

Article

A Novel Combined Treatment Process of Hybrid Biosorbent–Nanofiltration for Effective Pb(II) Removal from Wastewater

Asma Hanif ^{1,2}, Shaukat Ali ², Muhammad Asif Hanif ^{2,*}, Umer Rashid ^{3,*} , Haq Nawaz Bhatti ², Muhammad Asghar ⁴, Ali Alsalmeh ⁵  and Dimitrios A. Giannakoudakis ^{6,7} 

¹ Department of Chemistry, Government College Women University, Faisalabad 38000, Pakistan; asmarana_hanif@yahoo.com

² Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan; shaukatchemist@hotmail.com (S.A.); haq_nawaz@uaf.edu.pk (H.N.B.)

³ Institute of Nanoscience and Nanotechnology (ION2), Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia

⁴ Department of Biochemistry, University of Agriculture, Faisalabad 38040, Pakistan; mabajwapk@yahoo.com

⁵ Chemistry Department, College of Science, King Saud University, Riyadh 1145, Saudi Arabia; aalsalme@ksu.edu.sa

⁶ Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland; dagchem@gmail.com

⁷ Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

* Correspondence: drmuhammadasifhanif@gmail.com (M.A.H.); dr.umer.rashid@gmail.com (U.R.); Tel.: +60-3-9769-7393 (U.R.)



Citation: Hanif, A.; Ali, S.; Hanif, M.A.; Rashid, U.; Bhatti, H.N.; Asghar, M.; Alsalmeh, A.; Giannakoudakis, D.A. A Novel Combined Treatment Process of Hybrid Biosorbent–Nanofiltration for Effective Pb(II) Removal from Wastewater. *Water* **2021**, *13*, 3316. <https://doi.org/10.3390/w13233316>

Academic Editors: Xanel Vecino and Mònica Reig

Received: 24 September 2021
Accepted: 8 November 2021
Published: 23 November 2021

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Abstract: The untreated effluents discharged by different industries, such as metallurgy, fertilizers, pesticide, leather, mining, electroplating, surface finishing, aerospace, and electroplating, have increased the risk of the contamination of bodies of water by heavy metals. Herein, hybrid biosorbent–nanofiltration processes for Pb(II) removal from wastewater was studied. The hybrid biosorbent was prepared from date seed waste and *Ganoderma lucidum*. Hybrid biosorbent characterization was performed by SEM and FTIR. SEM micrographs showed that the HB surface is irregular. For the adsorption studies, various sorption parameters were optimized. The maximum biosorption capacity of immobilized heat-inactivated hybrid biosorbent was 365.9 mg/g, with the Langmuir isotherm model to present the best fit. Desorption experiments were conducted for regenerating immobilized heat-inactivated hybrid biosorbent for three consecutive cycles using different desorption agents, with acetic acid to be the optimum. Going a step further, nanofiltration was also applied as a post-treatment process to elevate the remediation effectiveness for wastewater of high Pb(II) initial concentrations. The reasonably low cost and high removal of Pb(II) make hybrid biosorbent–nanofiltration processes a prosperous and potentially attractive hybrid approach against heavy-metal-polluted wastewater.

Keywords: hybrid biosorbent; desorption; thermodynamic; nanofiltration

1. Introduction

For wastewater management, strict environmental rules are developed in many countries [1]. Among the plethora of potential pollutants that wastewaters can contain, toxic heavy metals (HMs) are assumed to be major pollutants due to their existence in ground, marine, industrial, and even treated wastewater in low concentrations [2,3]. Heavy metal ions in wastewater must be regulated and their concentration retained at lower than established values. Rampant anthropogenic activities result in the excessive release of metals in water systems. Being non-biodegradable, inorganic heavy metal ions cause health risks to living biota even at low concentrations [4]. Due to their accumulation tendency and persistence, heavy metals lead to toxicity and complications in living organisms and environments. Pb (II) is a hazardous environmental pollutant. Upon insertion to human

body, it can limit the oxygen-carrying capacity of red blood cells and cause harmful effects to the hearing, nervous system, and kidneys. In drinking water, the maximum allowable level of lead is 15 µg/L according to EPA [5].

Different processes for heavy metal removal are available, among which electrolysis, evaporation, ion exchange, adsorption, and coagulation–flocculation are the most used ones [6,7]. However, these techniques have several demerits, such as high chemical requirements (such as expensive organic solvents, which produce side-polluted wastes), high operational costs, and in various cases low efficiency. The development of economical water treatment techniques, which will be more environmentally friendly and in general more practical in real-life application than the traditional methods, is always an open research and development goal. A modern strategy towards the development of effective technologies has led to hybrid processes, advanced chelating materials, enhanced membrane filtration, and specific adsorbents in the production of reclaimed water. The use of appropriate biological methods for the uptake of wastewater pollutants includes bioaccumulation and biosorption. Biosorption is the sequestering of organic or inorganic pollutants by active or dead/inactive biomass. Bioaccumulation refers to intracellular accumulation of pollutant [8].

Various pressure-driven membrane filtration systems such as nanofiltration (NF), microfiltration, ultrafiltration, and reverse osmosis have become popular treatment technologies for wastewater. Among these approaches, nanofiltration is comparatively the newest wastewater treatment process. The characteristics of NF membranes are between ultrafiltration and reverse osmosis [9]. NF membranes are used for water purification due to higher flux, lower operational pressure, less energy consumption, lower monovalent ions rejection, and higher rejection of divalent ions. Therefore, NF process can be extensively used in the retention of dyes [10], treatment of drinking and industrial wastewater [11], and removal of micropollutants [12].

Considering all the aforementioned, the goal of this work was to explore the potential of using simple and cost-effective biosorbent and nanofiltration membranes to treat wastewater containing Pb(II) using immobilized hybrid biosorbent–nanofiltration processes.

2. Materials and Methods

2.1. Chemicals

All the chemicals were purchased from Sigma-Aldrich and Merck. Stock Pb(II) solution was prepared by dissolving 1.60 g of lead nitrate in 1 L DDW. The required solutions were prepared by diluting metal stock solution. A total of 1M NaOH/ HCl was used to adjust the pH of solutions.

