


## Article

# Greener Method for the Removal of Toxic Metal Ions from the Wastewater by Application of Agricultural Waste as an Adsorbent

Rabia Baby Shaikh <sup>1,\*</sup>, Bullo Saifullah <sup>2</sup>  and Fawad ur Rehman <sup>2</sup> <sup>1</sup> Education Department, Sukkur IBA University, Sukkur, Sindh 65200, Pakistan<sup>2</sup> Henan-Macquarie Universities Joint Center for Biomedical Innovation, Henan University, Jin-Ming Avenue, Kaifeng 475004, China; bullosaif1@gmail.com (B.S.); dawarvet@hotmail.com (F.u.R.)

\* Correspondence: rabia.shaikh@iba-suk.edu.pk; Tel.: +92-71-564-4000

Received: 12 July 2018; Accepted: 6 September 2018; Published: 23 September 2018



**Abstract:** The presence of inorganic pollutants such as metal ions ( $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{6+}$ ) in water, probably by long-term geochemical changes and from the effluents of various industries, causes diseases and disorders (e.g., cancer, neurodegenerative diseases, muscular dystrophy, hepatitis, and multiple sclerosis). Conventional methods for their removal are limited by technical and economic barriers. In biosorption, low-cost and efficient biomaterials are used for this purpose. In this study, *Brassica Campestris* stems from the agriculture waste and has been used for the removal of  $\text{Ni}^{2+}$ ,  $\text{Cr}^{6+}$  and  $\text{Pb}^{2+}$  ions from an aqueous solution containing all the ions. Effect of different parameters, e.g., pH, contact time, metal ion initial concentration, adsorbent dose, agitation rate and temperature were analyzed and optimized. The adsorbent worked well for removal of the  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$  as compared to  $\text{Ni}^{2+}$ . The atomic absorption spectrophotometer (AAS) and FTIR investigation of adsorbent before and after shows a clear difference in the adsorbent capability. The highest adsorption percentage was found at 98%, 91%, and 49% respectively, under the optimized parameters. Furthermore, the Langmuir isotherm was found better in fitting to the experimental data than that of the Freundlich isotherm.

**Keywords:** water purification; heavy metal contamination; adsorption; sorbent; kinetics; Chromium (VI); Lead (II); Nickel (II); *Brassica Campestris*

## 1. Introduction

The situation of water pollution is getting worse and worse worldwide with industrialization and urbanization [1–5]. Moreover, the inorganic pollutants such as metal ions ( $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{6+}$ ) are mixed in drinking water through rivers as industrial waste water [6]. The removal of toxic metals from wastewater is necessary because they disrupt the human organelles, consumed through the food cycle as non-biodegradable contaminants [7]. The main sources of heavy metals into water are industrial waste, likewise from electroplating, the mining process of metals, metallurgical engineering, primary and secondary battery productions, the manufacturing of paints and pigments, nuclear power stations, and ceramic and glass factories. Similarly, pewter, enamels, film and photography, galvanometric, mining, alloys (especially magnetic steels and stainless steels), electronics, porcelain and radioisotope therapy, fertilizer, petrochemicals, tanneries, paper and pulp, oil refinery, fossil fuel burning, pharmaceutical and gasoline additives, stainless steel, aircraft industries, nickel electroplating, stabilizers and thermoplastics also contribute to heavy metal pollution [1,8,9]. Different conventional techniques are widely utilized for the removal of toxic metal ions from aqueous solutions namely reverse osmosis, precipitation, evaporation, colorimetric and radiometric fluorescent, fungi biosorption,

biosorption with bacteria, phytoextraction, electrodeposition, ion exchange, membrane separation and coagulation [10–18]. Because of the energy consumption, high cost and low volume concentration removal of metal ions, they are not as effective as suggested in many studies [8]. Research studies suggest that the adsorption of agricultural waste is the most potential method as it is economical, requires lesser chemical reagents and is eco-friendly for removing toxic metal ions from wastewater [19]. Research studies have proved that plants like *Azadirachta indica* (Neem tree) bark, peapods, leaves, stems, peanut seeds, tree pulps, saltbush (*Atriplex canescens*) leaves, banana pith, tree fern, a stalk of grape waste are highly capable to uptake the heavy metals from wastewater [20]. The presence of active functional groups of amino, carboxyl, and esters which metal ions helps in biosorption complexation. Other bio sorbents have been used in the method for making it more effective. *Brassica Campestris* plant is also recognized as an excellent phytoextraction material [21,22]. The finest and prospect usage of different *Brassica* family stems are used from its necessary acceptance to poisonous metals and fairly small sized powdered biomaterial assembly [20,23]. The aim of this study was to assess the potential use of *Brassica Campestris* stem as low cost, easy availability, non-modified biosorbent for the  $\text{Pb}^{2+}$ ,  $\text{Cr}^{6+}$  and  $\text{Ni}^{2+}$  ions removal in the field of biosorption.

## 2. Materials and Methods

### 2.1. Chemical Reagents and Instruments

Two % formaldehyde,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , 0.1 M HCl, 0.1 M NaOH were bought from Sigma-Aldrich (St. Louis, MO, USA). Atomic Absorption Spectrophotometer (Perkin Elmer AA-100 Analyst, (Waltham, MA, USA) digital pH meter (Mettler, Toledo, OH, USA), FTIR Thermoscientific (Waltham, MA, USA) and thermometers were applied throughout studies.

#### 2.1.1. Sample Collection and Preparation of Stock Solutions

The samples of *Brassica Campestris* waste stem as *biomass* were collected from agriculture farmland. The biomass was washed with tap water and dehydrated in the sunlight for 3 days. Dried mass was then rinsed with distilled water for another time and sprayed with 2% formaldehyde solution to protect it from organic leakages and mold formation at batches in adsorption by following the previously reported protocol [9]. The different stages of biomass preparation are shown in the Supplementary Figures S1–S4. The salt solution of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  of 1 ppm concentration were prepared and dispensed separately in three different 1000 mL volumetric flasks and leveled with double distilled water. A pH value of 5 was maintained by hydrochloric acid and sodium hydroxide solutions for further steps.

#### 2.1.2. Biosorption Studies

An appropriate amount of biosorbents were added to 50 mL aqueous salts solutions of nickel, chromium, and lead in all experiments. They were shaken in the environmental shaker for different time points at the optimized rpm and room temperature. After that, the samples were filtered by Whatmann filter paper ME cellulose 0.45  $\mu\text{m}$ . The filtrate was scrutinized for the metal ions by Atomic Absorption Spectrophotometer (Perkin Elmer AA-100 Analyst, (Waltham, MA, USA) for metal ions quantification and adsorption capacity [24], by the equation given below;

$$q_e = (C_o - C_e) \times V/m \quad (1)$$

Removal efficiency, E (%) was measured by

$$(\%) = [(C_o - C_e)/C_o] \times 100 \quad (2)$$

Respectively, whereas  $q_e$  (mg/g) is equilibrium adsorption mass,  $C_o$  represents the initial metal ion concentration (mg/L),  $C_e$  shows the equilibrium concentration in (mg/L),  $V$  shows the volume and  $W$  is biomass amount in (g).

## 2.2. Adsorption Experiments

### 2.2.1. Adsorbent Dosage and Initial Metal Concentration

The adsorbent dose was utilized in 0.2, 0.4, 0.6, 0.8, 1 gm and optimized by keeping the other factors constant. The initial metal concentration effect is the characteristic parameter on equilibrium in adsorption studies and is analyzed by adding a 1.0 g dosage of adsorbent in 50 mL of metal solutions of initial concentrations ranging from (20 to 120 mg/L). The batch trembled for 1 h in 5 pH at 30 °C and 150 rpm for all the metal ions in a water bath. The final equilibrium values were fixed to the Langmuir [25] and Langmuir-Freundlich isotherm model [26].

