Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23580

144 (2019) 345–354
March

Chemically treated cactus (*Opuntia*) as a sustainable biosorbent for the removal of heavy metals from aqueous solution: characterization and adsorption capacity

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Received 7 March 2018; Accepted 13 August 2018

ABSTRACT

The purpose of this study was to evaluate the efficiency of chemically treated (NaOH or HCl) cactus for the removal of Zn^{2+} and Mn^{2+} ions from aqueous solution via biosorption. The characteristics of the adsorbents were studied using Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and Brunauer-Emmett-Teller analyses. In addition, the effects of biosorbent dose, initial metal ion concentration, contact time, initial solution pH, and temperature were investigated. Adsorption kinetics, equilibrium, and isotherm studies were also conducted. The FTIR results indicated that chemical treatment changed the stretching vibration. The elemental analysis showed that NaOH treatment increased the oxygen content by 56.91% and decreased the carbon content by 26.44%. The highest removal efficiencies of Zn^{2+} and Mn^{2+} were found with the NaOH-treated cactus, followed by the HCl-treated cactus. The biosorption efficiency of Zn^{2+} increased from 36.0% to 95.9% and from 36.0% to 84.6% when the raw biosorbent was treated with NaOH and HCl, respectively. For Mn^{2+}, the biosorption efficiency increased from 33.2% to 88.6% and from 33.2% to 71.0% when the raw biosorbent was treated with NaOH and HCl, respectively. Moreover, a rapid increase in binding efficiency was observed under conditions of pH up to 5, with Zn^{2+} adsorption greater than that of Mn^{2+}. Metal ion biosorption increased with increasing contact time and initial metal ion concentration. The pseudo-second-order model was more appropriate than the pseudo-first-order model for explaining the biosorption processes of Zn^{2+} and Mn^{2+} by cactus due to its higher R^2 value. From this study, it can be concluded that chemical pretreatment of raw cactus (*Opuntia*) with NaOH strongly enhanced its biosorption potential for the studied metals.

Keywords: Modified cactus; Biosorption capacity; Sustainable biosorbent; Heavy metal removal

1. Introduction

The industrial discharge of heavy metals into the aquatic environment from industries such as metal plating, mining, fertilizer production, textile manufacturing, and tanneries is causing severe environmental pollution. The disposal of industrial effluents into natural waters causes damage to the aquatic environment and presents a risk to human health, with even small amounts of certain metals known to cause severe physiological effects [1,2]. Removal of heavy metals from wastewater has progressed significantly in recent years and has been applied to protect the environment and human health.

To date, several treatment methods for metal ion removal from aqueous solutions have been established, i.e., chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, evaporative recovery, and solvent extraction. However, most of these methods are expensive, and their use is often

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Presented at the 2017 International Environmental Engineering Conference & Annual Meeting of the Korean Society of Environmental Engineers (IEEC 2017), 15–17 November 2017, Jeju, Korea.

restricted because cost factors override the importance of pollution control. This makes their application unfeasible for local communities in nonindustrialized countries. Among available water treatment technologies, biosorption offers several advantages owing to its convenience, ease of operation, and simplicity of design [3,4]. It is also eco-friendly because, instead of generating toxic sludge [4], biosorbents have various functional groups that can bind to heavy metal ions, such as hydroxyl, amino, carboxyl, phosphate, sulfonate, and ether groups [5]. However, raw biosorption materials may also possess groups that inhibit biosorption capacity; thus, chemical elimination of these inhibiting groups may produce more effective biosorbent materials [5,6]. Chemical pretreatment with base and acid solutions has been preferred owing to its simplicity and efficiency [7,8].

In the present study, the application of chemically treated cactus (*Opuntia*), which is regarded as native to Mexico and considered an invasive plant in countries including Ethiopia, Eritrea, South Africa, and several Mediterranean countries, was investigated. Cactus (*Opuntia*) provides considerable socioeconomic benefits to rural economies; its fruits and stems are used in traditional medicines in several countries for treatment of conditions such as diabetes, hypertension, asthma, ulcers, rheumatic pain, inflammation, wounds, joint pain, stress, and fatigue [9–13]. *Opuntia* has received a large amount of attention for application in water treatment [14,15]. To our knowledge, *Opuntia* was first used for the biosorption of Mn^{2+} from water, with the highest reported removal efficiency of 36.0% with 0.5 g of biosorbent [16]. However, studies on the possibility of increasing the removal efficiency of heavy metals by applying modified *Opuntia* and the surface characteristics of such a modified biosorbent are not prevalent in the literature.

