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Plant-Based *Tacca leontopetaloides* Biopolymer Flocculant (TBPF) Produced High Removal of Heavy Metal Ions at Low Dosage

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Abstract: High removal of heavy metals using plant-based bioflocculant under low concentration is required due to its low cost, abundant source, and nontoxicity for improved wastewater management and utilization in the water industry. This paper presents a treatment of synthetic wastewater using plant-based *Tacca leontopetaloides* biopolymer flocculant (TBPF) without modification on its structural polymer chains. It produced a high removal of heavy metals (Zn, Pb, Ni, and Cd) at a low concentration of TBPF dosage. In our previous report, TBPF was characterized and successfully reduced the turbidity, total suspended solids, and color for leachate treatment; however, its effectiveness for heavy metal removal has not been reported. The removal of these heavy metals was performed using a standard jar test procedure at different pH values of synthetic wastewater and TBPF dosages. The effects of hydroxide ion, pH, initial TBPF concentration, initial metal ion concentration, and TBPF dosage were examined using one factorial at the time (OFAT). The results show that the highest removal for Zn, Pb, Ni, and Cd metal ions were 98.4–98.5%, 79–80%, 97–98%, and 92–93%, respectively, using 120 mg/L dosage from the initial concentration of 10% TBPF at pH 10. The final concentrations for Zn, Pb, Ni, and Cd metal ions were 0.043–0.044, 0.41–0.43, 0.037–0.054, and 0.11–0.13 mg/L, respectively, which are below the Standard B discharge limit set by the Department of Environment (DOE), Malaysia. The results show that TBPF has a high potential for the removal of heavy metals, particularly Zn, Pb, Ni, and Cd, in real wastewater treatment.

Keywords: *Tacca leontopetaloides* biopolymer flocculant (TBPF); heavy metal; flocculation mechanism; hydroxide ion; polymer flocculant

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1. Introduction

Polluted water with high heavy metal ion content remains a serious worldwide problem, especially in developing countries. Heavy metals such as Zn, Pb, Cd, and Ni are often discharged by metal plating, metal cleaning and fabrication, battery manufacturing, chemical manufacturing, and paint and pigment industries [1]. The effluent discharged by these industries indirectly contaminates the sources of water supply in the soil/groundwater system. Without proper treatment, these heavy metals have long been associated with various health problems, especially to human life. Although some of these heavy metals such as Mn, Fe, Cu, and Zn are essential nutrients at low levels, others, such as Pb, Cd, and Hg, could bring severe physiological or neurological consequences even in small amounts [1,2]. Meanwhile, high exposure of Ni can lead to several types of cancer, such as oral, skin, and lung cancers [3].

In Malaysia, the discharge limits for these heavy metals, i.e., Zn, Pb, Ni, and Cd, are 0.5, 1.0, 0.02, and 1.0 mg/L, respectively, based on the Standard B discharge limit as stipulated in Malaysia Sewage and Industrial Effluent Regulations (1979) [4]. Due to this stringent regulation to ensure the treated effluent complies with the standard limit set by the authorities, many technologies have been used to reduce these heavy metal ion content. Common technologies for the removal of heavy metals from water solution include chemical precipitation, ion exchange, solvent extraction, reverse osmosis, and membrane filtration, but these methods are relatively expensive [5]. Therefore, alternative methods with low cost and efficient treatment of heavy metals removal are needed to ensure treated effluent is safe to be discharged into water streams.

Hydroxide precipitation is a common treatment method to remove metal ions in industries' effluent. This process involves coagulation–flocculation–settling mechanism, followed by the separation of the unsettled flocs particles from the wastewater stream by the filtration process. The coagulation–flocculation process is common for the treatment of heavy metals because the colloidal particles, some soluble compounds, and very fine solid suspensions initially present in the wastewater by destabilization and formation of flocs will be removed through this process [1].

Water-soluble synthetic and natural macromolecules are the most efficient materials used as flocculants in water clarification, especially in heavy metals removal [5]. Many studies have been carried out to treat synthetic wastewater with a high concentration of heavy metals using integrated natural flocculants with polymer content. Wu et al. [6] reported that a pH-responsive amphoteric starch derivative (PRAS) with the presence of methyl ethyl in its polymer structure was used to treat 74 mg/L of synthetic water containing Zn ions in alkaline phase (pH 9). The Zn removal reported was high (91%), but 20 mg/L of PRAS was able to catch one type of heavy metal only. In another study by Kolya and Triphaty [5], polymer flocculant from hydroxyethyl starch grafted with poly-*N*,*N*-dimethyl acrylamide (HES-g-PDMA), with the presence amino and carboxyl group in its structure, was used to treat 355 mg/L of mixed synthetic water containing Zn, Pb, and Ni ions. The use of this integrated starch at a high dosage of 2000 mg/L and in acidic condition (pH 5.5) was only able to remove 25%, 10%, and 14% of synthetic water containing Zn, Pb, and Ni, respectively [5]. Meanwhile, Ibarra-Rodríguez et al. [7] used nopal pectin with carboxylate and the methoxylate group in its polymer structure to treat various metal concentrations of 344.14, 701.28, 457.54, and 399.66 mg/L of Zn, Pb, Ni, and Cd, respectively. The 90 mg/L of 0.2% nopal pectin at pH 3 was required to remove 99%, 67%, 90%, and 40% of Zn, Pb, Ni, and Cd, respectively. Even though the dosage of nopal pectin was low, the removals of Pb and Cd were less efficient, and the treatment needs to be in the acidic region, which demands high cost.

For chemical flocculant, Lopez et al. [8] reported that 67 mg/L of polydiallyldimethylammonium chloride (polyDADMAC) was used to treat 99% of 626 mg/L Pb ions in electroplating wastewater with the presence of hydroxide ion and cationic polyelectrolyte as flocculant aid. Meanwhile, Pang et al. [1] used 80 mg/L of polyaluminum chloride (PaCl) with Koaret PA 3230 and hydroxide ion as flocculant aid to treat 99% of 10 mg/L Pb ions in mixed Pb and Zn ion solution. Both studies found the alkaline region as a suitable operating phase and only considered the removal of Pb ions. The preparation of this kind of polymer flocculant was reported as too complicated. Although some natural flocculant can be used at a low concentration, the removal of some metals remains low.