2.2. Hybrid Biosorbent Preparation and Characterization

The date seed waste (A2) left after oil extraction was collected from the Nano and Biomaterials Laboratory, Department of Chemistry, University of Agriculture, Faisalabad-Pakistan. The date seed waste was washed twice with distilled water and then oven dried at 60 °C to obtain constant mass and stored in sealed plastic box. *Ganoderma lucidum* (A1) was preserved by sub culturing on PDA plates and stored at 4 °C for further study. The desired amount of growth medium was prepared in conical flasks. The fungal inoculums were prepared from properly grown, uncontaminated slants. The inoculum media for *Ganoderma lucidum* were prepared following compositions given in the literature [13]. A total of 1M NaOH/ HCl was used to adjust the pH of media at 4.5. Conical flasks containing 100 mL of growth medium were sterilized by autoclaving at 121 °C for 15 min. After cooling to a lower temperature (≈40 °C), spores of *Ganoderma lucidum* were aseptically added to the growth medium and incubated in an orbital shaker (120 rpm) at 30 °C for 7 days. After the incubation period, homogenous suspensions of *Ganoderma lucidum* spores were formed.

The pre-weighed, oven-dried date seed waste was transferred to Erlenmeyer flasks containing growth medium and autoclaved for 15 min at 121 °C. Then, 5.0 ± 0.025 mL *Ganoderma lucidum* mycelium suspension was added to these flasks and agitated at 100 rpm,

for 7 days at 30 °C. After seven days, *Ganoderma lucidum* biomass was found growing on the date seed waste to produce a hybrid biosorbent (HB). The dry weight of A1 within A2 was calculated as the weight difference of A2 before and after A1 growth on it, when dried at 70 °C overnight [14].

The hybrid biomass (HB) was autoclaved at 121 °C for 15 min and then oven dried for 72 h at 70 °C to obtain heat-inactivated hybrid biosorbent (HI HB). The material was crushed by means of a food processor (Moulinex, France) and U.S. A standard sieve was used for sieving. The fraction with 50 mesh size was selected for further studies and stored in sealed plastic box. Two per cent Na-alginate was used to immobilize the heat-inactivated hybrid biosorbent (HI HB). To dissolve sodium alginate, the solution was heated and then cooled down. Then, 1g/100 mL of HI HB was mixed with the above solution to obtain a homogeneous mixture, which was taken in a burette and introduced into 0.1M CaCl₂·2H₂O solution. The prepared beads were washed twice and stored in 0.05M CaCl₂·2H₂O [15].

The surface morphologies of samples were analyzed by SEM (FEI Quanta 400F electron microscope), and the chemical characteristics of hybrid biosorbent were interpreted by FTIR Agilent N630, with the samples prepared as KBr discs.

2.3. Biosorption Studies

The immobilized HI HB potential for Pb(II) biosorption was determined in batch mode (Figure 1). The effects of pH (2–4.5), biosorbent dose (0.05–0.3 g/L), initial metal ion concentration (25–400 ppm), and temperature (30–70 °C) were checked by varying one parameter, while keeping other parameters constant. The effects of the presence of Mg⁺², Al⁺³, Cu⁺², and Zn⁺² on the adsorption capacity of immobilized HI HB in binary system for Pb(II) were also studied. The concentration of lead ions was fixed at 100 ppm, while the concentration of other metal ions was varied from 25 to 400 ppm. Blank solutions without hybrid biosorbent were run in parallel at the same conditions. The samples were shaken at 120 rpm for a specific duration using an orbital shaking incubator (PA250/25H). Atomic absorption measurements were performed using a Varian AA240, GTA 120 instrument to determine lead concentration in solutions. The removal capacity was determined using the following equation:

$$q_e = \frac{(C_o - C_e)V}{W}$$

where C_o and C_e (mg/L) denote the initial and equilibrium metal ion concentration, respectively, V (L) is the volume of the solution, and W (g) is the amount of HB used [16].

2.4. Biosorption Isotherm Models

The equilibrium adsorption data were fitted to the following isotherms according to equations given in the literature, including: Freundlich model [17], Langmuir model [18], Temkin [17], and Harkins and Jura [19], to determine the adsorption mechanism for Pb (II) removal by hybrid biosorbent.

2.5. Biosorption Thermodynamics

The study of thermodynamic parameters is essential to determine the orientation and feasibility of an adsorptive reaction. The thermodynamic behavior of metal ions' biosorption using immobilized HI HB can be estimated by various thermodynamic parameters, such as change in free energy (ΔG), entropy (ΔS) and enthalpy (ΔH) using equations given in the literature [20].

2.6. Desorption

After biosorption experiments, Pb(II) ions were desorbed from the hybrid matrix. Three sorption/regeneration cycles for immobilized HI HB were conducted using various eluents. Sorption of metal ions was performed at optimum pH by adding 0.05 g hybrid biosorbent in 100 mg/L Pb (II) solution at 30 °C for 3 h. After the solution was filtered and dried, the metal ions loaded immobilized HI HB into the oven at 60 °C. Then, the dried

biomass was shaken with 0.1M HCl, HNO₃, acetic acid, and EDTA. Desorption efficiency (%) was estimated using following equation:

$$\text{Desorption efficiency (\%)} = \frac{q_{de}}{q_{ad}} \times 100$$

Combined Treatment

Hybrid Biosorbent treatment

Nanofiltration treatment

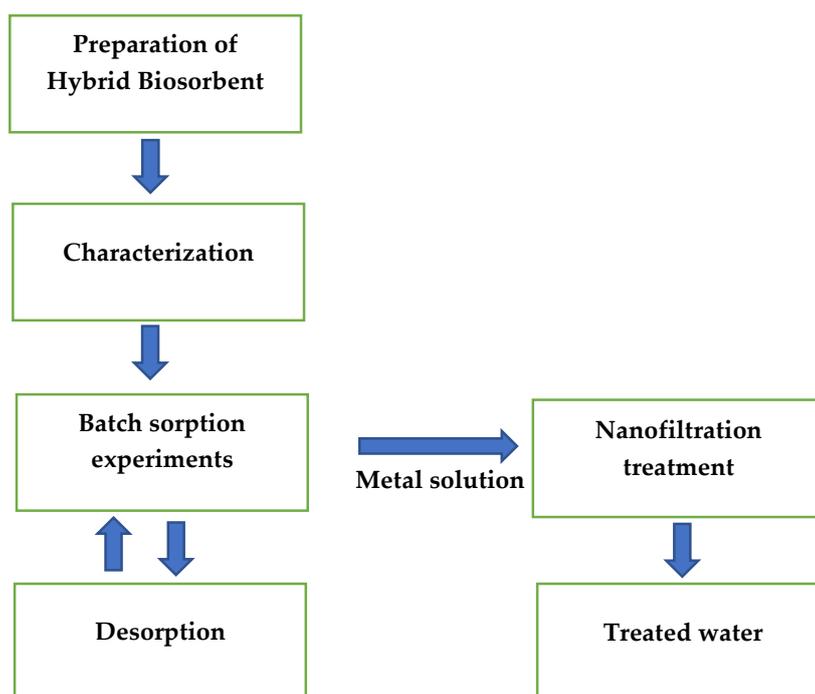


Figure 1. Schematic design of hybrid biosorbent–nanofiltration process.

2.7. Nanofiltration

Wastewater was treated through integrated processes by adsorption as a pretreatment, with nanofiltration (NF) as a post-treatment in this study. A commercially available NF membrane was used. After adsorptive removal using immobilized HI HB, the lead ions were subjected to the NF membrane unit. The main properties of the NF membrane are summarized in Table 1.

Table 1. Characteristics of NF membrane.

| Parameters | Nanofiltration |
|---------------|----------------------|
| Membrane type | Flat sheet |
| Material | PA (polyamide) |
| Membrane area | 0.006 m ² |
| Pressure | 5 bar |

Membrane Filtration Experiments

For removal studies, a dead-end NF unit was utilized. The NF unit consisted of a reservoir, a membrane module, and a high-pressure pump. This NF unit was operated at a pressure of 5 bar. The membrane was immersed in deionized water before being used in any experiment and pressurized at 5 bar for 1 h to prevent compression effects

and to determine leak tightness. In these experiments, after adsorptive removal, metal ion solutions were pumped out of the membrane module. The influence of important process parameters such as pH, temperature and initial metal ion concentration upon lead ions removal was estimated. The percentage removal was calculated through the following relationship:

$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

2.8. Statistical Analysis

All the experiments were performed in triplicate. The results were analyzed statistically by applying regression analysis.

3. Results and Discussion

3.1. Biosorption Study

3.1.1. Characterization

The morphological uniqueness of biosorbents can be evaluated using SEM. The SEM micrograph of hybrid biosorbent (HB) is shown in (Figure 2a), where all the morphological characteristics were taken at $5000\times$ magnification. The SEM micrograph of HB before biosorption revealed an irregular, rough, and porous surface. Such a structure significantly enlarges the available adsorptive surface, which results in increased binding capabilities of Pb(II) ions (Figure 2b). Therefore, HB is more conducive for the adsorption process. After biosorption of metals and dyes the pores are filled with sorbate ions on the surface of the biosorbents [21,22].

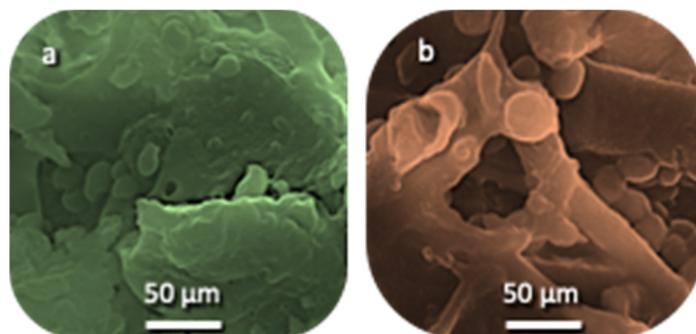


Figure 2. (a) SEM micrograph of hybrid biosorbent (HB). (b) SEM micrograph of HB loaded with Pb(II) ions.

The Fourier transform infrared spectroscopic study reveals important information about the chemical environment of biomaterials responsible for sorption. The spectrum of HB shows a strong and broad unbounded O-H stretching band centered at 3349 cm^{-1} . The peaks at 2924 and 2853 cm^{-1} were due to C-H symmetric and asymmetric stretching vibrations. The peak observed at 1735 cm^{-1} corresponds to C=O stretching vibration due to non-ionic -COOH groups. The peak at 1507 cm^{-1} corresponds to the amide II band of protein peptide bonds. In addition, the peak at 1032 cm^{-1} is attributable to the C-N and C-O bonds (Figure 3) [23]. This indicates that the hydroxyl and carboxyl groups of HB participated in the Pb(II) ions biosorption by sharing or exchanging electrons among sorbent and sorbate.