The objectives of this study were to (1) characterize the modified cactus (HCl-treated cactus and NaOH-treated cactus) using a range of characterization techniques and (2) to determine the biosorption efficiency of chemically treated cactus for the removal of Zn^{2+} and Mn^{2+} ions from aqueous solution. Tests were conducted to investigate a range of parameters, including biosorbent dose, solution pH, contact time, and initial ion concentration.

2. Materials and methods

2.1. Materials

A cactus pad was collected from an area located close to Mekelle University, Ethiopia. Solutions of Zn^{2+} and Mn^{2+} used in the biosorption experiment were prepared using zinc(II) chloride (Duksan Chemical Co., Ltd, Korea) and manganese(II) chloride (Sigma-Aldrich, USA), respectively, while NaCl (99.5%) and HCl (30%) were purchased from Sigma-Aldrich (USA). All other chemicals used were reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized distilled water was used in all experiments.

2.2. Preparation and characterization of biosorbents

The raw cactus pad was washed with distilled water several times, sliced into smaller pieces, and then dried in an oven at 80°C for 24 h. The resultant dried cactus was ground, sieved using a 1.25-mm sieve, and then stored at 4°C. For the chemical pretreatment, 10 g of raw cactus powder was treated with 100 mL of a 1M solution of NaOH or HCl for 2 h. The suspension was then filtered and washed with distilled water until neutral pH was reached and then dried at 80°C for 24 h. The pretreated cactus was then stored in glass bottles and labeled as either NaOH-treated cactus or HCl-treated cactus, as appropriate.

To analyze the characteristics of the biosorbents, Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700 spectrometer, Thermo Fisher Scientific, USA), X-ray photoelectron spectroscopy (XPS; VG Microtech ESCA 2000 system, JEOL Ltd., Japan), field emission scanning electron microscopy (SEM; JSM-7600F, JEOL Ltd., Japan), and Brunauer-Emmett-Teller (BET) analyses (Autosorb-iQ-MP, Quantachrome Instruments, USA) were used.

2.3. Biosorption experiment

The biosorption experiment was conducted using stock solutions (1,000 mg/L) of Zn^{2+} and Mn^{2+}, which were diluted in deionized distilled water to the required concentrations before use. The effects of 0.1–4 g doses of raw cactus, HCl-treated cactus, and NaOH-treated cactus were evaluated under fixed experimental conditions of 40 mL aqueous solutions of Zn^{2+} and Mn^{2+}, respectively, with an initial concentration of 10 mg/L placed in 50-mL conical tubes and shaken at 150 rpm at 25°C for 24 h. To evaluate the effect of contact time on Zn^{2+} and Mn^{2+} adsorption, a 0.5 g/L dose of raw cactus, HCl-treated cactus, and NaOH-treated cactus biosorbent was used in a sample containing10 mg/L of metal ions, respectively. Samples were shaken during the experiments, and the contact time for adsorption varied from 0.5 to 24 h. To evaluate the effect of initial metal ion concentration, the concentration was varied between 5 and 300 mg/L under fixed experimental conditions of an adsorbent dose of 0.5 g/L shaken at 150 rpm at 25°C for 24 h. The effect of pH was investigated in a pH range of 2–6 by adding 0.1 mol/L HCl at the start of each experiment. At the end of the predetermined contact time, each adsorption sample was filtered using a 0.45 μm filter (cellulose acetate, Hyundai Micro Co., Ltd., Korea) and analyzed with inductively coupled plasma-atomic emission spectrometry (ICP-AES; IRIS, Thermo Jarrell Ash Co., USA) to measure the concentrations of Zn^{2+} and Mn^{2+} ions. The ICP-AES apparatus was calibrated using standard metal ion solutions.

The amount of Zn^{2+} and Mn^{2+} adsorbed at equilibrium (q_e, mg/g) with the raw cactus, HCl-treated cactus, and NaOH-treated cactus adsorbents was calculated using the following equation:

$$q_e = V \times \frac{C_i - C_e}{m} \tag{1}$$

where C_i and C_e are the initial and equilibrium metal ion concentrations in solution (mg/L), respectively; V is the volume of the aqueous solution (L); and m is the mass of the adsorbent (g).