Plant-based flocculant, *Tacca leontopetaloides*, comes from a wild distribution along a sandy beach of the Peninsular Malaysia, which has an active agent reported as biosorbent for heavy metal removal. Like other starches, *Tacca leontopetaloides* biopolymer flocculant (TBPF) consists mainly of polysaccharides of the monosaccharide, alpha- D- (+) glucopyranose type. In our previous study [9], TBPF has a amylose/amylopectin polymer mixture, viscosity, and zeta potential of 26:74, 0.037–0.04 Pa·s, and −13.14 mV, respectively, which helped in flocculating activity. During isolation process, the loss of birefringence and crystalline order in starch occurred due to the breaking of the double helix in the crystalline region and the leaching of amylose. Amylose consists of a linear, helical chains of roughly 500 to 20,000 alpha-D-glucose monomers linked together through alpha (1–4) glycosidic bonds. Meanwhile, despite amylopectin's relatively large molecular weight of ~$10^{7–8}$ and each branched polymer of glucose containing between one and two million residues, amylopectin remained in the structure [10,11]. The presence of –COOH and –OH structures in TBPF was also identified at the polymer adsorption active side. This reduced the turbidity, total suspended solids (TSS), and color of the leachate from 218 nephelometric turbidity unit(NTU), 214 mg/L, 14,201 PtCo to 45.8–54.5 NTU, 19.3–19.9 mg/L, and 852–994 PtCo, respectively, using 240 mg/L of TBPF at pH 3 [9]. However, the removal of heavy metals was not examined. Thus, the aim of this study was to evaluate the potential of TBPF for heavy metal removal at a low concentration through the coagulation–flocculation process with hydroxide ion.

2. Materials and Method

The experiment was conducted at room temperature in the laboratory. Four batch experiments were conducted to evaluate mixed metal ion removal efficiency. The effect of pH (hydroxide ion) in 2.0 mg/L of mixed Zn, Pb, Ni, and Cd metals ion solution was determined, followed by the effect of pH 3 to 12 on the metals ion removal using 240 mg/L dosage (from previous study) from an initial concentration of 3% TBPF in a 2.0 mg/L concentration of metal ions. The optimum pH, TBPF dosage, and initial metal ion concentration were kept constant while the initial TBPF concentration was varied at 3%, 5%, and 10%. The preparation and characterization of TBPF was carried out from our previous study [9]. Next, the effect of metal ion removal was examined by varying the metal ion concentration from 1.5 to 3.0 mg/L at fixed pH, dosage, and initial TBPF concentration. Finally, the effect on metal ion removal at various TBPF dosages was examined. The highest metal ion removal at optimum variables was compared with the standard regulated discharge limit set by the Department of Environment (DOE), Malaysia. All of the pieces of equipment used were immersed overnight with pure nitric acid to avoid any miscellaneous substance that would affect the consistency of results. The precautions and standard analysis were conducted following the standard method from the official method for analysis by the Association of Official Analytical Chemists [12].

2.1. Chemicals and Reagents

$Zn(NO_3)_2{\cdot}H_2O$, $Pb(NO_3)_2{\cdot}H_2O$, $Ni(NO_3)_2{\cdot}H_2O$, and $Cd(NO_3)_2{\cdot}H_2O$ used in this study were of analytical grade (R&M,Petaling jaya,Malaysia) with purity more than 99.9%. Each synthetic metal ion stock solution of 1000 mg/L was prepared separately using deionized water. For the preservation of the stock solution, pure nitric acid was added to a pH of less than 2. The desired concentration of each metal ion solution was prepared from the stock solution, and the pH was adjusted with 0.1 M NaOH (Merck Millipore,Subang jaya,Malaysia) and 0.1 M HCl (Merck Millipore,Subang jaya,Malaysia). The desired metal ion concentration was freshly prepared to avoid any inconsistent result due to metal precipitate.

2.2. Preparation of TBPF

Tacca leontopetaloides biopolymer flocculant (TBPF) was prepared following from our previous study [9]. A 3 g (3%) of Tacca starch was immersed in 80 °C of 100 mL distilled water. The mixture was vigorously stirred using a magnetic stirrer at 200 rpm for 1 h heating. The mass of Tacca starch was varied to 5 and 10% for study the effect initial TBPF concentration.

2.3. Coagulation–Flocculation Experiments

The coagulation–flocculation experiments were carried out based on our previous study [9]. The effects of pH, initial concentrations of TBPF and heavy metal solution, and TBPF dosage on the heavy metal removal were determined using the one-factor-at-a-time

(OFAT) method. The synthetic heavy metal solution containing Zn, Pb, Ni, and Cd metal ions was used to study the potential of TBPF in the heavy metal removal. A total of 500 mL of mixed metal ion solution consisted of Zn, Pb, Ni, and Cd was transferred into 1 L of six cylindrical beakers with different pH values varying from 3 to 12, adjusted using 0.1 M of HCl or NaOH. The metal ion solution was mixed rapidly (200 rpm) using a flat paddle impeller (75 × 25 mm) for 4 min. The speed of the stirrer was reduced to 40 rpm for 30 min. TBPF with the desired dosage was added during the slow speed phase. The mixture was left for 30 min, and then the supernatant was collected 5 cm from the surface of the suspension for metal analysis using the standard method. The effects of HCl and NaOH in the range of 3 to 12, initial TBPF stock (3%, 5%, and 10%), initial metal ion concentration (1.5–3 mg/L), and TBPF dosage (40–1200 mg/L) were studied. All analyses were performed in triplicate and assigned as run 1. The same experiment with a different batch was repeated and assigned as run 2.

2.4. Analysis of the Metal Ion Removal

The pH values throughout this study were measured using a standard portable MILWAUKEE (MW100) pH meter with 0.1 pH resolution. The concentrations of metal ions before and after pH variation, and after being treated with TBPF were determined using an atomic absorption spectrophotometer (Hitachi High-Technologies, Tokyo, Japan). A standard calibration curve was obtained by determining the absorbance at various concentrations of each metal ion. The effects of HCl, NaOH, and TBPF on metal ion removal were calculated using the following formula:

$$Metal\ ion\ removal\ (\%) = \frac{(Ci - Cf)}{Ci} \times 100 \quad (1)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively.