### 2.2.2. Optimization of Agitation Rate and Optimization of pH

The variation in shaking rate on equilibrium was studied by loading 1.0 g of adsorbent solutions with 50 mL of ppm metal solutions (single-component) and shaking time was 1 h with a range from 50 to 250 rpm at pH 5 at 30 °C. The pH effect was examined by involving 1.0 g of ground biomass with 50 mL metal ions solutions. The pH values were kept between 3 and 11 and were constantly adjusted throughout the experiment by micro-additions of  $HNO_3$  of 0.1 M or  $NaOH$  of 0.1 M. The batch was shaken for 1 h, 250 rpm rate at 30 °C [27].

### 2.2.3. Contact Time and Optimization of Temperature

Kinetic studies were conducted by keeping the mass in 'g' of biomass with 50 mL metal ions solutions and shaken with optimized pH, temperature and at a rate of rpm found in last batches. Samples were analyzed after fixed intervals (15–75 min). The effect of pH on adsorption studies was determined by maintaining the pH of adsorbate, a dose of adsorbent contact time constant while increasing the temperature from 30–75 °C.

### 2.2.4. FT-IR Characterization and Sorption Isotherm

FT-IR is a technical process, and supports the intermixing of IR rays and taster materials in either solid, liquid or gaseous state. Standardized and treated ground biosorbent particles with metal ions were examined on the surface of the ZnS plate of attenuated pressure and reflectance, keeping the range of  $4000\text{--}400\text{ cm}^{-1}$  FTIR [28]. The kinetic experiment values have been studied with the equations of Langmuir and Freundlich isotherms for fixing the equilibrium of metals adsorption on *Brassica Campestris* stem. The two forms of Linear equations are followed in Formula 3 and 4. [25]

$$Q_e = (bQ_m C_e)/(1 + bC_e) \quad (3)$$

Linearly,

$$C_e/q_e = (C_e/q_m) + 1/(bq_m), \quad (4)$$

where  $C_e$  is an equilibrium concentration of metals (mg/L),  $q_e$  and  $q_m$  are the amounts of metals adsorbed (mg/g) and the concentrated amount of metals adsorbed (mg/g) per unit mass of sorbent, respectively.  $K_a$  is the adsorption constant related to the isotherm models of Freundlich, and show

$$Q_{eq} = K_f \times C_{eq} \times 1/n, \quad (5)$$

$$\text{Log } q_e = \text{log } K_f + 1/n \times \text{log } C_e, \quad (6)$$

where,  $Q_{eq}$  and  $C_{eq}$  are similar to Langmuir's equation while  $K_f$  and  $1/n$  are Freundlich co-efficients. Fifteen different models of isotherms have been introduced up to the present time [29].

### 3. Results

Different Batches were kept at different values of parameters for the studies of adsorption of *Brassica Campestris*. The stem on lead (II), Chromium (VI) and Nickel (II) metal ions.

#### 3.1. Effect Dosage of Adsorbent

Figure 1 shows the trends in the metal ions adsorption which shows the direct relation with the quantity of biomass, i.e., metal ions adsorption increases with an increase in the amount of biomass [30]. This is because of the more the biomass more the linkages for formation of complexes with metal ions. Further increment does not bring about a significant change, suggesting that the presence of the linkages saturated with ions and equilibrium has been established between the biomass and ions. The percentage adsorption of Nickel and Lead were found to be 53% and 71%, while the Chromium ions showed the highest adsorption of 97.3% respectively, in 1000 mg and 600 mg of adsorbent dosage, while keeping the other optimized conditions constant, e.g., initial concentration of 1000 mg/L, 1 h time, 150 rpm rate, pH 5, temp.  $30 \pm 2$  °C, the volume of 50 mL of stock solution.

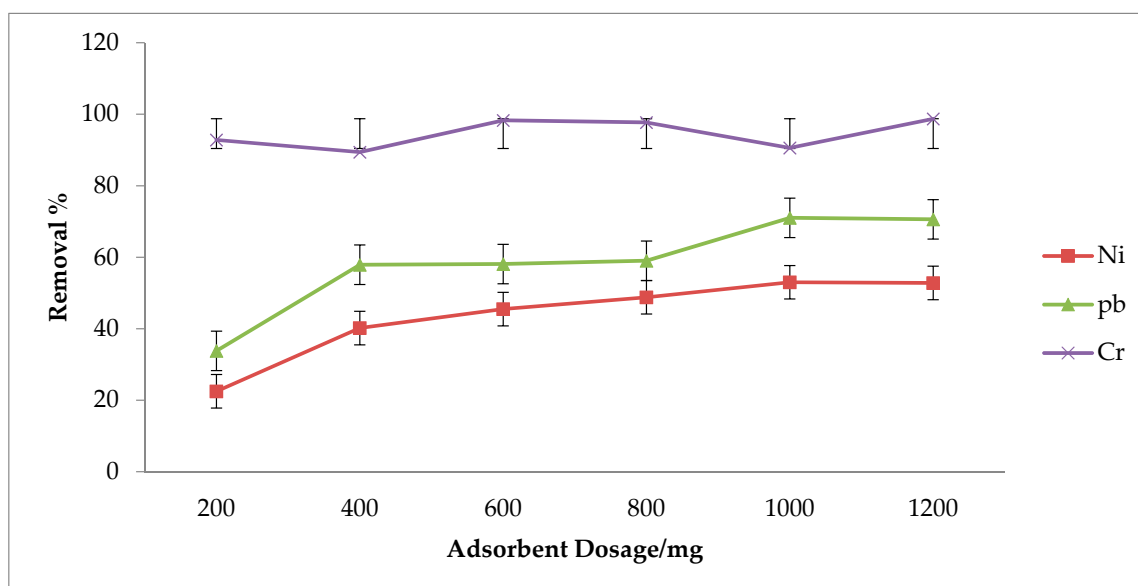
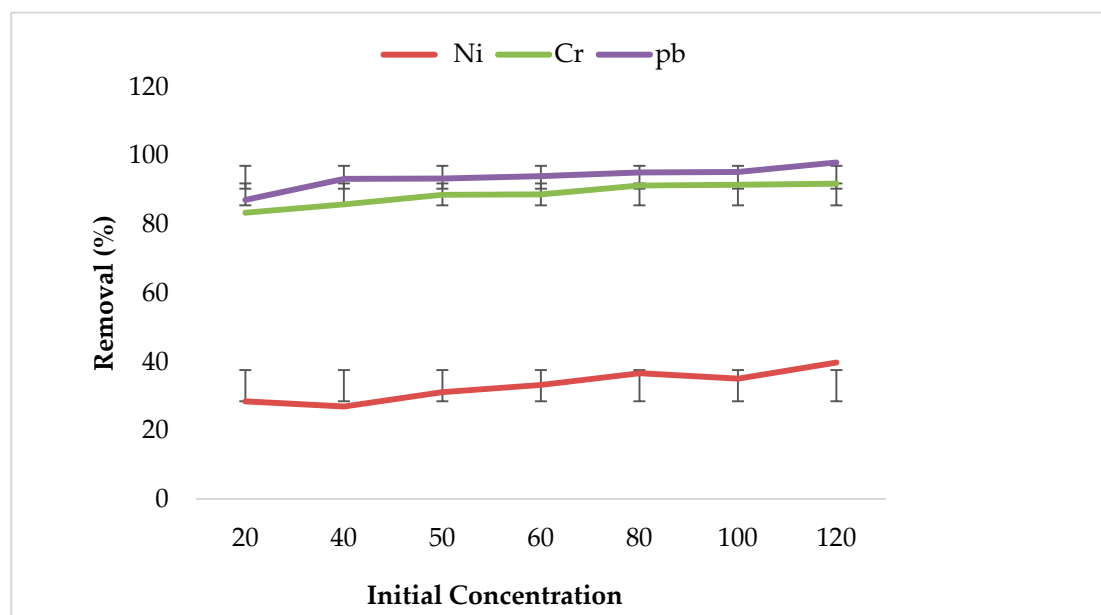


Figure 1. Adsorbent dosage effect on removal of metal ions of Ni, Pb and Cr.

