgments: Authors are thankful to provide laboratory, administrative and technical support by Thapar Institute of Engineering and Technology, Patiala, Punjab and Amity University Uttar Pradesh, Noida, India.

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- Singh, R.; Gautam, N.; Mishra, A.; Gupta, R. Heavy metals and living systems: An overview. *Indian J. Pharmacol.* 2011, 43, 246. [CrossRef] [PubMed]
- Muthusamy, P.; Murugan, S.; Smitha, M. Removal of nickel ion from industrial waste water using maize cob. Int. Res. J. Biol. Sci. 2012, 1, 7–11.
- Plouffe, G.; Bulle, C.; Deschênes, L. Case study: Taking zinc speciation into account in terrestrial ecotoxicity considerably impacts life cycle assessment results. J. Clean. Prod. 2015, 108, 1002–1008. [CrossRef]
- 4. Kumar, V.V.; Kaladharan, P. Biosorption of Metals from Contaminated Water Using Seaweed. Curr. Sci. 2006, 90, 1263–1267.
- Bind, A.; Goswami, L.; Prakash, V. Comparative analysis of floating and submerged macrophytes for heavy metal (copper, chromium, arsenic and lead) removal: Sorbent preparation, characterization, regeneration and cost estimation. *Geol. Ecol. Landsc.* 2018, 2, 61–72. [CrossRef]
- El-Naggar, N.E.-A.; Hamouda, R.A.; Mousa, I.E.; Abdel-Hamid, M.S.; Rabei, N.H. Biosorption optimization, characterization, immobilization and application of Gelidium amansii biomass for complete Pb<sup>2+</sup> removal from aqueous solutions. *Sci. Rep.* 2018, *8*, 13456. [CrossRef]
- 7. Abbas, S.H.; Ismail, I.M.; Mostafa, T.M.; Sulaymon, A.H. Biosorption of Heavy Metals: A Review. J. Chem. Sci. Technol. 2014, 3, 74–102.
- 8. Vijayaraghavan, K.; Balasubramanian, R. Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions. *J. Environ. Manag.* 2015, *160*, 283–296. [CrossRef]
- Foroutan, R.; Esmaeili, H.; Rishehri, S.D.; Sadeghzadeh, F.; Mirahmadi, S.; Kosarifard, M.; Ramavandi, B. Zinc, nickel, and cobalt ions removal from aqueous solution and plating plant wastewater by modified Aspergillus flavus biomass: A dataset. *Data Brief* 2017, 12, 485–492. [CrossRef]
- Mishra, V.; Balomajumder, C.; Agarwal, V.K. Biological removal of heavy metal zinc from industrial effluent by Zinc sequestering bacterium VMSDCM. *Clean Technol. Environ. Policy* 2014, 16, 555–568. [CrossRef]
- Abdullah, N.; Yusof, N.; Lau, W.J.; Jaafar, J.; Ismail, A.F. Recent trends of heavy metal removal from water/wastewater by membrane technologies. J. Ind. Eng. Chem. 2019, 76, 17–38. [CrossRef]
- 12. Ibarra-Rodríguez, D.; Lizardi-Mendoza, J.; López-Maldonado, E.A.; Oropeza-Guzmán, M.T. Capacity of 'nopal' pectin as a dual coagulant-flocculant agent for heavy metals removal. *Chem. Eng. J.* **2017**, *323*, 19–28. [CrossRef]
- 13. Zhang, T.; Wang, W.; Zhao, Y.; Bai, H.; Wen, T.; Kang, S.; Song, G.; Song, S.; Komarneni, S. Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. *Chem. Eng. J.* **2021**, 420, 127574. [CrossRef]