3. Results and Discussion

3.1. Effect of pH on the Removal of Zn, Pb, Ni, and Cd

The results of the Zn, Pb, Ni, and Cd ion removal by hydroxide precipitation and TBPF against pH are shown in Figure 1a–d. During the preparation of the metal solution, the nitrate salts of each metal were diluted in deionized water, causing the metal salts to split into its components, as shown in Equation (2), and turn into their original state as nitrate salts. When hydrochloric acid was added to the metal ion solution until pH 3, the metal ion removal was negative, indicating the increased amount of metal ions. This result occurred due to the presence of excess H^+ digesting the salt compounds to maintain its state as a single metal ion, thus yielding negative metal ion removal. In another situation where the pH was adjusted, the hydroxide ions provided chemical precipitation with the metal ion, thus directly assisting in the removal of metal ions. When the hydroxide ion was introduced, the metal ion formed an ionic compound with the hydroxide ion, thus forming precipitation, as shown in Equation (3) [13]. Due to this chemical precipitation, the removal of the ions at pH 12 increased to 74%, 52%, 84%, and 88% for Zn, Pb, Ni, and Cd, respectively. The metal precipitation was as follows: PB > Zn > Cd > Ni. The sequences were followed based on their chemical characteristic behavior, such as atomic weight, ionic radius, electronegativity, etc. [14] Among these metal ions, Pb (Figure 1b) removal was significant when the pH was adjusted from 5 to 9, decreased slightly at pH 10, and achieved equilibrium until pH 12.

$$M(NO_3)_2 \rightarrow M^{2+} + 2NO_3^- \quad (2)$$

$$M(\mathrm{OH})_2 + 2\mathrm{OH}^- \leftrightarrow M\mathrm{OH}_4^{2-} \quad (3)$$

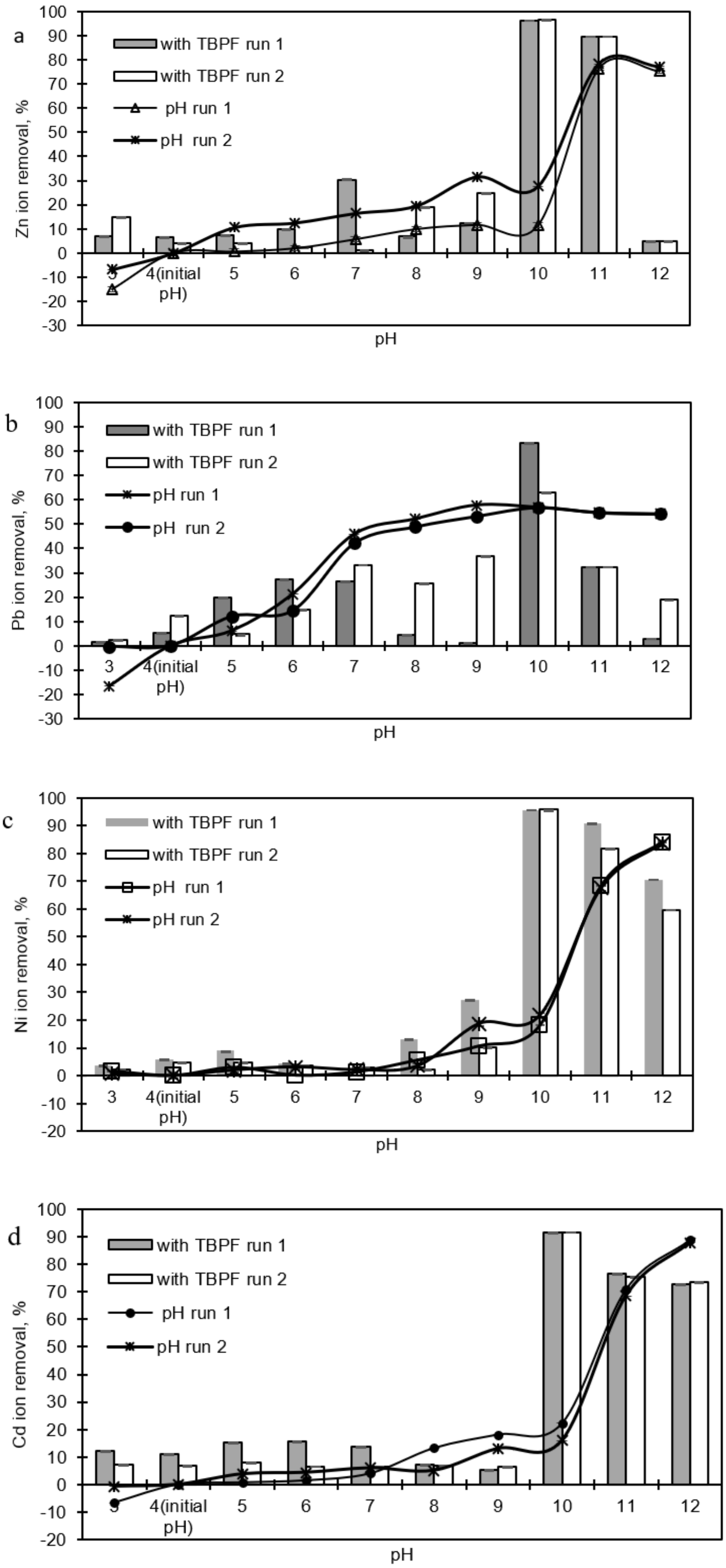

Figure 1. Effect of pH on metal ion removal: (**a**) Zn, (**b**) Pb, (**c**) Ni, and (**d**) Cd at a concentration of 2.0 mg/L.

From Figure 1, the minimum solubility for Zn, Pb, Ni, and Cd were at pH 11, 9, 12, and 12, respectively. At these pH values, the highest metal ion removals by hydroxide ions were 76%, 55%, 84%, and 88% from the initial concentration of 2.0 mg/L. Although the highest removal was approximately 88%, the final dissolved concentration (i.e., 0.24 mg/L for Cd) still exceeded the standard discharge limit set by DOE Malaysia.

Although metal ions can be treated using hydroxide ions, a huge amount of hydroxide ions is required, producing an excessive sludge that requires further treatment to achieve the standard limit discharge. Furthermore, it has problems such as slow metal precipitation, poor settling, aggregation of precipitation, and the long term of sludge disposal [15]. Therefore, *Tacca leontopetaloides* biopolymer flocculant (TBPF) was introduced as a polymer flocculant to promote polymer adsorption between the metal hydroxide and the polymer chain for bridging, and also as a charge neutralization mechanism to settle and remove the heavy metal ions.