#### 3.2. Effect of Initial Metal Ions Concentration

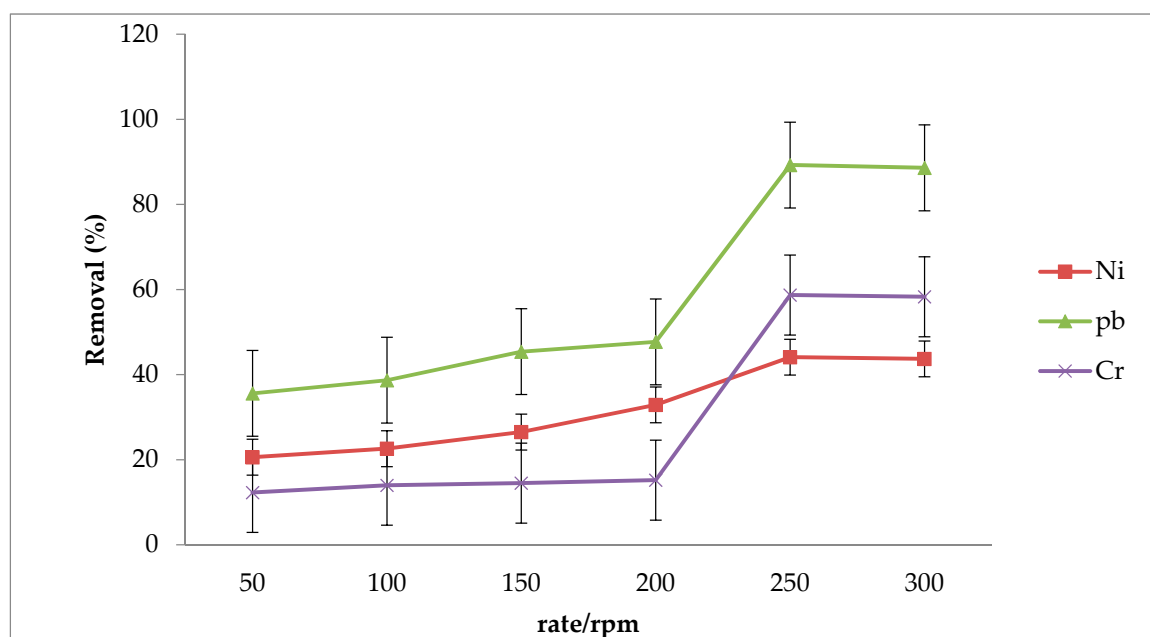
With the higher metal ions concentration, the removal percentage falls due to the accessibility of binding sites and overloading on biomass. As the concentration of metallic ions concentration increases from 20 mg/L to 120 mg/L, the relation of metallic ions adsorption increases with the equilibrium due to the higher concentration gradient force to stunned. Furthermore, all resistance mass transfer between the liquid and solid phases increases the probable striking between metal ions and biomass, thus resulting in higher metal ions adsorption [6,31]. In these adsorption studies, 120 ppm initial metal ions concentrations of  $Pb^{2+}$ ,  $Ni^{2+}$  and  $Cr^{6+}$ , and their adsorption was found to be 98%, 40% and 91.8% respectively, which clearly shows that  $Pb^{2+}$  ions have a greater extracted than  $Ni^{2+}$  and  $Cr^{6+}$  ions by keeping optimized parameters constants e.g., 30 °C, 1 gm/50 mL dose for lead and Nickel, while for Cr 60 mg/50 mL for 60 min, 150 rpm, pH 5, initial ion concentrations range from 20, 40, 50, 60, 80, 100, and 120 mg/L. Figure 2 shows the effect of initial ion concentration on biosorption process.



**Figure 2.** Effect of initial concentration of metal ions for their adsorption on biomass.

### 3.3. Effect of Shaking Rate

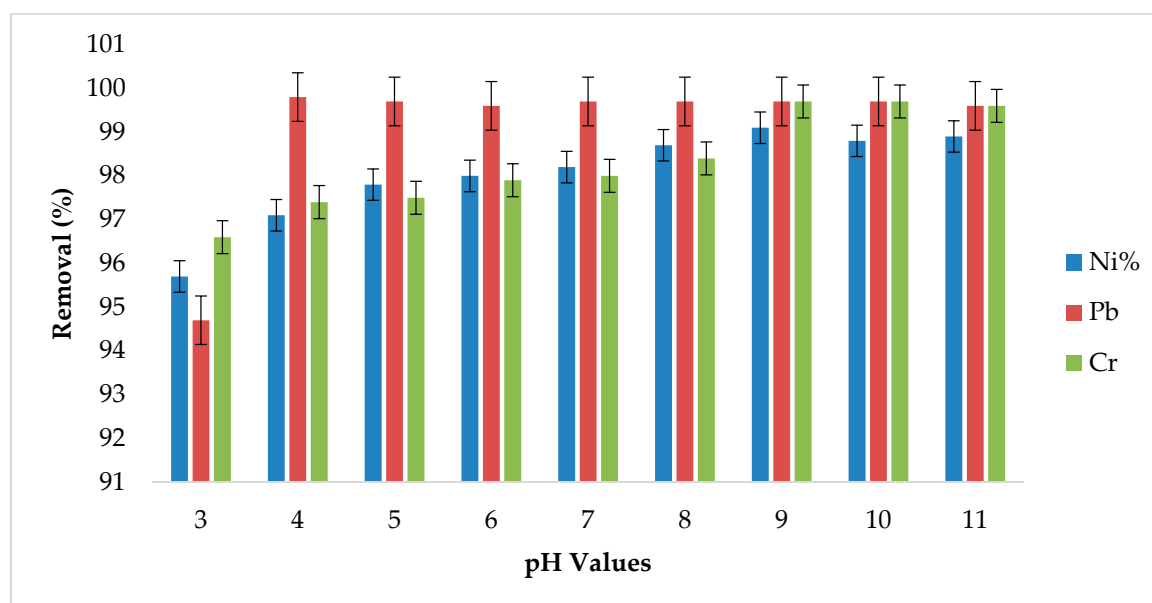
The greater shaking rate, the higher push up of all surface links for metal ions adsorption. The shaking parameters were optimized using different shaking rates, and 250 rpm was found to be best and was selected for further experiments. The maximum adsorption of Nickel, Lead, and Chromium ions were found to be 44%, 89%, and 58% respectively, clearly indicating that Lead ions are more highly adsorbed by biomass than Chromium and Nickel ions, while all the other parameters were kept constant e.g., temperature 30 °C, with a dose of 1.0 gm/50 mL for  $Pb^{2+}$  and  $Ni^{2+}$ , and 0.6 gm/50 mL for  $Cr^{6+}$  with 1 h time, 50, 100, 150, 200, 250 rpm, pH 5 and an initial conc. Of 120 ppm. Figure 3 shows the effect of shaking rate on the removal trends of metal ions.