The removal percentage of Zn^{2+} and Mn^{2+} was calculated using the following equation.

$$\%\text{removal} = \frac{C_i - C_e}{C_i} \times 100\% \tag{2}$$

3. Results and discussion

3.1. Characterization of raw cactus, HCl-treated cactus, and NaOH-treated cactus

The pretreatment modified the surface characteristics/groups and enhanced the capacity of biosorbents for cationic metals through the extraction of soluble organic or inorganic components from the raw biomass and/or by changing its biochemistry. Alkali or acid pretreatment of *Opuntia* significantly increased the Zn^{2+} and Mn^{2+} uptake capacities.

3.1.1. FTIR analysis

Several characterization techniques were employed to understand the surface functional groups, elemental analysis components, surface morphology, and pore size. The FTIR spectra of the raw cactus, HCl-treated cactus, and NaOH-treated cactus are presented in Fig. 1. The raw cactus spectrum indicated various surface functional groups. The peaks around 2,920–2,850 cm^{-1} corresponded to the vibrational stretching of the methyl groups, thereby indicating the presence of O–H and C–H groups [17]. The peaks around 1,750–1,600 cm^{-1} represented C=O stretching and aromatic C=C bending vibration [18]. The peak at 1,450 cm^{-1} was assigned to the asymmetric bending of CH_3 of the acetyl moiety [19,20]. The peak at 1,380 cm^{-1} was due to amide or sulfamide bonding [21], whereas the peak around 1,240 cm^{-1} indicated the presence of carbonyl stretching. Furthermore, the occurrence of peaks around 1,220–1,030 cm^{-1} showed the presence of C–O vibrational stretching [20].

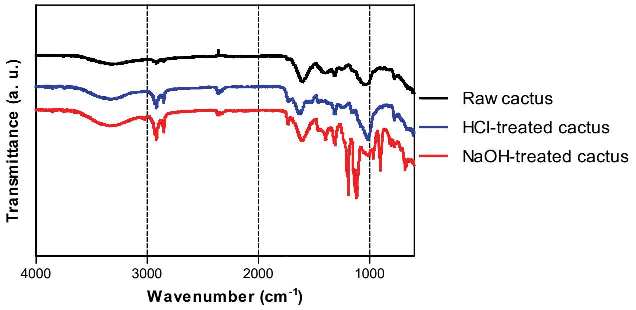


Fig. 1. Fourier transform infrared spectra of the raw cactus, HCl-treated cactus, and NaOH-treated cactus.

To elucidate the changes in functional groups from biosorption, the FTIR spectra of the HCl-treated cactus and NaOH-treated cactus biosorbents were compared with that of the raw cactus biosorbent (Fig. 1). For the NaOH-treated cactus biosorbent, the increasing intensity of the peak at 1,450 cm^{-1} was attributed to asymmetric bending of CH_3. The peak around 1,380 cm^{-1} (amide or sulfamide bond) increased in size for the NaOH-treated cactus biosorbent. The peak at 1,240 cm^{-1} (C–O stretching of COOH) shifted to 1,250 cm^{-1} for the NaOH-treated cactus, which indicated an increase in carbonyl groups via treatment of the raw biosorbent with a base, i.e., sodium hydroxide, thereby increasing the metal-binding ability of the biosorbent [22]. Moreover, methyl ester bonds could be saponified to carboxyl (–COOH), carboxylate (–COO), and alcoholic (–OH) ligands [23,24]. Treatment with a base also leads to a decrease in the degree of polymerization and crystallinity, as follows:

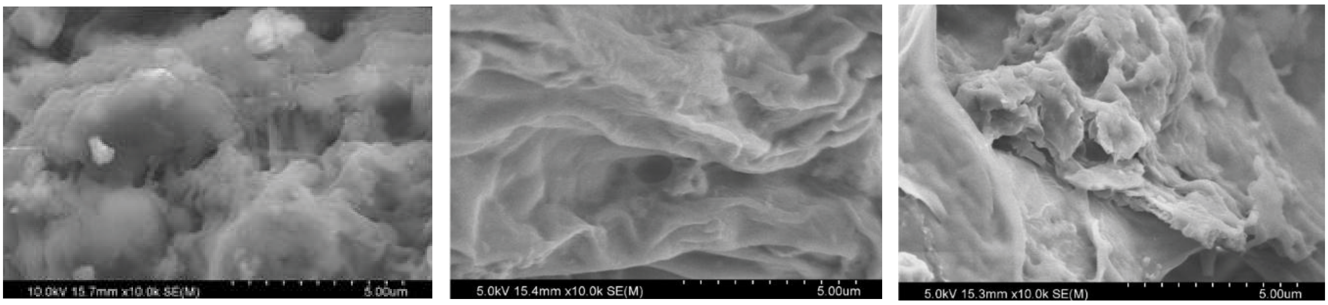
$$R-COOH+NaOH\rightarrow R-COO^{-}+CH_3OH+Na^{+}$$