Upon the addition of TBPF, the removal of Zn, Pb, Ni, and Cd improved significantly in the alkaline environment when compared with the acidic environment (Figure 1a–d). The treatment with 240 mg/L of 3% TBPF in 2.0 mg/L metal ion solutions worked well, providing more than 80% removal of Zn, Cd, and Ni in the pH range of 10 to 11. The final concentrations of Zn, Pb, Ni, and Cd at the maximum removal were 0.04–0.08, 0.74–0.9, 0.1, and 0.18 mg/L, respectively, which exceed the discharge limits of Standard A and B The removal of Pb was the lowest at 55–63% but still showed the maximum removal in the alkaline phase. This shows that TBPF has more reactive sites to form linkages in the following sequence: Zn > Ni > Cd > Pb, and it worked efficiently in the alkaline phase when compared with the acidic phase. This is due to the difference in the stability constant of the metal ions and ligands [5]. Furthermore, the hydroxyl and carboxyl functional groups in TBPF could ionize into sodium salt at high pH (alkaline region), thus increasing solubility [16]. Upon increasing pH value, the carboxylic groups on TBPF were progressively deprotonated and reached full dissociation, while the flocculant was dissolved in water because of the high ionizability of the anionic groups, and it formed a more extended conformation [6]. Polymer bridging and charge neutralization took place between the negatively charged TBPF and cationic metal ions, increasing the flocculation efficiency. The removals of Zn, Pb, Ni, and Cd at pH 4 (initial pH solution) were only 4–11%, 9–12%, 4–5%, and 6–11%, respectively, significantly contrasting with the removals at pH 10 (Figure 1). In the case of suspension of the metallic solution at a low pH, the distorted configuration of the polymer reduced its size, and the polymer adsorbed on the surface with the chain train in close contact with many surface sites. This caused strong bonding between the polymer mixture chain (amylose/amylopectin) and metallic surface but with limited close contact. At pH 7, the negative charge of the suspension increased; thus, the polymer adsorbed in loops due to the increased electrostatic repulsion, and it started bridging and forming floc. At pH 10, a further increase in charge increased the repulsion between the metallic surface and the polymer. The extended polymer chains provided a large surface area for the adsorption and bridging mechanism, thus leading to the formation of large floc [16]. The flocculation mechanism as a function pH and absorption of metallic surface on TBPF polymer are shown in Figure 2.

3.2. Effect of Initial Concentration of TBPF on the Removal of Zn, Pb, Ni and Cd Ions

The effect of TBPF dosages (3%, 5%, and 10%) on the removals of Zn, Pb, Ni, and Cd in 2.0 mg/L metal ion concentration at pH 10 is shown in Figure 3. There was no effect of the different initial concentrations of TBPF on the removals of Zn, Ni, and Cd, but a significant effect on Pb ion removal was observed. Increasing the initial concentration of TBPF increased the removal of Pb ion. However, the removal of all metal ions was more than 95% at pH 10 compared with the use of hydroxide ions alone, which was less than 18%. At a high pH of the metal ion solution, the high concentration of TBPF increased the degree of interchain interaction between the polymer mixture chain and metal hydroxide; thus sufficient polymer aggregate formation occurred [6]. In addition, the content of polymer mixture leached (amylose and amylopectin) in TBPF increase as the concentration increase. The same result pattern was obtained by Ma et al. [17] who used the highest amount of methacryloxy ethyl trimethyl ammonium chloride (DMC) from 10, 20, 30, and 40 wt% on kaolin suspension. Therefore, 10% of the initial TBPF concentration was further used in subsequent experiments.

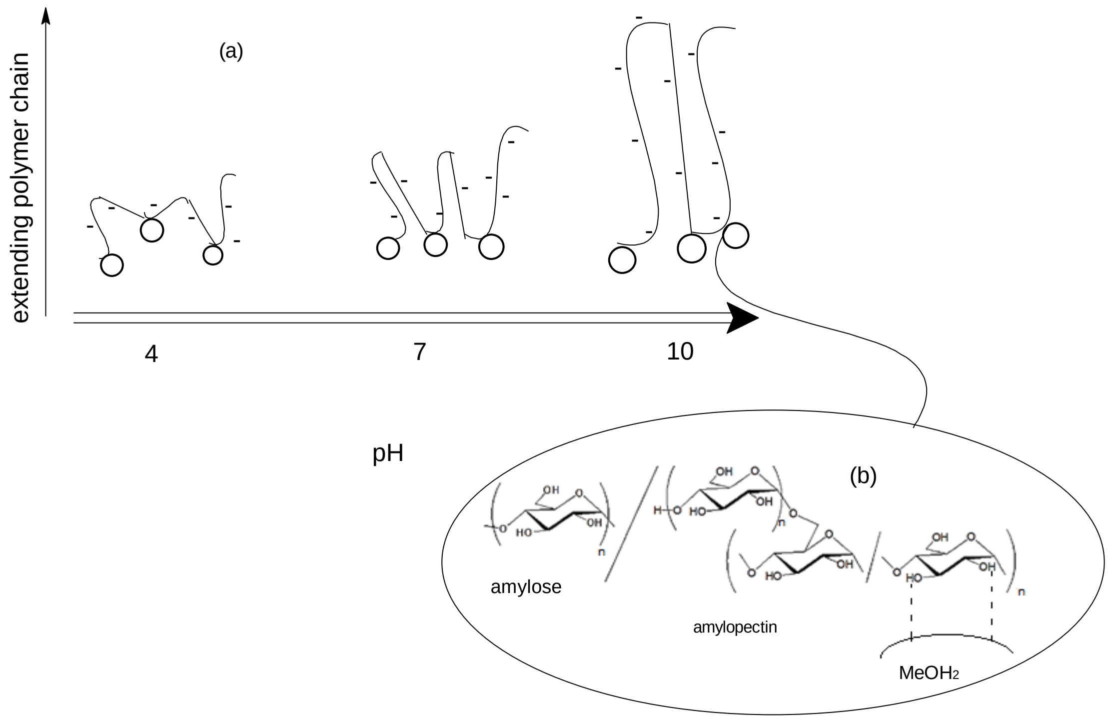

Figure 2. (**a**) Flocculation mechanism in increasing pH and (**b**) absorption of $Me(OH)_2$ on the *Tacca leontopetaloides* biopolymer flocculant (TBPF) surface.