**Figure 3.** Shaking rate effect on the removal of metal ions of Ni, Pb and Cr.

### 3.4. Effect of pH Variation

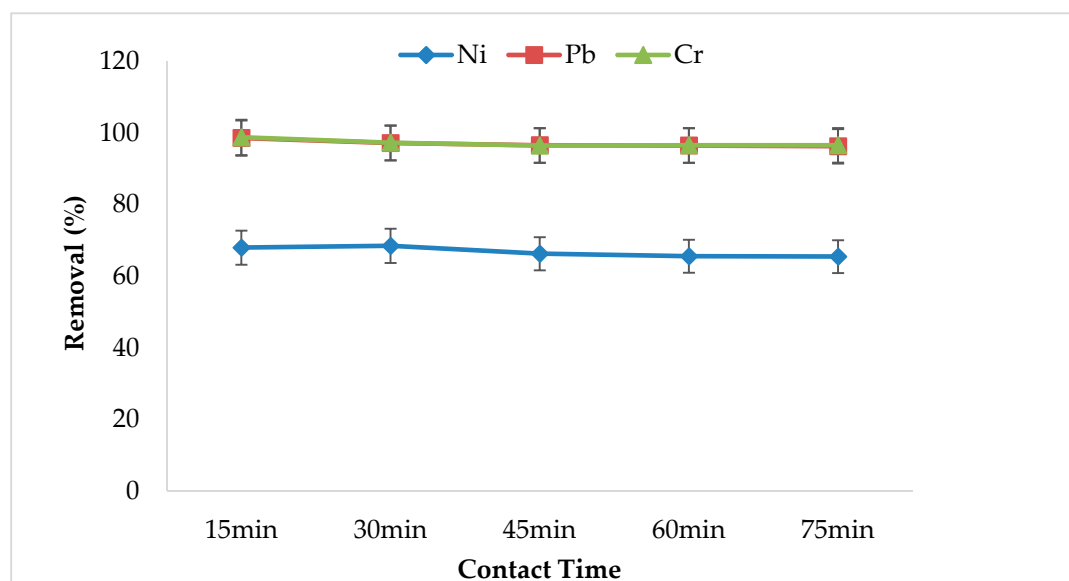
Figure 4 shows the effect of pH change on the biosorption of Nickel, Chromium, and Lead ions on *Brassica Campestris* stem. The pH range of 3 to 11 pH were selected for evaluating its effect on metal ions biosorption. The metal ions of Ni (II) and Cr (VI) were found to be highly adsorbed at pH 9 while  $Pb^{2+}$  ions highly adsorbed at pH 4. As pH 2 and pH 3 are considered to be more acidic, that hampers metallic ions uptake due to the repulsion of similar charge of  $H^+$  and metal ions resulting in a decrease in the adsorption. The biomass surface having partially negative and positive surface molecules depends on the pH of the solution in suspensions; the removal capability of metal ions by adsorbent could differ with the pH of the solution [4,7,24].



**Figure 4.** Effect of pH on the removal of metal ions  $Ni^{2+}$ ,  $Pb^{2+}$  and  $Cr^{6+}$ .

### 3.5. Effect of Contact Time

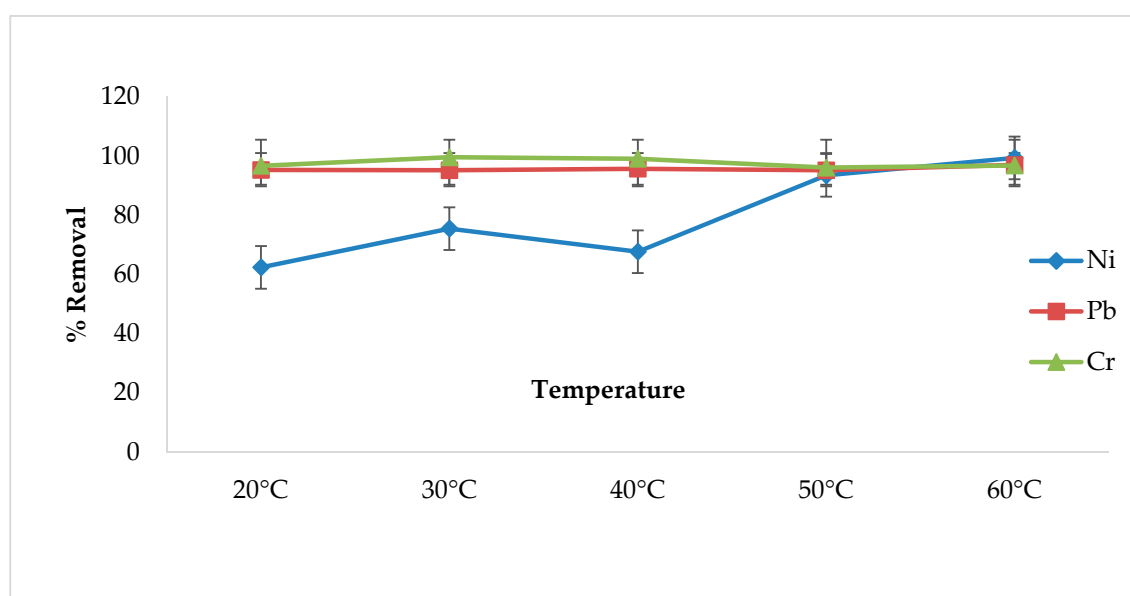
The biosorption process was evaluated against the contact time for the metal ions of Nickel, Lead, and Chromium. Different durations of contact between metal ions and biomass ranging from 15 min to 75 min were assessed. However, the effect after 15 min to 75 min was found to be more or less similar, as the lines are roughly straight, which shows the better adsorption capability of the adsorbent. The adsorption was found to be 65%, 96.6% and 96.5% for Lead, Nickel, and Chromium ions respectively, while keeping the other parameters constant, as shown in Figure 5.



**Figure 5.** Effect of contact time of adsorbent on the removal of metal ion  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$ .

### 3.6. Effect of Temperature

The effect of temperature on the biosorption of metal ions of Nickel, Chromium, and Lead by Brassica stem was evaluated by varying the temperature from 20–60 °C. An increase in temperature leads to an increase in the rate of adsorption, and gradually viscosity factor of the solution goes down [32,33]. Figure 6 shows the percentage adsorption of 99%, 97%, and 96% for Nickel, Lead and Chromium ions at 60 °C. Furthermore, it was found that  $\text{Ni}^{2+}$  is at first point of adsorption than  $\text{Pb}^{2+}$  and then  $\text{Cr}^{6+}$ ; while keeping other optimized conditions constant, e.g., pH 9 of Ni, pH 4 of  $\text{Pb}^{2+}$ , pH 9 of  $\text{Cr}^{6+}$ , with 120 ppm of  $\text{Ni}^{2+}$ , with 1.0 gm of sorbent of  $\text{Pb}^{2+}$  &  $\text{Ni}^{2+}$ , 0.6 gm for  $\text{Cr}^{6+}$ , 50 mL volume, 250 rpm rate and 60 min of time.

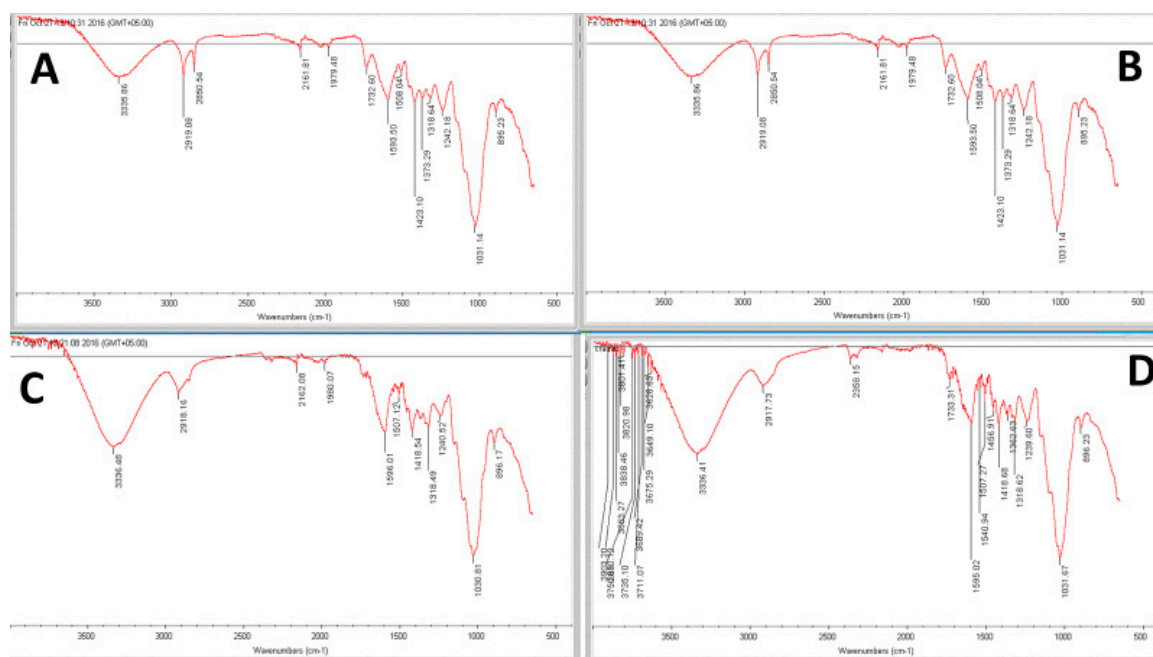


**Figure 6.** Temperature effect on the removal of metal ion  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$ .

### 3.7. FTIR Spectroscopic Analysis

FTIR spectra of blank adsorbent, (adsorbent + Nickel ions), (Adsorbent + Chromium ions), and (adsorbent + Lead ion) are given in Figure 7A–D, respectively. The polar linkage of the adsorbent