For the FTIR spectrum of the HCl-treated cactus, the peak at 1,570 cm^{-1} shifted to 1,600 cm^{-1}, thereby indicating C=C stretching vibrations. This was because HCl can protonate unavailable functional groups in the structure of the biosorbent by oxidizing the functional groups and transforming them into carboxylic groups [25,26].

Compared with the raw cactus peaks, the peaks of the HCl-treated cactus and NaOH-treated cactus showed significant changes. In particular, the peaks at 1,220–1,030 cm^{-1} increased after chemical pretreatment, and the shift in functional groups of the NaOH-treated cactus biosorbent was slightly higher than that for the HCl-treated cactus. These results supported the notion that chemical treatment changed the stretching vibration of the amide or sulfamide bond, methyl groups, and carbonyl groups on the surface of the cactus and that they can serve as active sites for the biosorption of Zn^{2+} and Mn^{2+} [20,27,28].

3.1.2. Scanning electron microscopy

SEM images of the raw cactus, HCl-treated cactus, and NaOH-treated cactus are shown in Fig. 2. The surface morphology of the raw cactus changed after the treatment process because of the chemical reaction between the raw material and the activating agent (HCl or NaOH). Nevertheless, Fig. 2 shows that raw cactus, HCl-treated cactus, and



Raw cactus HCl-treated cactus NaOH-treated cactus

Fig. 2. Scanning electron microscope images of the raw cactus, HCl-treated cactus, and NaOH-treated cactus.

NaOH-treated cactus appeared to have low porosity. This result revealed that nanopores of the biosorbents do not play a significant role in the adsorption capacity.

3.1.3. Elemental analysis

The elemental analysis results of the raw cactus, HCl-treated cactus, and NaOH-treated cactus are shown in Table 1. The content of the raw cactus material mainly consisted of carbon and oxygen, with smaller proportions of calcium. The large proportions of carbon and oxygen were attributed to polysaccharides, such as cellulose, hemicellulose, and lignin, in the cactus (*Opuntia*) [29]. After the treatment with NaOH, an increase in oxygen content of 56.91% was observed. Conversely, the carbon and calcium contents decreased. For the HCl-treated cactus, both the oxygen and calcium contents increased, while the amount of carbon decreased by 26.44%. The weight fraction of oxygen increased when the cactus was modified with NaOH and HCl because oxygenated groups were introduced onto the surface of the biosorbent during the modification. Although the result was unable to show the main biosorption sites, it indicated that the amino, carboxyl, and hydroxyl groups took part in the formation of the complexes and had an interaction or synergistic action in the biosorption process [30]. These results revealed that the oxygen atoms in the biosorbents contributed to the biosorption of Zn^{2+} and Mn^{2+}, which correlated strongly with the FTIR results.

3.1.4. XPS analysis

The levels of C1s and O1s in the XPS spectra for the raw cactus, HCl-treated cactus, and NaOH-treated cactus are presented in Fig. 3 and Table 2. The results indicated that the atomic concentration (AC) (%) of the aliphatic carbon (C–C) groups increased with NaOH modification. This increase in C–C groups could be interpreted as resulting from the addition of alkyl groups [31]. However, the AC of –C–O or O–H groups decreased. For the HCl-treated cactus, the AC of the C–C groups decreased and the AC of the –C–O or O–H groups increased. The increase in –C–O or O–H groups could have been due to the increase in carbonyl (–CO) and alcoholic (–OH) ligands on the biosorbent surface.