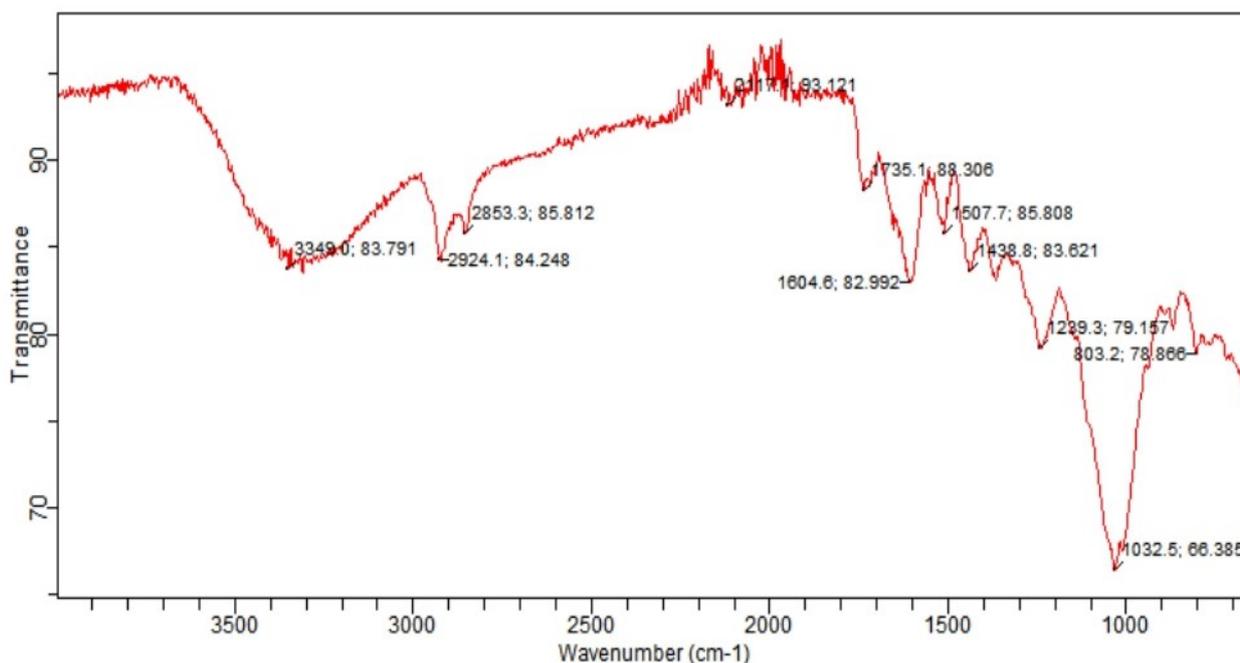


Figure 3. FTIR spectra of hybrid biosorbent (HB).

3.1.2. Batch Study

The different pH binding profiles for these components can be explained based on the different chemical interactions of each species with the adsorbent's surface. The influence of the initial pH (2–4.5) on Pb (II) adsorption was determined at 30 °C by fixing the initial metal ion concentration at 100 mg/L and 0.05 g/L biosorbent dose. The maximum removal of Pb (II) ions was found as 365.9 mg/g at pH 4.5 by immobilized heat-inactivated hybrid biosorbent (Figure 4). The lower uptake of metal ions in stronger acidic conditions (pH 2–4) by hybrid biosorbent can be ascribed to the large number of hydrogen or/and hydronium ions competing with Pb (II) ions for the binding at sorption sites of biosorbent, as has been reported by other authors [24,25]. The concentration of H⁺ decreased with the increase in pH, leading to an increased uptake of lead ions [26]. The increase in the rate of adsorption with increasing pH was due to a combination of various effects: (i) less ionic competition due to metal binding sites' deprotonation, (ii) at higher pH values, decrement in solubility of heavy metal ions. However, precipitation occurs at higher pH (>7.0) due to the increased concentration of hydroxyl ions in the medium [27].

The adsorption capacity can be strongly affected by the biosorbent dosage [28]. To determine the biosorbent dosage effect on adsorption, optimum adsorption conditions were determined for better biosorption. The influence of biosorbent dosage on the removal efficiency of hybrid biosorbent against Pb(II) was examined in the range of 0.05–0.3 g/L, when pH (4.5), metal ion concentration (100 mg/L), and temperature (30 °C) were kept constant (Figure 5). The results presented in Figure 5 indicate that the equilibrium biosorption capacity for metal ions decreased when the immobilized HI HB dosage increased. The uptake capacity of hybrid biosorbent decreased with the increase in biomass dosage, whereas the reverse was true for percentage removal. The maximum metal ion removal was observed at 0.05 g/L. It was noticed that the removal efficiency (both as an absolute value or expressed as per adsorbent mass) of the hybrid biomass was a function of biomass amount. The metal ions' removal declined with the increase in biomass dose. The decremental trend of Pb(II) ions' removal by the increase in the utilized biomass is due to poor utilization and the agglomeration of biomass at a higher dosage leading to a lower extent of available adsorption sites [29]. This observation clearly suggested that maximum adsorption sets in after a particular biomass dose, thus, the ratio of ions bound to hybrid biosorbent to free ions became constant even when more biomass was added [30]. The selection of such

a biomass concentration when both metal uptake capacity and percentage removal have suitable high values is practically very important, since the optimization of the minimum desired amount has a direct positive effect on the cost.

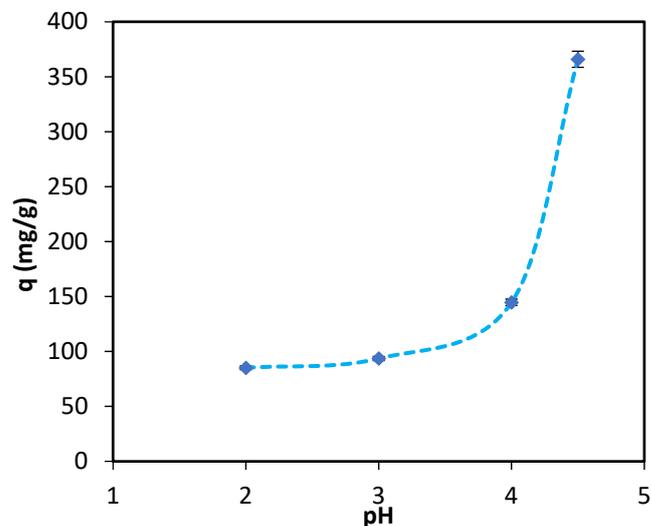


Figure 4. Effect of pH on the Pb(II) ions' removal by immobilized heat-inactivated hybrid biosorbent (HI HB).