with heavy metal ions,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{6+}$ , and  $\text{Pb}^{2+}$  was analyzed as they can make the polar linkages with O-H, N-H, C-O functional groups. The mechanism identifies biotic accumulation of metal ions by *Brassica* stem species [34]. The major IR groups of the stretching bands of the OH group were shifted very slightly from  $3335\text{ cm}^{-1}$  to  $3336\text{ cm}^{-1}$  (8), to  $3338\text{ cm}^{-1}$  (9), and to  $3340\text{ cm}^{-1}$  (10) due to the loading of Nickel, Lead and Chromium ions associations with the polar surface of the adsorbent. The carbonyl group of carboxylic acid having a band at  $1732\text{ cm}^{-1}$  in blank and  $\text{Ni}^{2+}$ ,  $\text{Cr}^{6+}$ , and  $\text{Pb}^{2+}$  after loading carbonyl peaks were slightly shifted. In summary, all FTIR spectra of *Brassica* (BCS) plant loaded with  $\text{Ni}^{2+}$ ,  $\text{Cr}^{6+}$ , and  $\text{Pb}^{2+}$ , showed bands with slight shifts at about  $1365$ ,  $1362$ ,  $1352\text{ cm}^{-1}$  which can possibly be attributed to Ni-O, Cr-O and Pb-O bonds, respectively [35].

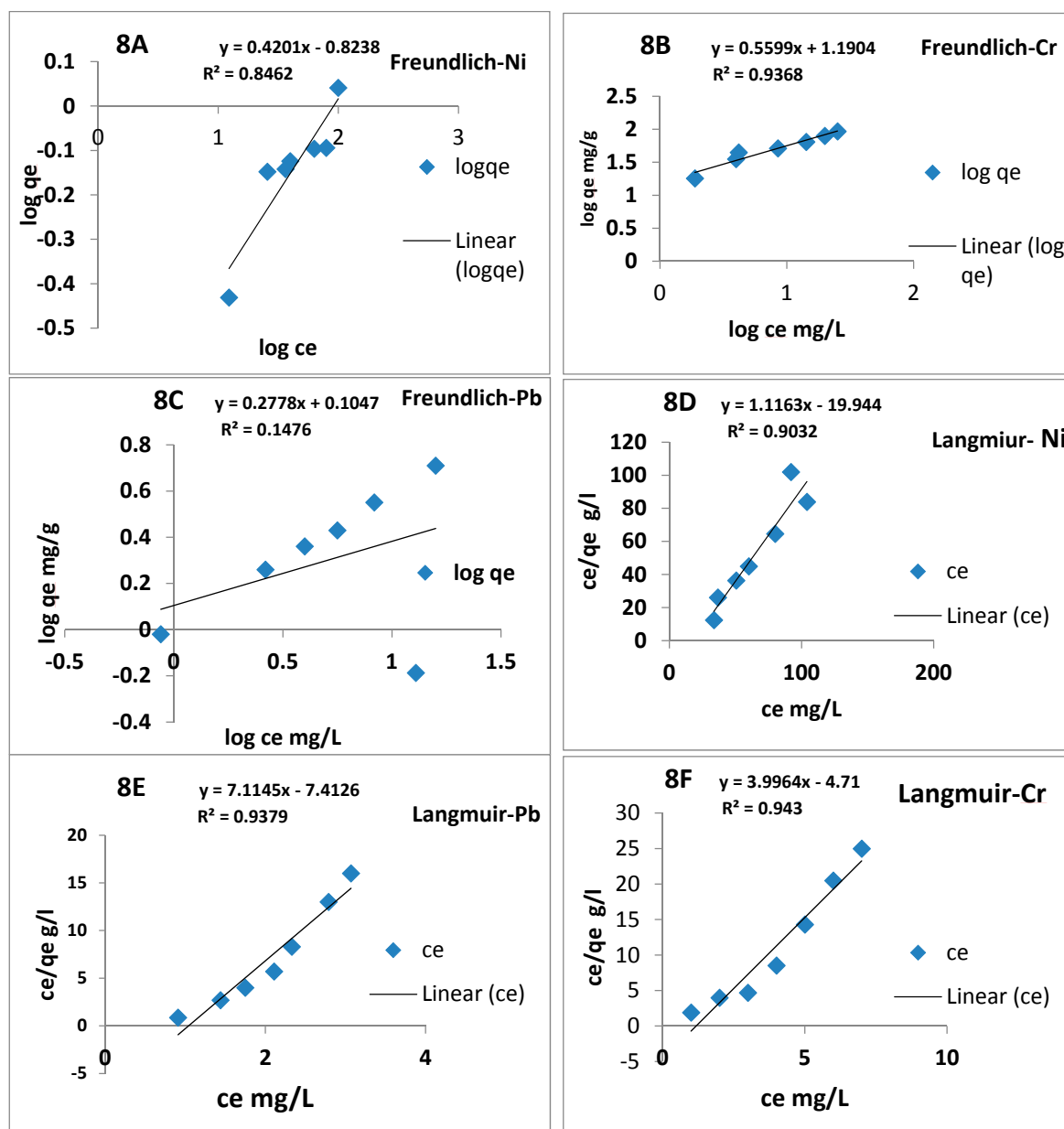


**Figure 7.** (A–D) showing FTIR Spectra of *Brassica campestris* stem (BCS) adsorbent,  $\text{Ni}^{2+}$ , with an adsorbent,  $\text{Cr}^{6+}$ , with adsorbent and  $\text{Pb}^{2+}$  with the adsorbent.

### 3.8. Adsorption Isotherms Analysis

Solid-liquid sorption examination determines the equilibrium of batch sorption analysis and dynamic flow sorption researches. Adsorption constants were examined from isotherms, and correlation coefficients ( $R^2$ ) defining the relation with parameters were found to be 0.56 to 0.98 in Langmuir's Model and 0.156 to 0.87 in Freundlich.  $1/n$  is the strength function of the employed sorbent thus When  $1/n > 1$ . The mass of adsorbate was also adjusted by Langmuir' isotherm. Whereby Nickel ions were adsorbed  $1.1\text{ mg/g}$ , Chromium  $95\text{ mg/gm}$  while  $78.5\text{ mg/gm}$  of Lead ions. The metal ions are selected free on monolayer type of binding site in the Freundlich model hence the first metal ion does not disturb the other ion process. The Figure 8D–F shows that the Freundlich model of isotherms for Nickel ions is not a straight line, and testifies for the linear equation as compared to Lead and Chromium ions, while Figure 8A–F show that that Langmuir Model of isotherm is fitted best for the adsorption parameters. Table 1 shows the Constants of Langmuir and Freundlich adsorption isotherms and correlation coefficients ( $R^2$ ).





**Figure 8.** (A–C) Freundlich isotherm diagram of  $\text{Ni}^{2+}$ ,  $\text{Cr}^{6+}$  and  $\text{Pb}^{2+}$  adsorbents respectively and Figure 8 (D–F) shows the Langmuir isotherm diagram of  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cr}^{6+}$  adsorbents at  $30 \pm 2^\circ\text{C}$  respectively.