3.1.5. BET surface area and porosity

The textural characteristics of the raw cactus, HCl-treated cactus, and NaOH-treated cactus are listed in Table 3. The surface area of the cactus modified with NaOH was slightly higher than that of the unmodified raw cactus. For the HCl-treated cactus, the surface area was found to be smaller than that of the raw cactus. However, the areas recorded were smaller than those of common activated carbons. The average pore volume and average pore diameter of the modified

Table 1
Elemental analysis of the raw cactus, HCl-treated cactus, and NaOH-treated cactus biosorbents

Biosorbent	Percentage (%)			
	C	O	K	Ca
Raw cactus	75.70	23.05	0.29	0.68
HCl-treated cactus	67.42	32.09	0.00	0.49
NaOH-treated cactus	55.68	40.50	0.00	3.74

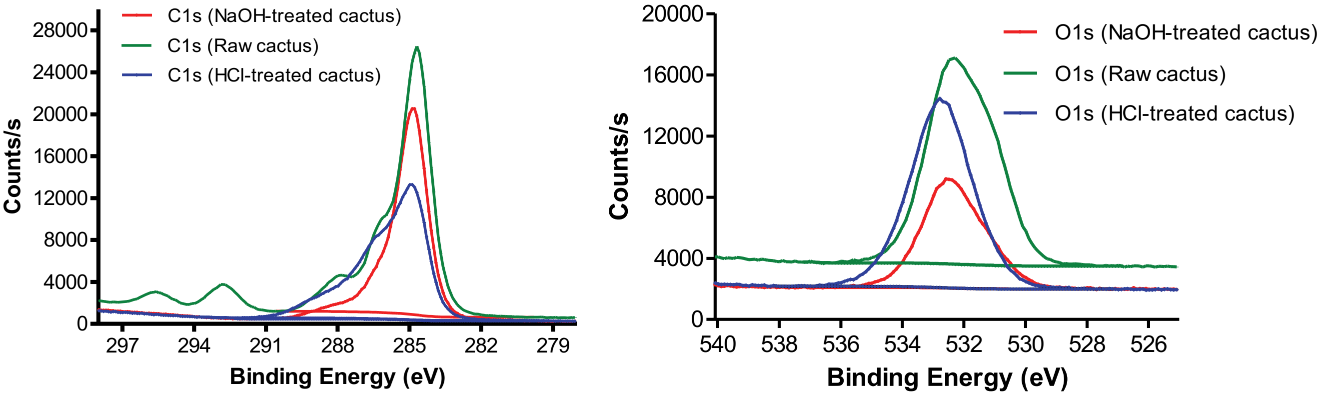


Fig. 3. X-ray photoelectron spectroscopy spectra of the raw cactus, HCl-treated cactus, and NaOH-treated cactus biosorbents.

Table 2
Assignment of main spectral bands based on their binding energy (BE) and atomic concentration (AC) for the raw cactus, HCl-treated cactus, and NaOH-treated cactus

Element	Raw cactus		HCl-treated cactus		NaOH-treated cactus		Assignment
	BE (eV)	AC (%)	BE (eV)	AC (%)	BE (eV)	AC (%)	
C1s	284.70	78.98	285.08	75.85	284.87	84.93	C–C
O1s	532.18	21.02	532.74	24.15	532.44	15.07	–C–O or O–H

Table 3
Textural characteristics of the raw cactus, HCl-treated cactus, and NaOH-treated cactus

Adsorbent	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
Raw cactus	1.402	0.00555	15.824
HCl-treated cactus	0.894	0.00323	14.472
NaOH-treated cactus	1.680	0.00454	10.802

cactus were similar to those of the unmodified cactus. These results indicated that the anatomic structure of the alkaline- and acid-modified cactus changed little. This may have been due to the higher content of organic carbon in *Opuntia* because organic materials do not dissolve in acid or base solutions; thus, their structure is relatively stable with such treatments [32].

3.2. Biosorption performance

3.2.1. Effect of adsorbent dose

Adsorbent dose is one of the main parameters that require optimization for application purposes. Figs. 4(a) and (b) show the removal percentage of Zn^{2+} and Mn^{2+} versus biosorbent dose at a concentration of 10 mg/L and a pH of 5. An increase in biosorbent dose from 0.1 to 4 g/L resulted in the incremental removal of Zn^{2+} from 22.6% to 95.9% for the NaOH-treated cactus, from 14.9% to 83.9% for the HCl-treated cactus, and from15.3% to 36.0% for the raw cactus (Fig. 4(a)). For Mn^{2+}, the removal efficiency increased with increasing dose from 14.6% to 88.7% for the NaOH-treated cactus, from 8.8% to 71.0% for the HCl-treated cactus, and from 8.1% to 33.0% for the raw cactus (Fig. 4(b)). The increases in Zn^{2+} and Mn^{2+} uptake could have been due to an increase in adsorption sites resulting from the increased biosorbent dose [33]. In addition, chemical pretreatment of the raw cactus with NaOH was found to strongly enhance the biosorption capacity of the biosorbent for the tested metals.