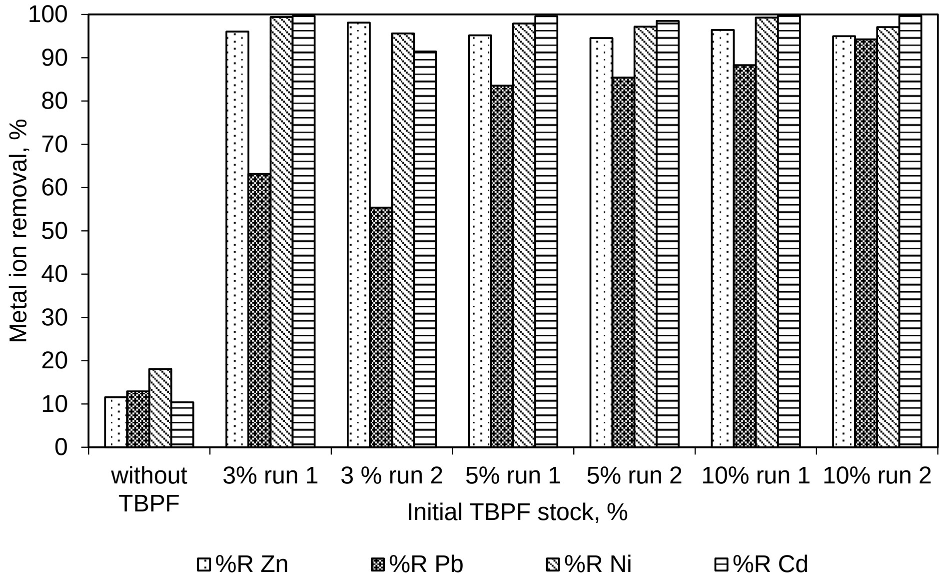

Figure 3. Effect of initial concentration of TBPF (3%, 5%, and 10%) on metal ion removal (Zn, Pb, Ni, and Cd) at pH 10 in a 2.0 mg/L metal ion concentration.

3.3. Effect of Initial Metal Ion Concentration on Metal Ion Removal

The presence of a multi-metal solution influences the sorption of metal due to the presence of a competitive process between metal ions and the TBPF surface. The active site on the TBPF surface is competitively divided among the metal ions. It is difficult to identify the competitive process between the metal ions and the TBPF surface. Nevertheless, it has been reported in the literature [14,18–20] that the atomic weight, electronegativity, electrode potential, ionic radius, hydration energy, softness capacity for hydroxylation, and position in the Irving–Williams series could be a factor of sorption affinity. Based on Figure 4, as the initial concentration of metal ions increased from 1.5 to 2.5 mg/L, the removal of metal ions increased sharply at pH 10 and 800 mg/L of 10% TBPF due to the presence of a large number of vacant sites on the metal ions and polymer chains [14], while it decreased in the metal ion solution of 3 mg/L. At a higher concentration, the numbers of metal ions were relatively higher than the available sites on the fixed TBPF dosage, hence decreasing the removal percentage. The removal of Pb (Figure 4b) was lower compared with the removals of Zn, Ni, and Cd. Factors such as ionic radius could be considered further and may fit the results, as the lower the ionic radius of metal, the higher the sorption affinity [14,19,21]. Therefore, Ni displayed the highest removal due to the fact that Ni has the lowest ionic radius (0.69 Å), followed by Zn (0.74 Å), Cd (0.95 Å) and Pb (1.19 Å). The highest removals of Zn, Pb, Ni, and Cd at 2.5 mg/L metal ion solutions were in the ranges of 94–98%, 77–80%, 93–99%, and 90–93%, respectively.

3.4. Effect of TBPF Dosage on Metal Ion Removal

The removal of metal ions was further evaluated with the effect of various TBPF dosages (Figure 5). At pH 10, a 2.5 mg/L concentration of metal ion solution, and 10% of initial TBPF concentration, the dosage of TBPF in the metal ion solution varied between 40 and 1200 mg/L. The removal of Pb (Figure 5b) was lower, and the trend of Pb removal was significant towards the various TBPF dosages compared with the other metal ions. The removals of Zn, Pb, Ni, and Cd increased to 98.4–98.5%, 79–80%, 97–98%, and 92–93%, respectively upon increasing the TBPF dosage from 40 to 120 mg/L. At a low dosage, the number of anionic sites was insufficient for complete neutralization of the cationic metal ions, resulting in weak destabilization of colloids [6,14]. The maximum metal ion removal by TBPF was recorded at 120 mg/L. When the dosage of TBPF increased further, the removal of metal ions recorded no further increment because there were many flocculants in the aqueous solution to obstruct the interaction between the flocculant molecules and heavy metals due to electrostatic repulsion [22], and the number of metal ions surrounding the polymer chains was limited when compared to the available active sites on the polymer chains. This is in agreement with Wu et al. [6]. The optimum dosage obtained was lower when compared with that initial used, probably because of the effect of the initial concentration, as studied earlier. The content monomer in TBPF increased as the concentration increased, and, thus, the optimal dosage evidently decreased [17].

3.5. Comparison of Final Treatment of Heavy Metals with the Standard Limit Set by DOE Malaysia

The final treated heavy metal ions using 120 mg/L of 10% TBPF at pH 10 in a 2.5 mg/L metal ion concentration and their comparison with the standard limits set by DOE Malaysia are shown in Table 1. The targeted heavy metal removal must be based on the standard discharge requirement set by DOE Malaysia, under the discharge effluent limit. Standard A is the effluent discharge in the upstream of the water supply, and Standard B is the effluent discharge in the downstream. At pH 10 and with a 120 mg/L TBPF dosage with 10% initial concentration, the best removal of metal ions was achieved at 2.5 mg/L. The final concentrations after hydroxide precipitation of Zn, Pb, Ni, and Cd were 2.75, 2.05, 1.89, and 1.80 mg/L, respectively. After the treatment with TBPF, the final concentrations were 0.04, 0.41–0.43, 0.04–0.05, and 0.11–0.13 mg/L, respectively. The final concentrations of Zn, Pb, and Ni complied with Standard B. Only the concentrations of Zn and Ni complied with Standard A. However, the concentration of Cd did not comply with either standard discharge limits.