**Table 1.** Evaluated Constant of Langmuir and Freundlich adsorption isotherms and correlation coefficients ( $R^2$ ).

Metals Ions	BCS Adsorbent						
	Langmuir's Constant			Freundlich Constant			
	$Q_m$	$b$	$R^2$	$q_e$ mg/g	$1/n$	$K_f$	$R^2$
$\text{Ni}^{2+}$	1.1	0.9	0.56	1.1	1.7	1.8	0.887
$\text{Cr}^{6+}$	3.9	1.2	0.91	95	2.70	1.6	0.877
$\text{Pb}^{2+}$	7.8	0.9	0.98	78.5	1.80	2.3	0.15

#### 4. Discussion

Heavy metal contamination in water is one of the major health concerns around the globe, and this can cause severe health disorder not only for humans but also for every living creature [36–39]. There are different sources causing heavy metal pollution in water such as industrial waste; mining, pharmaceutical, textile, fertilizers, petrochemicals mostly contribute to heavy metal ions such as i.e., Zn, Ni, Cu, Cr, Pb, Cd, Ar, Mn ions [2,40–42]. Different approaches have been made for the detection and removal of heavy metals for the water purification purpose such as bioremediation where bacteria as biosorbents as some of the microbes (i.e., Citrobacter, Pseudomonas, Streptomyces, Bacillus, etc.) have the potential to uptake heavy metals from different media [2,43,44]. However, growing bacteria and their maintenance is also hectic, burdensome work and their control is also a major concern. Algae both in living and nonliving forms have been utilized for the heavy metal removal from water and have several advantages such as low cost and no prior treatment is needed; Bilal et al. 2018 reviewed in detail the algae application as biosorbents [45,46]. In addition to algae, fungi have also been applied for the biosorption of heavy metals; Ahmed El-Gendy et al. 2017 applied Fungi for the removal of heavy metal ions (e.g.,) cadmium ( $\text{Cd}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), and lead ( $\text{Pb}^{2+}$ ) [47]. Bano A et al. 2018, applied fungi for the removal of iron and zinc elements from water [48]. Gupta et al. 2016 wrote a comprehensive review of the application of fungi, algae and other microbes in heavy metal biosorption [49].

Another useful and effective approach is the application of plant biomass for the removal of heavy metals from water [50]. Plant biomass has the tremendous ability to uptake the heavy metals and plant biomass is cheaper and easily available in large quantities as it is generated from agriculture waste [51]. Many heavy metals have been removed by the application of plant-based materials. Recently, M. Zhang et al. 2017 removed heavy metal ions namely Zn(II), Fe(III), Cu(II), and Cr(III) from water using waste biomass of soybean dregs [52]. Lingamdinne et al. 2016 utilized the biomass-based material of the *Lonicera japonica* flower for the removal of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  [53,54]. The Table 2 shows the adsorbent Brassica stem comparison on adsorption of Ni (II), Cr (IV) and Pb (II) with other biomasses.

**Table 2.** The adsorbent Brassica stem comparison on adsorption of Ni (II), Cr (IV) and Pb (II) with other biomasses.

S.No	Adsorbent/Agricultural Waste	Metal Ion	$Q_m$ mg/gm
1	Brassica Campestris stem (BCS)	$\text{Ni}^{2+}$	1.1 mg/gm
2	Brassica Campestris Stem (BCS)	$\text{Cr}^{6+}$	95 mg/gm
3	Brassica Campestris Stem (BCS)	$\text{Pb}^{2+}$	78 mg/gm
4	Cashew nut shell (raw)	$\text{Ni}^{2+}$	3 gm/L
5	Brassica satin	$\text{Ni}^{2+}$	0.02 mg/kg
6	Orange peel	$\text{Cr}^{3+}$	18.73 mg/gm
7	Sugarcane bagasse	$\text{Cr}^{3+}$	1.76 mg/gm
8	Neem sawdust	$\text{Cr}^{3+}$	58.28 mg/gm
9	Lentil husk	$\text{Pb}^{2+}$	81.73 mg/gm
10	Cabbage	$\text{Pb}^{2+}$	60.57 mg/gm
11	Cauliflower	$\text{Pb}^{2+}$	47.63 mg/gm

In this study, agricultural waste of *Brassica Campestris* stem was used for the removal of heavy metal ions, namely ( $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{6+}$ ) from the water. The effect of different parameters on the removal capability of adsorbent *Brassica campestris* stem was evaluated and optimized. The effect of dosage of adsorbent *Brassica campestris* stem was found to be a direct relation, as the increased dosage increases the removal of metal ions. The percentage removal of Nickel and Lead were found to be 53% and 71% while Chromium shows the highest percentage of 97.3% in 1000 and 600 mg of adsorbent dosage. Effect of initial metal ions concentration revealed that increasing concentration of metal ions also results in higher percentage removal until the accessibility of binding sites of adsorbent is fully covered.

After reaching equilibrium, metal ions removal capacity decreases due to the lack of availability of binding sites in the adsorbent. It was found that at 120 ppm, initial metal ion concentrations of  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cr}^{6+}$ , and their removal percentage was found to be 98%, 40%, and 91.8%, respectively. Faster shaking can mix the adsorbent well which resulted in the better removal of metal ions and shaking speed was set to 250 rpm. Effect of pH variation was also evaluated for the removal efficiency of ions. Different pH values were assessed from 3 to 11 and it was observed that 9 Ni, Cr were highly adsorbed and pH 4 was found to be good for  $\text{Pb}^{2+}$  adsorption. Different contact times were used to evaluate the effect of metal ions adsorption, from 15 min to 75 min and it was observed that adsorption was roughly similar through 15 min to 75 min, which suggests the greater capacity of faster adsorption of metal ions. The other parameter tested was the effect of different temperatures on metal ions adsorption. For Nickel, adsorption increased with an increase in temperature, while  $\text{Cr}^{6+}$  and  $\text{Pb}^{2+}$  were more or less similar from 20–60 °C. FTIR results revealed the shifts in absorption bands before and after adsorption, suggesting loading of the ions on the adsorbent. AAS was used to determine the metal ions concentrations after adsorption. The Langmuir isotherm was found to be better in fitting to the experimental data than that of the Freundlich isotherm.

## 5. Conclusions

In this study, a greener method was designed for the removal of toxic metal ions by the utilization of the agricultural waste. The *Brassica Campestris* stems were utilized for the removal of toxic ions from the water. The different parameters were optimized such as temperature, pH, concentrations, and shaking, etc. The highest removal percentage of  $\text{Pb}^{2+}$  98%,  $\text{Cr}^{3+}$  91% and  $\text{Ni}^{2+}$  ions 49% was established at optimized conditions (pH 4 with 60 min of contact time, 1 g adsorbent dose and 120 ppm concentration, 250 rpm, and at 60 °C), (pH 9 with 120 ppm of concentration and 60 min of contact time 0.6 g/50 mL, 250 rpm and at 60 °C ) and (pH 9, 120 ppm of concentration, 60 min of contact time, 1 g/50 mL, 250 rpm and 60 °C), respectively. This study suggests that the Freundlich model is better to set for Chromium comparatively Nickel and Lead ions, while Langmuir is appropriate isotherm for the experimental data, however, the  $R^2$ -Coefficient of Langmuir isotherm is greater than Freundlich isotherm for  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and Cr metal ions. The highlighted values clearly follow that *Brassica Campestris* stem as a cheap, active and strong source for the  $\text{Cr}^{6+} > \text{Pb}^{2+} > \text{Ni}^{2+}$  ions removal. This study suggests that the designed method can be an alternative greener protocol for heavy metal ions removal especially Lead, Nickel and Chromium from contaminated water.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4441/10/10/1316/s1>, Figures S1–S4 showing different stages for the preparation of adsorbent and FTIR spectra; Figures S5–S8 are given in the supplementary file.

**Author Contributions:** R.B.S. and B.S. designed and conducted the experiments, characterize and analyze the data and wrote the manuscript, F.u.R. draw the graphs and edited the manuscript and R.I.S. did the statistics.

**Funding:** This research received no external funding.

**Acknowledgments:** Authors acknowledge the funding support from ORIC SUKKUR IBA University and Higher Education Commission of Pakistan. Authors are also thankful to Ruqia Iqbal Shaikh for their kind assistance in statistical analysis.