- 14. Huang, J.; Qi, F.; Zeng, G.; Shi, L.; Li, X.; Gu, Y.; Shi, Y. Repeating recovery and reuse of SDS micelles from MEUF retentate containing Cd<sup>2+</sup> by acidification UF. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *520*, 361–368. [CrossRef]
- 15. Dabrowski, A.; Hubicki, Z.; Podkościelny, P.; Robens, E. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere* **2004**, *56*, 91–106. [CrossRef]
- 16. Heidmann, I.; Calmano, W. Removal of Cr(VI) from model wastewaters by electrocoagulation with Fe electrodes. *Sep. Purif. Technol.* **2008**, *61*, 15–21. [CrossRef]
- Yabe, J.; Nakayama, S.M.; Ikenaka, Y.; Yohannes, Y.B.; Bortey-Sam, N.; Oroszlany, B.; Muzandu, K.; Choongo, K.; Kabalo, A.N.; Ntapisha, J.; et al. Lead poisoning in children from townships in the vicinity of a lead–zinc mine in Kabwe, Zambia. *Chemosphere* 2015, 119, 941–947. [CrossRef]
- 18. Zhang, L.; Zhao, L.; Yu, Y.; Chen, C. Removal of lead from aqueous solution by non-living rhizopus nigricans. *Water Res.* **1998**, 32, 1437–1444. [CrossRef]
- 19. Ahmad, A.; Bhat, A.H.; Buang, A. Biosorption of transition metals by freely suspended and Ca-alginate immobilised with Chlorella vulgaris: Kinetic and equilibrium modeling. *J. Clean. Prod.* **2018**, 171, 1361–1375. [CrossRef]
- 20. Freundlich, H. Über die Adsorption in Lösungen. Z. Phys. Chem. 1907, 57, 385–470. [CrossRef]
- Sahmoune, M.N.; Louhab, K.; Boukhiar, A.; Addad, J.; Barr, S. Kinetic and equilibrium models for the biosorption of Cr(III) on Streptomyces rimosus. Toxicol. Environ. Chem. 2009, 91, 1291–1303. [CrossRef]
- 22. Volesky, B.; Holan, Z.R. Biosorption of heavy metals. *Biotechnol. Prog.* 1995, 11, 235–250. [CrossRef] [PubMed]
- 23. Manju, G.N.; Anoop Krishnan, K.; Vinod, V.P.; Anirudhan, T.S. An investigation into the sorption of heavy metals from wastewaters by polyacrylamide-grafted iron(III) oxide. *J. Hazard. Mater.* **2002**, *91*, 221–238. [CrossRef]
- 24. Paduraru, C.; Tofan, L.; Teodosiu, C.; Bunia, I.; Tudorachi, N.; Toma, O. Biosorption of zinc(II) on rapeseed waste: Equilibrium studies and thermogravimetric investigations. *Process Saf. Environ. Prot.* **2015**, *94*, 18–28. [CrossRef]
- 25. Ye, J.; Xiao, H.; Xiao, B.; Xu, W.; Gao, L.; Lin, G. Bioremediation of heavy metal contaminated aqueous solution by using red algae Porphyra leucosticta. *Water Sci. Technol.* **2015**, *72*, 1662–1666. [CrossRef]
- 26. Shah, J.; Jan, M.R.; ul Haq, A.; Zeeshan, M. Equilibrium, kinetic and thermodynamic studies for sorption of Ni (II) from aqueous solution using formaldehyde treated waste tea leaves. *J. Saudi Chem. Soc.* **2015**, *19*, 301–310. [CrossRef]
- 27. Nessim, R.B.; Bassiouny, A.R.; Zaki, H.R.; Moawad, M.N.; Kandeel, K.M. Biosorption of lead and cadmium using marine algae. *Chem. Ecol.* **2011**, *27*, 579–594. [CrossRef]
- 28. Abdel-Aty, A.M.; Ammar, N.S.; Abdel Ghafar, H.H.; Ali, R.K. Biosorption of cadmium and lead from aqueous solution by fresh water alga *Anabaena sphaerica* biomass. J. Adv. Res. 2013, 4, 367–374. [CrossRef]
- 29. Zou, H.-X.; Li, N.; Wang, L.-H.; Yu, P.; Yan, X.-F. Equilibrium and Kinetic Studies of Cd<sup>2+</sup> Biosorption by the Brown Algae Sargassum fusiforme. *PLoS ONE* **2014**, *9*, e95242. [CrossRef]
- Liu, X.; Chen, Z.-Q.; Han, B.; Su, C.-L.; Han, Q.; Chen, W.-Z. Biosorption of copper ions from aqueous solution using rape straw powders: Optimization, equilibrium and kinetic studies. *Ecotoxicol. Environ. Saf.* 2018, 150, 251–259. [CrossRef]
- Zhang, X.; Zhang, J.; Zheng, J.; Xin, D.; Xin, Y.; Pang, H. Streptomyces wuyuanensis sp. nov., an actinomycete from soil. Int. J. Syst. Evol. Microbiol. 2013, 63 Pt 8, 2945–2950. [CrossRef] [PubMed]
- Sahmoune, M.N.; Louhab, K.; Boukhiar, A. Studies of Chromium Removal from Tannery Effluents by Dead Streptomyces rimosus. Chem. Prod. Process Model. 2008, 3, 1–18. [CrossRef]
- 33. Dhanasekaran, D.; Thajuddin, N.; Panneerselvam, A. An antifungal compound: 4' phenyl-1-napthyl-phenyl acetamide from *Streptomyces* sp. Dptb16. *Med. Biol.* 2008, 15, 7–12.
- 34. Rho, J.Y.; Kim, J.H. Heavy Metal Biosorption and its Significance to Metal Tolerance of *Streptomycetes*. J. Microbiol. 2002, 40, 51–54.

**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.