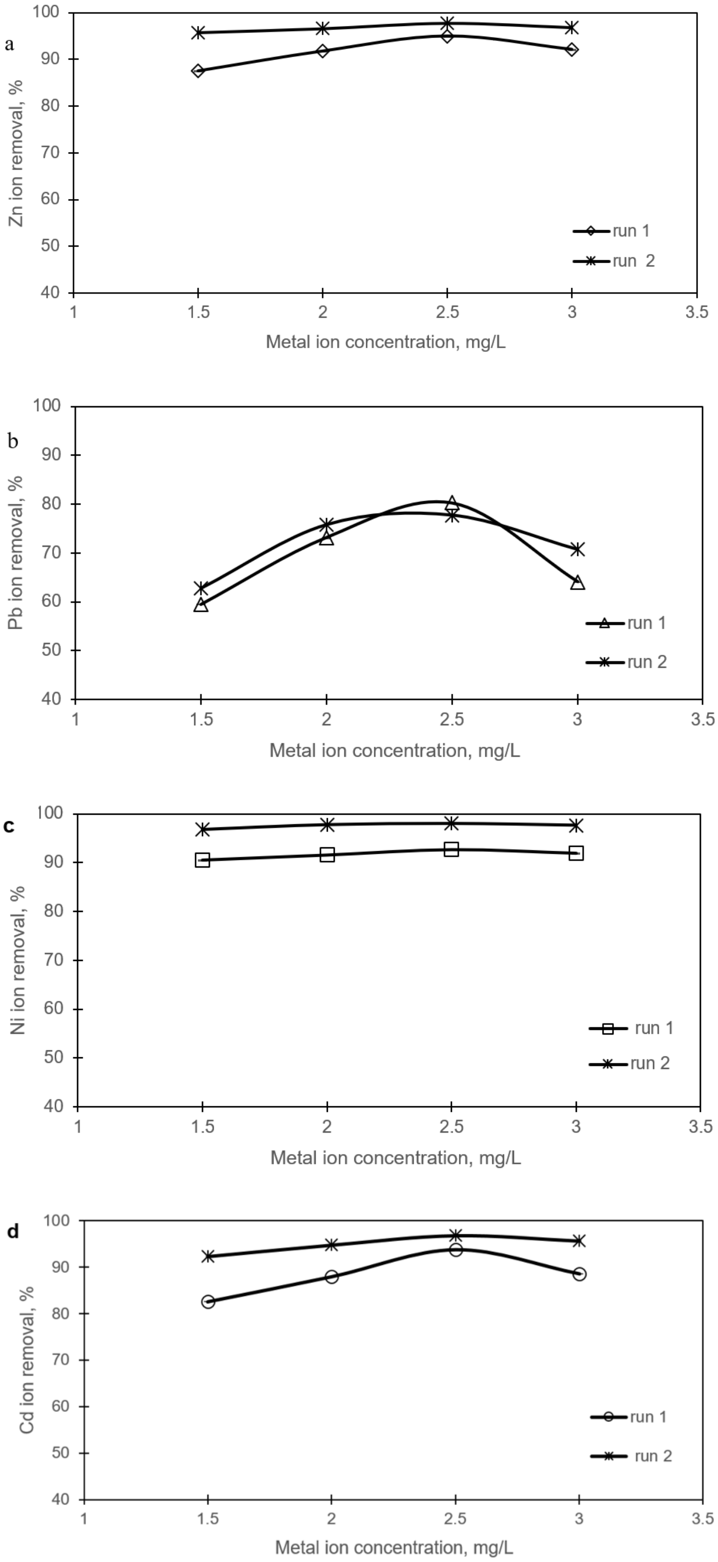

Figure 4. Effect on metal ion removal: (**a**) Zn, (**b**) Pb, (**c**) Ni, and (**d**) Cd at pH 10, using 800 mg/L of 10% TBPF in 1.5 to 3 mg/L metal ion concentrations.