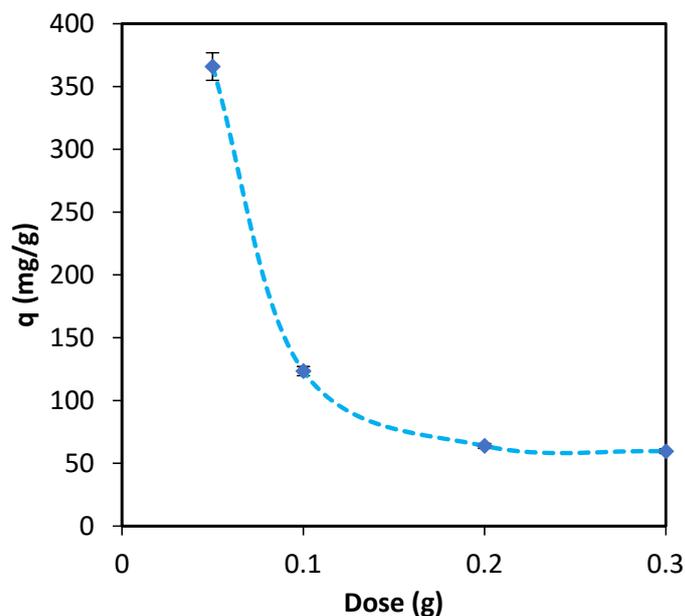


Figure 5. Effect of biosorbent dose on the removal of Pb(II) ions by immobilized HI HB.

The effect of initial Pb(II) concentration (25–400 mg/L) on adsorption efficiency of immobilized HI HB was studied at an optimum pH (4.5) and biosorbent dose (0.05 g) (Figure 6). It was observed that the adsorbed amount increased almost linearly as Pb(II) concentration increased up to 100 mg/L and remained stable for higher Pb(II) concentrations. The high initial metal ion concentration suggests an initial force to overcome pollutant mass transfer resistances between solid and aqueous phases. The incremental trend of adsorption at low initial Pb(II) concentration might be due to increased electrostatic interactions. The number of adsorbed metal ions was higher at high initial metal concentrations than at lower concentrations, because more binding sites were free for interaction [27]. At higher concentrations, the vacant sites of hybrid biosorbent became less, and sorption sites rapidly saturated due to constant amounts of adsorbent.

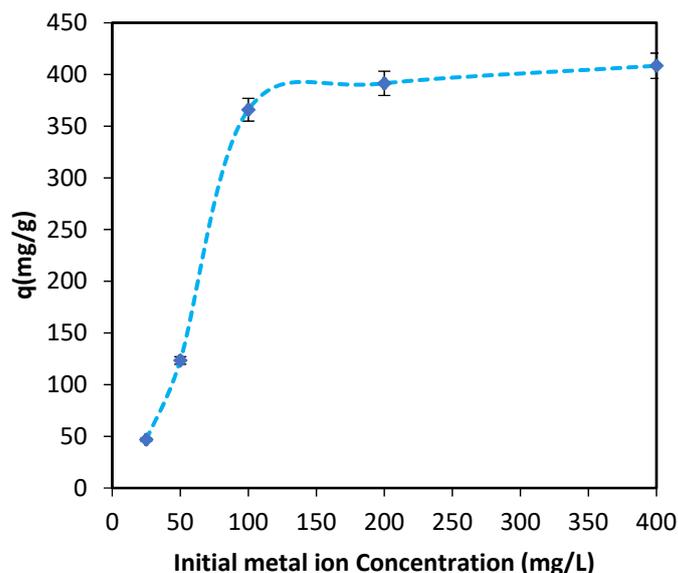


Figure 6. Effect of initial concentration on the removal of Pb(II) ions by immobilized HI HB.

Temperature change has an effect on adsorption capacity. The effect of temperature on Pb(II) removal using immobilized HI HB was investigated at five different temperatures; the results are shown in Figure 7. Adsorption capacity was at a maximum at 30 °C, then decreased steadily with an increase in temperature. The adsorption capacity decreased because the adsorptive forces responsible for Pb(II) biosorption on immobilized HI HB became weaker at higher temperatures. This might be due to the deactivation of sorption sites of biosorbent at high temperatures, which leads to decreased biosorption [31]. A similar trend was reported for Congo red uptake by surface-modified bentonite [32], and Direct Blue 106 dye adsorption onto pomegranate peels [33].

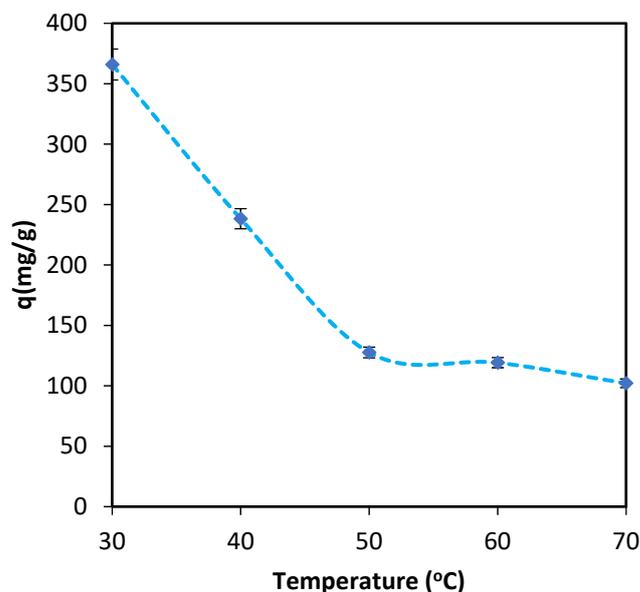


Figure 7. Effect of temperature on the removal of Pb(II) by immobilized HI HB.

3.1.3. Biosorption Isotherms

Different models of isotherms were studied to determine crucial remediation parameters and to have a better comparison with various other parameters reported in the literature materials. More precisely, four isothermal equations were used to study the adsorption process: Temkin, Langmuir, Freundlich, and Harkins–Jura, with all the calcu-

lated parameters shown in Table 2. The adsorption data (at 30 °C) fit well to the Langmuir isotherm ($R^2 = 0.993$) and were significantly close in value to experimental and calculated maximum capacity. Low values of R^2 in the case of the Temkin and Harkins–Jura isotherm model fittings suggested that experimental data for Pb(II) removal were not fitted satisfactorily. In addition, a poor fit to the Freundlich model was also observed. Even though the extraction of specific outcomes for the extent of fitting of the models should be very careful, it can be considered in general based on the above results that a monolayer of adsorption, but also a more heterogeneous adsorption process, took place.