**Conflicts of Interest:** The authors declare that they have no conflict of interest.

## References

1. Ibrahim, W.M.; Hassan, A.F.; Azab, Y.A. Biosorption of toxic heavy metals from aqueous solution by *Ulva lactuca* activated carbon. *Egypt. J. Basic Appl. Sci.* **2016**, *3*, 241–249. [CrossRef]
2. Jacob, J.M.; Karthik, C.; Saratale, R.G.; Kumar, S.S.; Prabakar, D.; Kadirvelu, K.; Pugazhendhi, A. Biological approaches to tackle heavy metal pollution: A survey of literature. *J. Environ. Manag.* **2018**, *217*, 56–70. [CrossRef] [PubMed]
3. Jiang, R.; Wang, M.; Chen, W.; Li, X. Ecological risk evaluation of combined pollution of herbicide siduron and heavy metals in soils. *Sci. Total Environ.* **2018**, *626*, 1047–1056. [CrossRef] [PubMed]

4. Naseem, K.; Farooqi, Z.H.; Ur Rehman, M.Z.; Ur Rehman, M.A.; Begum, R.; Huma, R.; Shahbaz, A.; Najeeb, J.; Irfan, A. A systematic study for removal of heavy metals from aqueous media using Sorghum bicolor: An efficient biosorbent. *Water Sci. Technol.* **2018**, *77*, 2355–2368. [[CrossRef](#)] [[PubMed](#)]
5. Rajeshkumar, S.; Liu, Y.; Zhang, X.; Ravikumar, B.; Bai, G.; Li, X. Studies on seasonal pollution of heavy metals in water, sediment, fish and oyster from the Meiliang Bay of Taihu Lake in China. *Chemosphere* **2018**, *191*, 626–638. [[CrossRef](#)] [[PubMed](#)]
6. Morosanu, I.; Teodosiu, C.; Paduraru, C.; Ibanescu, D.; Tofan, L. Biosorption of lead ions from aqueous effluents by rapeseed biomass. *New Biotechnol.* **2017**, *39*, 110–124. [[CrossRef](#)] [[PubMed](#)]
7. Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B.B.; Beeregowda, K.N. Toxicity, mechanism and health effects of some heavy metals. *Interdiscip. Toxicol.* **2014**, *7*, 60–72. [[CrossRef](#)] [[PubMed](#)]
8. Deniz, F.; Karabulut, A. Biosorption of heavy metal ions by chemically modified biomass of coastal seaweed community: Studies on phycoremediation system modeling and design. *Ecol. Eng.* **2017**, *106*, 101–108. [[CrossRef](#)]
9. Hadiani, M.R.; Darani, K.K.; Rahimifard, N.; Younesi, H. Biosorption of low concentration levels of Lead (II) and Cadmium (II) from aqueous solution by *Saccharomyces cerevisiae*: Response surface methodology. *Biocatal. Agric. Biotechnol.* **2018**, *15*, 25–34. [[CrossRef](#)]
10. Zouboulis, A.I.; Peleka, E.N.; Samaras, P. Removal of Toxic Materials from Aqueous Streams. In *Mineral Scales and Deposits*; Elsevier: Amsterdam, The Netherlands, 2015.
11. Singh, R.; Singh, S.; Parihar, P.; Singh, V.P.; Prasad, S.M. Arsenic contamination, consequences and remediation techniques: A review. *Ecotoxicol. Environ. Saf.* **2015**, *112*, 247–270. [[CrossRef](#)] [[PubMed](#)]
12. Vital, B.; Bartacek, J.; Ortega-Bravo, J.C.; Jeison, D. Treatment of acid mine drainage by forward osmosis: Heavy metal rejection and reverse flux of draw solution constituents. *Chem. Eng. J.* **2018**, *332*, 85–91. [[CrossRef](#)]
13. Zhao, X.; Liu, C. Efficient removal of heavy metal ions based on the optimized dissolution-diffusion-flow forward osmosis process. *Chem. Eng. J.* **2018**, *334*, 1128–1134. [[CrossRef](#)]
14. Rasheed, T.; Li, C.; Bilal, M.; Yu, C.; Iqbal, H.M. Potentially toxic elements and environmentally-related pollutants recognition using colorimetric and ratiometric fluorescent probes. *Sci. Total Environ.* **2018**, *640*, 174–193. [[CrossRef](#)] [[PubMed](#)]
15. Koller, M. *Introducing Heavy Metals*; IntechOpen: London, UK, 2018.
16. Ebrahim, S.E.; Hyder, N.H.; Yousif, Y.M. Biosorption of Heavy Metals onto Two Types of Fungi Biomass in Batch Experiments. *Assoc. Arab Univ. J. Eng. Sci.* **2018**, *23*, 55–69.
17. Bankar, A.; Nagaraja, G. Recent trends in biosorption of heavy metals by Actinobacteria. *New Future Dev. Microb. Biotechnol. Bioeng.* **2018**, 257–275.
18. Rasheed, T.; Bilal, M.; Nabeel, F.; Iqbal, H.M.N.; Li, C.; Zhou, Y. Fluorescent sensor based models for the detection of environmentally-related toxic heavy metals. *Sci. Total Environ.* **2018**, *615*, 476–485. [[CrossRef](#)] [[PubMed](#)]
19. Basu, M.; Guha, A.K.; Ray, L. Adsorption of Lead on Cucumber Peel. *J. Clean. Prod.* **2017**, *151*, 603–615. [[CrossRef](#)]
20. Ngabura, M.; Hussain, S.A.; Ghani, W.A.W.A.; Jami, M.S.; Tan, Y.P. Utilization of renewable durian peels for biosorption of zinc from wastewater. *J. Environ. Chem. Eng.* **2018**, *6*, 2528–2539. [[CrossRef](#)]
21. Hossain, M.A.; Ngo, H.H.; Guo, W.S.; Nghiem, L.D.; Hai, F.I.; Vigneswaran, S.; Nguyen, T.V. Competitive adsorption of metals on cabbage waste from multi-metal solutions. *Bioresour. Technol.* **2014**, *160*, 79–88. [[CrossRef](#)] [[PubMed](#)]
22. Jain, R.; Sikarwar, S. Adsorptive removal of Erythrosine dye onto activated low cost de-oiled mustard. *J. Hazard. Mater.* **2009**, *164*, 627–633. [[CrossRef](#)] [[PubMed](#)]
23. Jablonska, B.; Siedlecka, E. Removing heavy metals from wastewaters with use of shales accompanying the coal beds. *J. Environ. Manag.* **2015**, *155*, 58–66. [[CrossRef](#)] [[PubMed](#)]
24. Rahman, M.M.; Adil, M.; Yusof, A.M.; Kamaruzzaman, Y.B.; Ansary, R.H. Removal of Heavy Metal Ions with Acid Activated Carbons Derived from Oil Palm and Coconut Shells. *Materials* **2014**, *7*, 3634–3650. [[CrossRef](#)] [[PubMed](#)]
25. Montazer-Rahmati, M.M.; Rabbani, P.; Abdolali, A.; Keshtkar, A.R. Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae. *J. Hazard. Mater.* **2011**, *185*, 401–407. [[CrossRef](#)] [[PubMed](#)]