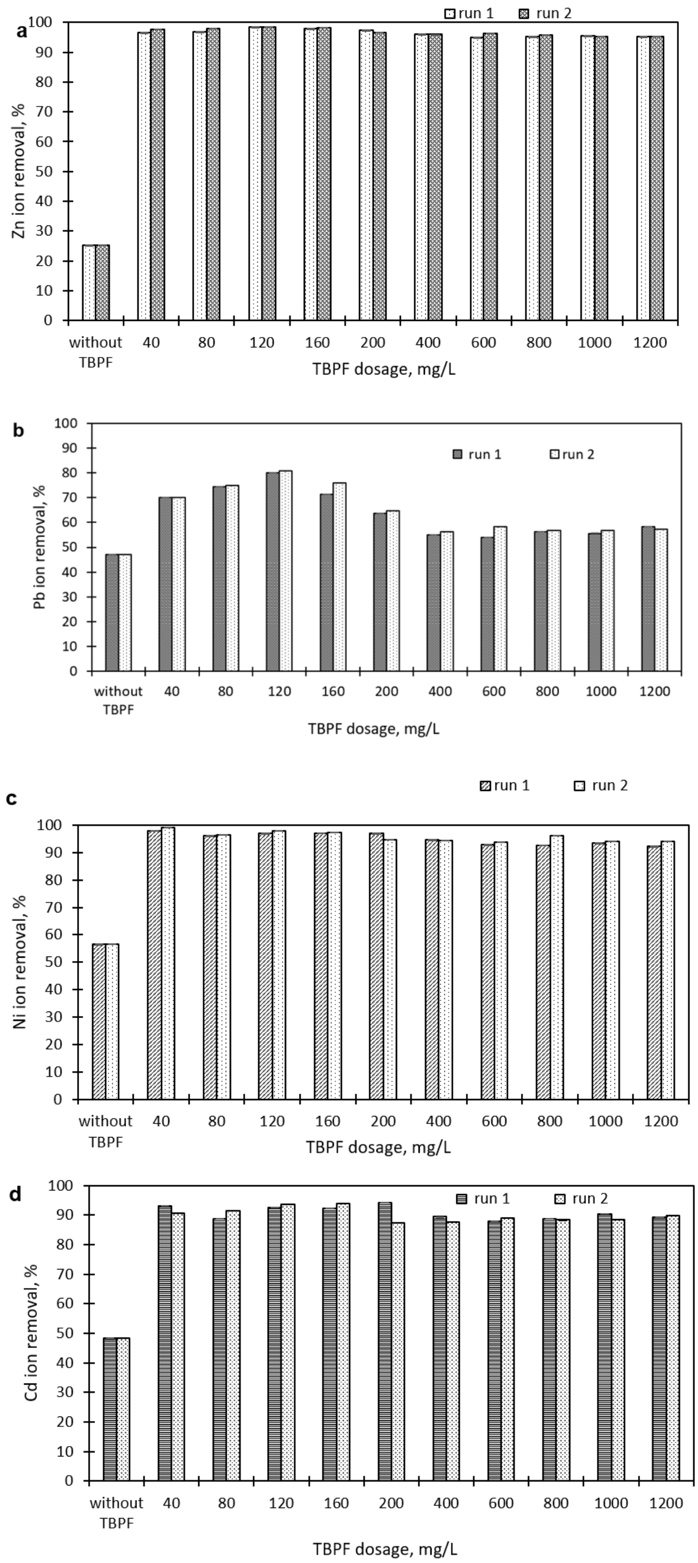

Figure 5. Effect of TBPF dosages on metal ion removal: (**a**) Zn, (**b**) Pb, (**c**) Ni, and (**d**) Cd at pH 10 in a 2.5 mg/L metal ion concentration.

Table 1. Comparison of final treatment of heavy metals with the standard limit set by the Department of Environment (DOE), Malaysia at 120 mg/L of 10% TBPF at pH 10 in a 2.5 mg/L metal ion concentration.

Metal Ion	Treatment		DOE Discharge	
	Before (mg/L)	After(mg/L)	Standard A (mg/L)	Standard B (mg/L)
Zn	2.75 ± 0.00	0.043 ± 0.00–0.044 ± 0.00	1.0	1.0
Pb	2.05 ± 0.01	0.41 ± 0.02–0.43± 0.01	0.1	0.5
Ni	1.89 ± 0.01	0.037 ± 0.00–0.054 ± 0.00	0.2	1.0
Cd	1.80 ± 0.00	0.11 ± 0.00–0.13 ± 0.00	0.01	0.02

3.6. Comparison of TBPF Performance with Other Natural and Chemical Flocculants

The performance of TBPF on metal ion removal was compared with other natural and chemical flocculants (Table 2). Most of the flocculants exhibited a functional group of carboxyl (COOH) as an active site for heavy metal removal. Other types of active sites in the polymer flocculant which also contribute to the removal of heavy metals are methyl ethyl in hydroxyethyl starch (HES), amino in pH-responsive amphoteric starch derivative (PRAS), methoxylate group in nopal pectin, and aluminum chloride in polyaluminum chloride (PaCl). In general, these flocculants performed better after being integrated into their functional structures. However, without the integration into its functional structure, TBPF showed more than 80% (up to 98%) removal of Zn, Pb, Ni, and Cd. TBPF can also capture all of the metal ions simultaneously, while pH-responsive amphoteric starch derivative (PRAS) can only capture Zn. PolyDAMAC + cationic polyelectrolyte and PaCl as chemical flocculants can only capture Pb ions. Even though TBPF was less effective in the removal of Pb when compared with commercial flocculant polyDADMAC + cationic polyelectrolyte, polyelectrolyte and Koaret PA 3230 + PaCl, most of the studies used high initial metal ion concentrations, while this study used a low concentration. The initial concentration of flocculant used in other studies recorded low removals when compared with TBPF. The suitable operating condition for TBPF was pH 10 (alkaline phase), and this is in agreement with the commercial flocculants. Some flocculants, such as nopal pectin (pH 3.3) and hydroxyethyl starch grafted with poly-*N*,*N*-dimethyl acrylamide (HES-g-PDMA) (pH 5.5), need acidic conditions to perform. Thus, further consideration is needed in regard to the cost of pH adjustment. The dosage of TBPF (120 mg/L) used in this study was in the range of the dosage used in other studies (19–2000 mg/L). TBPF has high potential to be used in the removal of heavy metals in real wastewater without being integrated into its functional structure, which makes it cost effective and easy to prepare.

Table 2. Comparison of metal ion removal by TBPF with other flocculants.

Natural/Chemical Polymer Flocculant	Nature of Wastewater	Flocculant Aid	Polymer Active Site	pH	Flocculant Initial Concentration (%)	Metal Ion Initial Concentration (mg/L)	Flocculant Dosage (mg/L)	Metal Ion Removal (%)				Reference
								Zn	Pb	Ni	Cd	
Natural Flocculants												
TBPF	Synthetic heavy metal	Hydroxide ion	Carboxylic and hydroxyl	10	10	2.5	120	98.4–98.5	79–80	97–98	92–93	This study
Hydroxyethyl starch grafted with poly-*N*,*N*-dimethyl acrylamide (HES-g-PDMA)	Synthetic heavy metal	Hydroxide ion	Amino and carboxyl	5.5	-	355	2000	25	10	14	-	[5]
pH-responsive amphoteric starch derivative (PRAS)	Synthetic heavy metal	-	Methyl ethyl and amide	9	1	74	70	91	-	-	-	[6]
Nopal pectin	Synthetic heavy metal	-	Carboxylate and methoxy-late group	3.4	0.2	Zn (344.14) Pb (701.28) Ni (1457.54) Cd (399.66)	19	99	67	90	44	[7]
Chemical Flocculants												
Polydiallyldim ethylammonium chloride (PolyDADMAC)_ + cationic polyelectrolyte	Electroplating wastewater	Hydroxide ion and polyDAD-MAC	-	9	0.011	626	67	-	99	-	-	[8]
PaCl	Synthetic heavy metal	Koaret PA 3230 + and hydroxide ion	Polyaluminum	8.0–9.3	-	Pb (7) Zn (10)	80	-	98	-	-	[1]

4. Conclusions

The removal of Zn, Pb, Ni, and Cd in synthetic wastewater based on several factors was successfully determined. The involved factors were pH, initial TBPF concentration, initial metal ion concentration, and TBPF dosage. The removals of 98%, 79–80%, 97–98%, and 92–93% of Zn, Pb, Ni, and Cd, respectively, were achieved at the dosage of 120 mg/L of 10% TBPF in 2.5 mg/L of metal ions at pH 10. The final concentrations of Zn, Pb, Ni, and Cd were 0.043–0.044, 0.41–0.43, 0.037–0.054, and 0.11–0.13 mg/L, respectively, which were below the Standard B discharge limit set by the Department of Environment (DOE), Malaysia. Among the metal ions studied, Pb showed different behavior towards these factors. The addition of TBPF after chemical precipitation by hydroxide ions enhanced the removal of metal ions. Therefore, TBPF successfully removed Zn, Pb, Ni, and Cd metal ions in synthetic wastewater; thus, it has high potential to be used in real wastewater treatment.