Table 2. Equilibrium modeling of data for the uptake of Pb(II) ions by immobilized HI HB.

| Parameters Derived from Isotherm Models | Values |
|---|--------|
| Langmuir | |
| q_m Calculated (mg/g) | 500 |
| q_m Experimental (mg/g) | 408.9 |
| b | 0.02 |
| R^2 | 0.993 |
| Freundlich | |
| K_F | 38.90 |
| n | 4.20 |
| R^2 | 0.821 |
| Temkin | |
| A | 5.25 |
| B | 0.009 |
| R^2 | 0.717 |
| Harkins–Jura | |
| A | 25.64 |
| B | 3.84 |
| R^2 | 0.590 |

3.1.4. Adsorption Thermodynamics

To evaluate the thermodynamic viability of the sorption process and to confirm its nature, different thermodynamic parameters were calculated for Pb(II) adsorption onto immobilized HI HB. The negative value of ΔH° (Table 3) indicates the exothermic nature of the adsorption process. The negative value of ΔS° suggests that the process is enthalpy driven. It also shows a decrease in randomness during Pb(II) biosorption onto immobilized HI HB [34].

Table 3. Thermodynamic parameters for the uptake of Pb(II) ions by immobilized HI HB.

| Temperature (K) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (Jmol ⁻¹ K ⁻¹) |
|-----------------|------------------------------|------------------------------|---|
| 303 | 33.4 | | |
| 313 | 34.5 | | |
| 323 | 35.6 | −38.9 | −110.3 |
| 333 | 36.7 | | |
| 343 | 37.8 | | |

3.1.5. Competitive Adsorption

A competitive adsorption process was studied to check the effect of other heavy metal ions on Pb(II) ion adsorption (Figure 8). The results demonstrate that as the concentration of the co-cations was increased from 25 to 400 mg/L in solution, immobilized HI HB adsorption capacity decreased. The adsorption capacity of immobilized HI HB decreased from 365.90 mg/g to 143.24 mg/g for the Pb(II) in the Pb(II) + Cu(II) binary system at 100 mg/L. In a binary solution, the sorption of primary metal was inhibited by the presence of secondary metal on the immobilized HI HB. However, copper ions have a stronger inhibitory effect during the sorption of lead as compared to the inhibitory effect of zinc in the adsorption of lead. The overall metal (Pb + Cu) sorbed from binary metal solution always remained lower than individual metal solutions by biosorbent. This indicates a competition between Cu(II), Zn (II), and Pb(II) for common binding sites on immobilized HI HB.

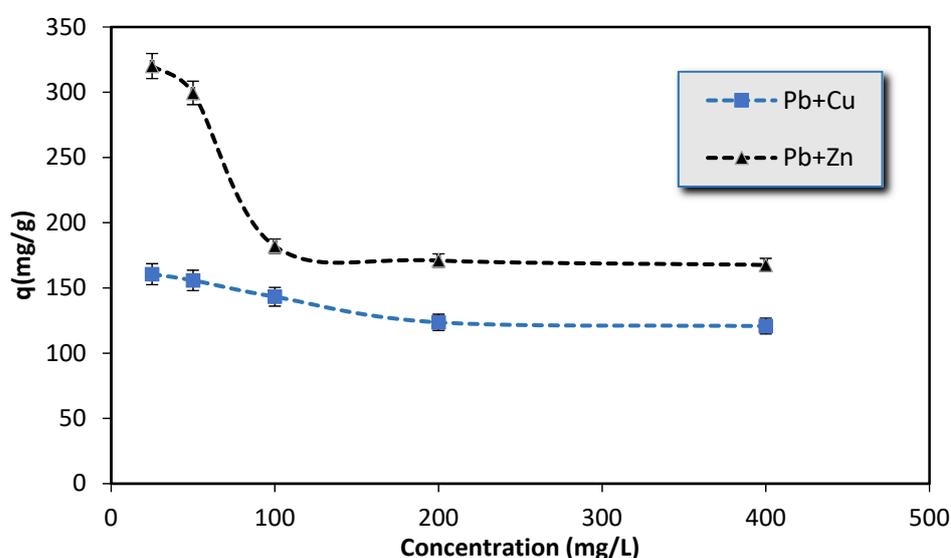


Figure 8. Effect of Cu(II) and Zn(II) concentrations on Pb(II) uptake by immobilized HI HB.

Several co-metal ions are always present in industrial wastewater. The adsorption of any metal depends upon metal chemistry, affinity for binding sites, and the presence of other metal ions in its vicinity. In this view, the effect of light metal ions such as Mg^{2+} and Al^{3+} on the uptake of lead ions by immobilized HI HB was evaluated (Figure 9). In general, metals with a higher atomic weight, ionic size, electronegativity, and electrode potential tend to exhibit a greater affinity for sorption [35]. The light atomic weight co-metal ions with greater charge competed/interfered more with the uptake of lead ions by immobilized HI HB and the competition for adsorption sites on biomass was in the following order $Al^{3+} > Mg^{2+}$.

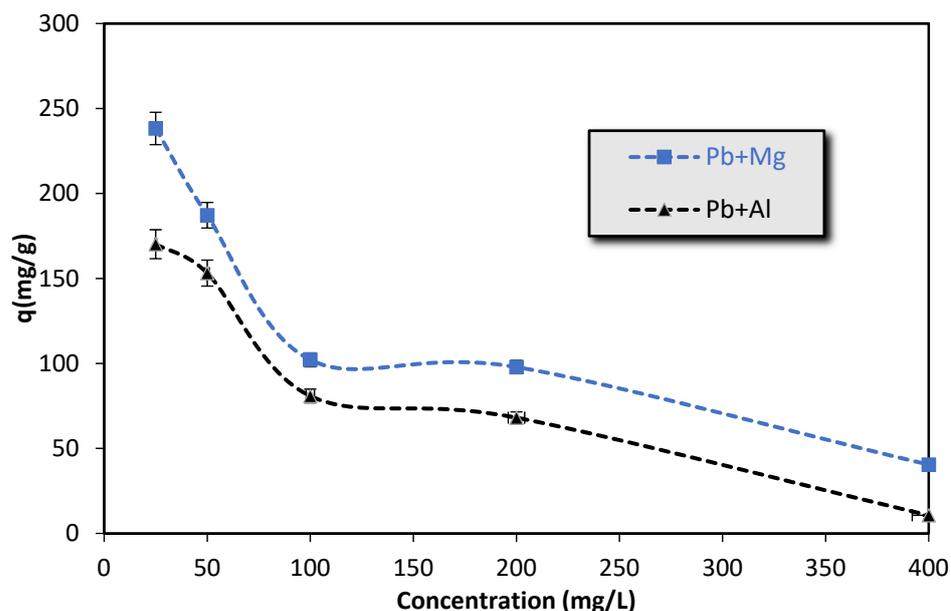


Figure 9. Effect of Mg²⁺ and Al³⁺ concentrations on Pb(II) uptake by immobilized HI HB.