26. Şeker, A.; Shahwan, T.; Eroğlu, A.E.; Yılmaz, S.; Demirel, Z.; Dalay, M.C. Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II), cadmium(II) and nickel(II) ions on *Spirulina platensis*. *J. Hazard. Mater.* **2008**, *154*, 973–980. [[CrossRef](#)] [[PubMed](#)]
27. Shen, Z.; Jin, F.; Wang, F.; McMillan, O.; Al-Tabbaa, A. Sorption of lead by Salisbury biochar produced from British broadleaf hardwood. *Bioresour. Technol.* **2015**, *193*, 553–556. [[CrossRef](#)] [[PubMed](#)]
28. Bertagnolli, C.; da Silva, M.G.C.; Guibal, E. Chromium biosorption using the residue of alginate extraction from *Sargassum filipendula*. *Chem. Eng. J.* **2014**, *237*, 362–371. [[CrossRef](#)]
29. Wu, Y.; Wang, L. Kinetic and Thermodynamic Studies of the Biosorption of Ni(II) by Modified Rape Straw. *Procedia Environ. Sci.* **2016**, *31*, 75–80. [[CrossRef](#)]
30. Taşar, Ş.; Kaya, F.; Özer, A. Biosorption of lead(II) ions from aqueous solution by peanut shells: Equilibrium, thermodynamic and kinetic studies. *J. Environ. Chem. Eng.* **2014**, *2*, 1018–1026. [[CrossRef](#)]
31. Long, J.; Li, H.; Jiang, D.; Luo, D.; Chen, Y.; Xia, J.; Chen, D. Biosorption of strontium(II) from aqueous solutions by *Bacillus cereus* isolated from strontium hyperaccumulator *Andropogon gayanus*. *Process Saf. Environ. Prot.* **2017**, *111*, 23–30. [[CrossRef](#)]
32. Vendruscolo, F.; da Rocha Ferreira, G.L.; Antoniosi Filho, N.R. Biosorption of hexavalent chromium by microorganisms. *Int. Biodeterior. Biodegrad.* **2017**, *119*, 87–95. [[CrossRef](#)]
33. Šoštarić, T.D.; Petrović, M.S.; Pastor, F.T.; Lončarević, D.R.; Petrović, J.T.; Milojković, J.V.; Stojanović, M.D. Study of heavy metals biosorption on native and alkali-treated apricot shells and its application in wastewater treatment. *J. Mol. Liq.* **2018**, *259*, 340–349. [[CrossRef](#)]
34. Yalcin, S.; Sezer, S.; Apak, R. Characterization and lead(II), cadmium(II), nickel(II) biosorption of dried marine brown macro algae *Cystoseira barbata*. *Environ. Sci. Pollut. Res. Int.* **2012**, *19*, 3118–3125. [[CrossRef](#)] [[PubMed](#)]
35. Suganthi, N.; Srinivasan, K. Adsorptive removal of nickel and lead ions from aqueous solutions using phosphorylated tamarind nut carbon. *J. Environ. Sci. Eng.* **2011**, *53*, 163–174. [[PubMed](#)]
36. Zhang, P.; Qin, C.; Hong, X.; Kang, G.; Qin, M.; Yang, D.; Pang, B.; Li, Y.; He, J.; Dick, R.P. Risk assessment and source analysis of soil heavy metal pollution from lower reaches of Yellow River irrigation in China. *Sci. Total Environ.* **2018**, *633*, 1136–1147. [[CrossRef](#)] [[PubMed](#)]
37. Zhang, L.; Zhu, G.; Ge, X.; Xu, G.; Guan, Y. Novel insights into heavy metal pollution of farmland based on reactive heavy metals (RHMs): Pollution characteristics, predictive models, and quantitative source apportionment. *J. Hazard. Mater.* **2018**, *360*, 32–42. [[CrossRef](#)] [[PubMed](#)]
38. Riani, E.; Cordova, M.R.; Arifin, Z. Heavy metal pollution and its relation to the malformation of green mussels cultured in Muara Kamal waters, Jakarta Bay, Indonesia. *Mar. Pollut. Bull.* **2018**, *133*, 664–670. [[CrossRef](#)] [[PubMed](#)]
39. Lu, H.; Yu, S. Spatio-temporal variational characteristics analysis of heavy metals pollution in water of the typical northern rivers, China. *J. Hydrol.* **2018**, *559*, 787–793. [[CrossRef](#)]
40. Mwinyihija, M. Main Pollutants and Environmental Impacts of the Tanning Industry. In *Ecotoxicological Diagnosis in the Tanning Industry*; Springer: New York, NY, USA, 2010.
41. Schaidt, L.A.; Senn, D.B.; Estes, E.R.; Brabander, D.J.; Shine, J.P. Sources and fates of heavy metals in a mining-impacted stream: Temporal variability and the role of iron oxides. *Sci. Total Environ.* **2014**, *490*, 456–466. [[CrossRef](#)] [[PubMed](#)]
42. Roberts, T.L. Cadmium and Phosphorous Fertilizers: The Issues and the Science. *Procedia Eng.* **2014**, *83*, 52–59. [[CrossRef](#)]
43. Dhanarani, S.; Viswanathan, E.; Piruthiviraj, P.; Arivalagan, P.; Kaliannan, T. Comparative study on the biosorption of aluminum by free and immobilized cells of *Bacillus safensis* KTSMBNL 26 isolated from explosive contaminated soil. *J. Taiwan Inst. Chem. Eng.* **2016**, *69*, 61–67. [[CrossRef](#)]
44. Hernandez-Vargas, G.; Sosa-Hernandez, J.E.; Saldarriaga-Hernandez, S.; Villalba-Rodriguez, A.M.; Parra-Saldivar, R.; Iqbal, H.M.N. Electrochemical Biosensors: A Solution to Pollution Detection with Reference to Environmental Contaminants. *Biosensors* **2018**, *8*, 29. [[CrossRef](#)] [[PubMed](#)]
45. Bilal, M.; Rasheed, T.; Sosa-Hernandez, J.E.; Raza, A.; Nabeel, F.; Iqbal, H.M.N. Biosorption: An Interplay between Marine Algae and Potentially Toxic Elements-A Review. *Mar. Drugs* **2018**, *16*, 65. [[CrossRef](#)] [[PubMed](#)]
46. Zeraatkar, A.K.; Ahmadzadeh, H.; Talebi, A.F.; Moheimani, N.R.; McHenry, M.P. Potential use of algae for heavy metal bioremediation, a critical review. *J. Environ. Manag.* **2016**, *181*, 817–831. [[CrossRef](#)] [[PubMed](#)]

47. Sağ, Y. Biosorption of heavy metals by fungal biomass and modeling of fungal biosorption: A review. *Sep. Purif. Method* **2001**, *30*, 1–48. [[CrossRef](#)]
48. Bano, A.; Hussain, J.; Akbar, A.; Mehmood, K.; Anwar, M.; Hasni, M.S.; Ullah, S.; Sajid, S.; Ali, I. Biosorption of heavy metals by obligate halophilic fungi. *Chemosphere* **2018**, *199*, 218–222. [[CrossRef](#)] [[PubMed](#)]
49. Gupta, A.; Joia, J.; Sood, A.; Sood, R.; Sidhu, C.; Kaur, G. Microbes as potential tool for remediation of heavy metals: A review. *J. Microb. Biochem. Technol.* **2016**, *8*, 364–372. [[CrossRef](#)]
50. Rodríguez Martín, J.A.; Gutiérrez, C.; Torrijos, M.; Nanos, N. Wood and bark of *Pinus halepensis* as archives of heavy metal pollution in the Mediterranean Region. *Environ. Pollut.* **2018**, *239*, 438–447. [[CrossRef](#)] [[PubMed](#)]
51. Rezanian, S.; Taib, S.M.; Md Din, M.F.; Dahalan, F.A.; Kamyab, H. Comprehensive review on phytotechnology: Heavy metals removal by diverse aquatic plants species from wastewater. *J. Hazard. Mater.* **2016**, *318*, 587–599. [[CrossRef](#)] [[PubMed](#)]
52. Zhang, M.; Song, L.; Jiang, H.; Li, S.; Shao, Y.; Yang, J.; Li, J. Biomass based hydrogel as an adsorbent for the fast removal of heavy metal ions from aqueous solutions. *J. Mater. Chem.* **2017**, *5*, 3434–3446. [[CrossRef](#)]
53. Lingamdinne, L.P.; Yang, J.-K.; Chang, Y.-Y.; Koduru, J.R. Low-cost magnetized *Lonicera japonica* flower biomass for the sorption removal of heavy metals. *Hydrometallurgy* **2016**, *165*, 81–89. [[CrossRef](#)]
54. Carolin, C.F.; Kumar, P.S.; Saravanan, A.; Joshiba, G.J.; Naushad, M. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *J. Environ. Chem. Eng.* **2017**, *5*, 2782–2799. [[CrossRef](#)]



© 2018 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 (<http://creativecommons.org/licenses/by/4.0/>).