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References

1. Pang, F.M.; Teng, S.P.; Teng, T.T.; Mohd Omar, A.K. Heavy metals removal by hydroxide precipitation and coagulation-flocculation methods from aqueous solutions. *Water Qual. Res. J. Can.* **2009**, *44*, 174–182. [CrossRef]
2. Ismail, Z.; Salim, K.; Othman, S.Z.; Ramli, A.H.; Shirazi, S.M.; Karim, R.; Khoo, S.Y. Determining and comparing the levels of heavy metal concentrations in two selected urban river water. *Meas. J. Int. Meas. Confed.* **2013**, *46*, 4135–4144. [CrossRef]
3. Rehman, K.; Fatima, F.; Waheed, I.; Akash, M.S.H. Prevalence of exposure of heavy metals and their impact on health consequences. *J. Cell. Biochem.* **2018**, *119*, 157–184. [CrossRef] [PubMed]
4. Embas, D.U. EQA ACT 1974 (Sewage) Regulation 2009. 2009; pp. 3884–3926. Available online: http://www.doe.gov.my/portalv1/wp-content/uploads/2015/01/Environmental_Quality_Sewage_Regulations_2009_-_P.U.A_432-2009.pdf (accessed on 23 November 2020).
5. Kolya, H.; Tripathy, T. Preparation, investigation of metal ion removal and flocculation performances of grafted hydroxyethyl starch. *Int. J. Biol. Macromol.* **2013**, *62*, 557–564. [CrossRef] [PubMed]
6. Wu, L.; Zhang, X.; Chen, L.; Zhang, H.; Li, C.; Lv, Y.; Xu, Y.; Jia, X.; Shi, Y.; Guo, X. Amphoteric starch derivatives as reusable flocculant for heavy-metal removal. *RSC Adv.* **2018**, *8*, 1274–1280. [CrossRef]
7. 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]
8. López-maldonado, E.A.; Oropeza-guzman, M.T.; Jurado-baizaval, J.L. Coagulation—flocculation mechanisms in wastewater treatment plants through zeta potential measurements. *J. Hazard. Mater.* **2014**, *279*, 1–10. [CrossRef] [PubMed]
9. Mohd Makhtar, N.S.; Idris, J.; Musa, M.; Andou, Y.; Ku Hamid, K.H.; Puasa, S.W. Plant-Based Tacca leontopetaloides Biopolymer Flocculant (TBPF) Produced High Removal of Turbidity, TSS, and Color for Leachate Treatment. *Processes* **2020**, *8*, 527. [CrossRef]
10. Li, H.; Fitzgerald, M.A.; Prakash, S.; Nicholson, T.M.; Gilbert, R.G. The molecular structural features controlling stickiness in cooked rice, a major palatability determinant. *Sci. Rep.* **2017**, *7*, 1–12. [CrossRef] [PubMed]
11. Alcázar-Alay, S.C.; Meireles, M.A.A. Physicochemical properties, modifications and applications of starches from different botanical sources. *Food Sci. Technol.* **2015**, *35*, 215–236. [CrossRef]
12. Helrich, K. AOAC: Official Methods of Analysis (Volume 1). *J. Assoc. Off. Agric. Chem.* **1990**, *1*, 237–242.
13. Abdullah, S.R.S.; Rahman, R.A.; Mohammad, A.B.; Mustafa, M.M.; Khadum, A.A.H. Removal of Mixed Heavy Metals by Hydroxide Precipitation. *J. Kejuruter.* **1999**, *11*, 85–101.
14. Matouq, M.; Jildeh, N.; Qtaishat, M.; Hindiyeh, M.; Al, M.Q. The adsorption kinetics and modeling for heavy metals removal from wastewater by Moringa pods. *J. Environ. Chem. Eng.* **2015**, *3*, 775–784. [CrossRef]

15. Barakat, M.A. New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem.* **2011**, *4*, 361–377. [CrossRef]
16. Shouci, L.; Pugh, R.J.; Forssberg, E. Chapter 7 Flocculation with polymers. In *Interfacial Separation of Particles*; Elsevier B.V.: Amsterdam, The Netherlands, 2005.
17. Ma, J.; Fu, K.; Fu, X.; Guan, Q.; Ding, L.; Shi, J.; Zhu, G.; Zhang, X.; Zhang, S.; Jiang, L. Flocculation properties and kinetic investigation of polyacrylamide with different cationic monomer content for high turbid water purification. *Sep. Purif. Technol.* **2017**, *182*, 134–143. [CrossRef]
18. Mattuschka, B.; Straube, G. Biosorption of metals by a waste biomass. *J. Chem. Technol. Biotechnol.* **1993**, *58*, 57–63. [CrossRef]
19. Igwe, J.; Abia, A.A. Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob. *Eclética Química* **2007**, *32*, 33–42. [CrossRef]
20. Ouyang, D.; Zhuo, Y.; Hu, L.; Zeng, Q.; Hu, Y.; He, Z. Research on the adsorption behavior of heavy metal ions by porous material prepared with silicate tailings. *Minerals* **2019**, *9*, 291. [CrossRef]
21. Goel, J.; Kadirvelu, K.; Rajagopal, C. Competitive sorption of Cu(II), Pb(II) and Hg(II) ions from aqueous solution using coconut shell-based activated carbon. *Adsorpt. Sci. Technol.* **2004**, *22*, 257–273. [CrossRef]
22. Sun, Y.; Shah, K.J.; Sun, W.; Zheng, H. Performance evaluation of chitosan-based flocculants with good pH resistance and high heavy metals removal capacity. *Sep. Purif. Technol.* **2019**, *215*, 208–216. [CrossRef]