3.1.6. Desorption

In developing a novel adsorbent for real-life applications, its reusability efficiency is vital. Thus, immobilized HI HB was reused in two successive adsorption–desorption cycles for Pb(II) during the current work. The Pb(II)-loaded immobilized HI HB was recovered using 0.1M EDTA, HCl, HNO₃, and acetic acid. The biomass regeneration efficiency of immobilized HI HB-loaded Pb(II) was in the following order: acetic acid < nitric acid < hydrochloric acid < EDTA. The highest metal recovery was 86.4% using acetic acid during the first cycle (Figure 10). On the other hand, the experimental data with EDTA revealed that this regenerating solution was unsuitable to recover metal ions from the sorbent in the next cycle. EDTA was not used in the second cycle because immobilized HI HB changed to an amorphous form after the first desorption cycle. The highest metal recovery was 54.43% and 33.5% using acetic acid after the second and third cycles respectively.

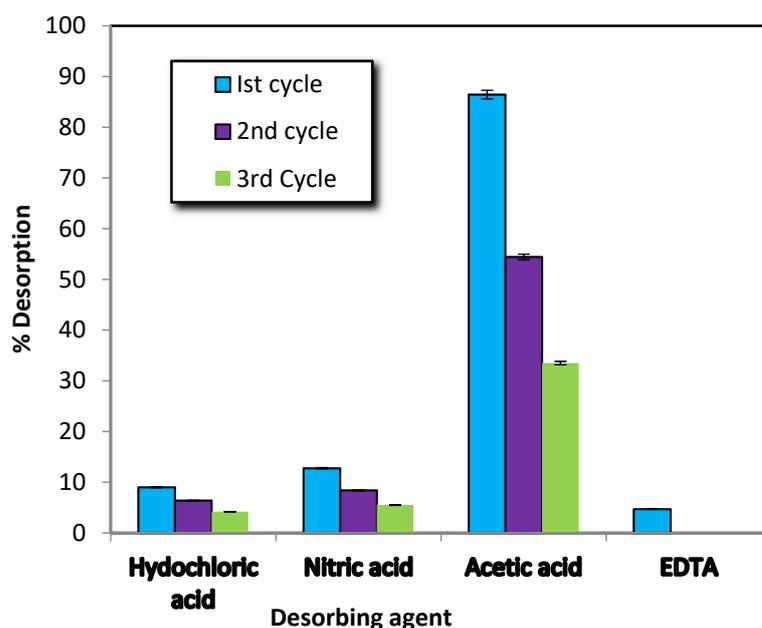


Figure 10. Desorption of Pb(II) ions from immobilized HI HB in three consecutive sorption–desorption cycles.

3.2. Nanofiltration Study

Parameters Affecting the Performance of NF Membrane

In the present study, wastewater is treated through adsorption, in combination with nanofiltration (NF) as a post-treatment process. The important operating parameter affecting the performance of flat sheet polyamide (PA) NF membrane is pH. Solution pH is an important factor in membrane-based processes, because it can affect a membrane's charge and therefore its rejection properties. The separation of ions by NF is achieved both by size exclusion and by electrical interactions between ions in feed aqueous solution and charged NF membranes [36,37]. Figure 11 presents the influence of pH on percentage removal of Pb(II) by PA nanofiltration membrane. It was found that the metal removal was very high across the whole pH range investigated. The results show that, in most cases, increasing pH from 2 to 5 enhanced the removal efficiency of metals >60% [38]. The positively charged ions, for example heavy metal ions, are rejected partly based on molecular weight. The nanofiltration membrane's performance is affected by pH in more than one way. NF membranes are charged due to functional groups' presence and their dissociation. At a higher or neutral pH, the functional groups (i.e., sulfonic group or carboxylic groups) present on the NF membrane's surface are negatively charged but lose their charge at an acidic pH. At a low pH, most RO and NF membranes had lower rejections. The solubility of ions changes by changing the pH and, therefore, the dissociation states of ions also change [39].

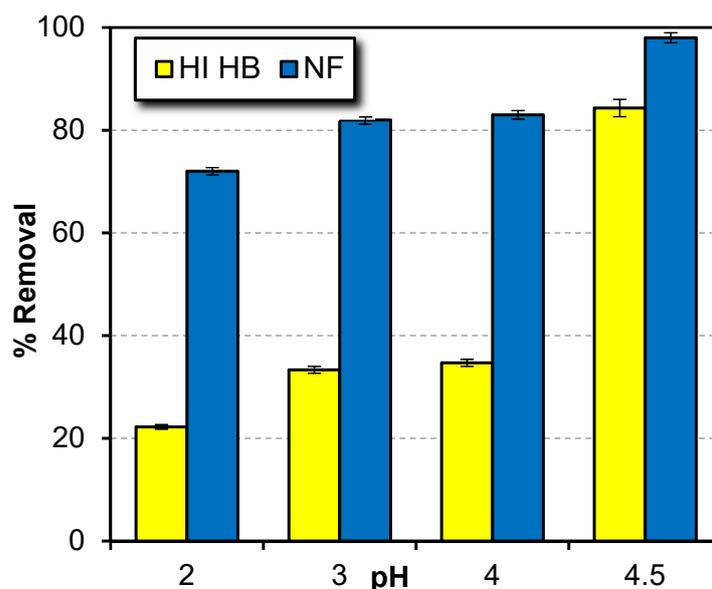


Figure 11. Influence of feed pH on Pb(II) ions' removal using immobilized HI HB and NF.

The effect of initial Pb(II) concentration (25, 50, and 100 mg/L) was studied keeping the applied pressure constant (results shown Figure 12). Very high percentage removal values (>90%) were obtained for all the above-mentioned initial concentrations. The metal removal with the use of NF was >95% in all cases, showing that NF membrane has very good separation properties.

The percentage Pb(II) removal was additionally evaluated as a function of temperature, as shown in Figure 13. It was observed that the Pb(II) percentage removal decreases with the increase in temperature, since removal at 30 °C is >98 % while at 70 °C it is 80%. This can be linked to the fact that the NF membrane flux increased due to a decrease in viscosity when the temperature was increased. However, the rejection by NF membranes is not considerably dependent on temperature [39,40] in comparison to batch removal experiments with immobilized HI HB.

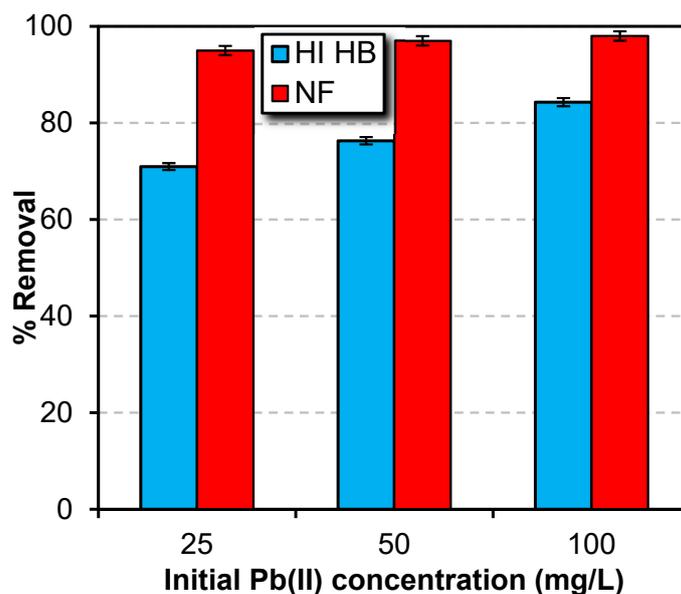


Figure 12. Influence of feed concentration on Pb(II) ions removal using immobilized HI HB and NF.

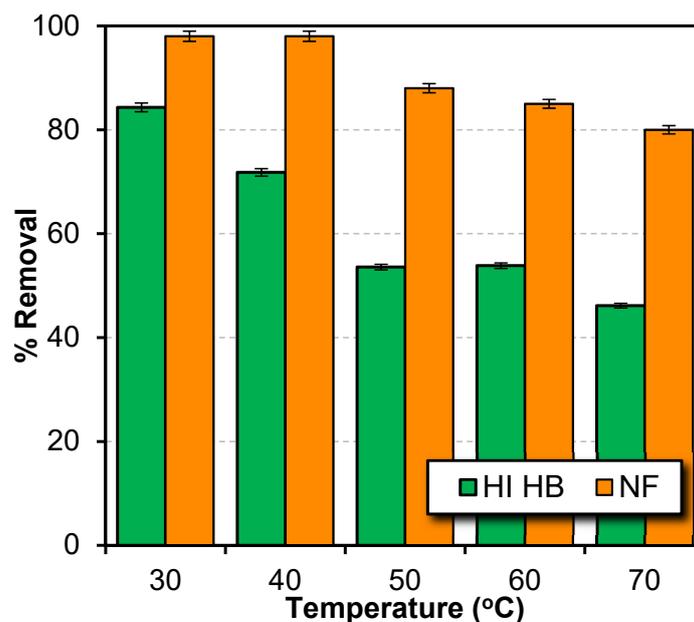


Figure 13. Influence of temperature on Pb(II) ions removal using immobilized HI HB and NF.

4. Conclusions

This research work attempted to combine two technologies, namely (bio)sorption and nanofiltration, towards wastewater treatment. In order to elevate the sorptive efficiency, the strategy of hybrid bio-sorbent was followed by combining two bio-sorbents. The maximum biosorption capacity (365.9 mg/g at 100 mg/L initial Pb(II) concentration) reported in this work is higher than that of various previously used biomaterials. The uptake of Pb(II) from aqueous solutions by hybrid biosorbent would be an addition to the list of high-metal-uptake-capacity biomaterials. The Langmuir isotherm model presents the best fitting. Different divalent metal ions' presence significantly decreased the adsorption capacity of immobilized HI HB. The FTIR results indicate the involvement of hydroxyl and carboxylic groups in the biosorption process. SEM micrographs showed that the HB surface is irregular and rough. Such a surface significantly enlarges the available surface of hybrid biosorbent, which results in increased binding capabilities of metal ions. Nanofiltration as a post treatment after adsorptive removal further increased the percentage removal of

metal ions. The main concluding remarks in this work are that the combination of the two treatments, the hybrid biosorbent and nanofiltration process, resulted in the removal of almost 98% of lead ions, providing better results than each technique separately.

Author Contributions: Conceptualization, M.A.H. and U.R.; data curation, A.H., S.A., H.N.B., M.A. and U.R.; formal analysis, A.H., M.A.H. and U.R.; funding acquisition, U.R., M.A.H. and A.A.; investigation, M.A., D.A.G. and U.R.; methodology, M.A.H., U.R. and D.A.G.; project administration, M.A.H., U.R. and A.A.; resources, M.A.H. and U.R.; visualization, M.A.H. and U.R.; writing—original draft, D.A.G., M.A.H., A.H. and U.R.; writing—review and editing, D.A.G., U.R., A.A. and M.A.H. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are thankful to the Higher Education Commission of Pakistan for providing funding (17-5(2Ps1-301)/HEC/Sch-Ind/2012) to conduct the present study. The APC is funded by Universiti Putra Malaysia (UPM), Malaysia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors extend their thanks to the Researchers Supporting Project (Ref: RSP-2021/78), King Saud University (Riyadh, Saudi Arabia).

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

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