Conversely, the equilibrium biosorption capacity of the biosorbents for Zn^{2+} decreased from 20.1 to 2.1 mg/g for the NaOH-treated cactus, from 13.8 to 1.9 mg/g for the HCl-treated cactus, and from 13.6 to 0.8 mg/g for the raw cactus, as shown in Fig. 4(a). For Mn^{2+}, the equilibrium adsorption capacity of the biosorbents decreased from 13.2 to 2.0 mg/g for the NaOH-treated cactus, from 8.0 to 1.6 mg/g for the HCl-treated cactus, and from 7.3 to 0.8 mg/g for the raw cactus when the biosorbent dose was increased from 0.1 to 4 g/L, as shown in Fig. 4(b). This could have been due to the increasing dose of biosorbent per given amount of adsorbate leading to unsaturation of biosorption sites as they exceeded the dose. Considering the balance between the removal percentage and biosorption capacity, the biosorbent dose was set at 0.5 g/L for the remaining biosorption studies.

3.2.2. Effect of pH

Solution pH is one of the most important parameters in the Zn^{2+} and Mn^{2+} biosorption process. The uptake of metal ions is influenced considerably by pH owing to metallic ion speciation in solution and the change in surface charge of the adsorbent [34,35]. As shown in Figs. 5(a) and (b), the biosorption of Zn^{2+} and Mn^{2+} was low in the acidic medium and increased with increasing pH. This increase in removal efficiency with pH could have been due to the deprotonation of the carboxyl and hydroxyl active sites, which enhances metal binding [34]. The maximum metal ion biosorption was achieved at pH of 5. However, for the raw cactus, the maximum biosorption was found at pH 4. These changes in optimum conditions and biosorption efficiencies could be explained by differences in the functional groups on

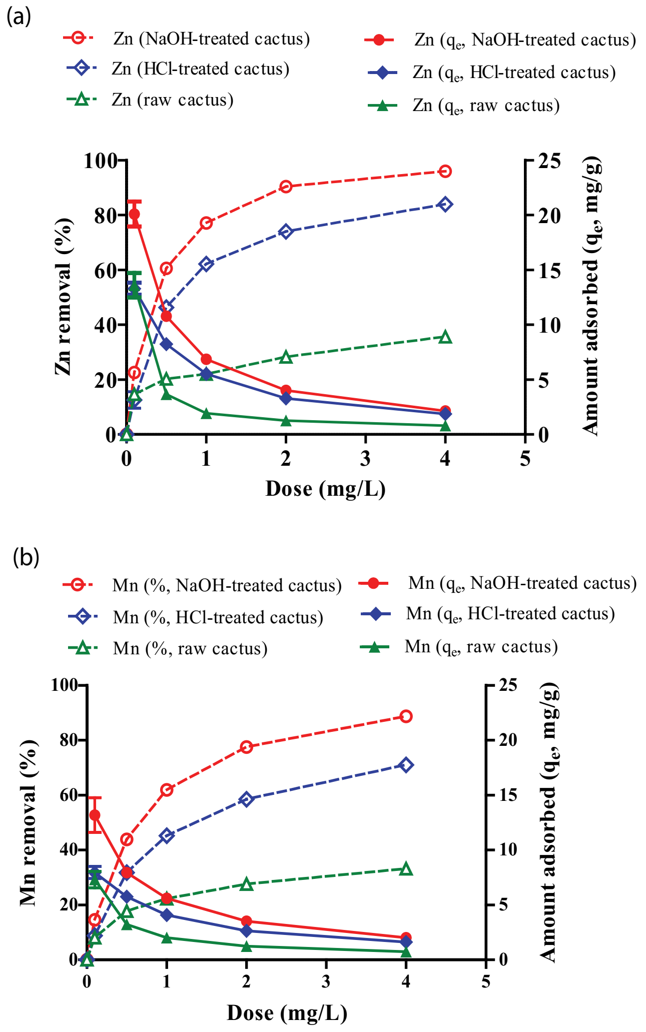


Fig. 4. Effect of biosorbent dosage on (a) Zn^{2+} and (b) Mn^{2+} removal (adsorbent dose: 0.1–4.0 g/L; initial metal ion concentration: 10 mg/L; temperature: 25°C; pH: 5; contact time: 24 h).

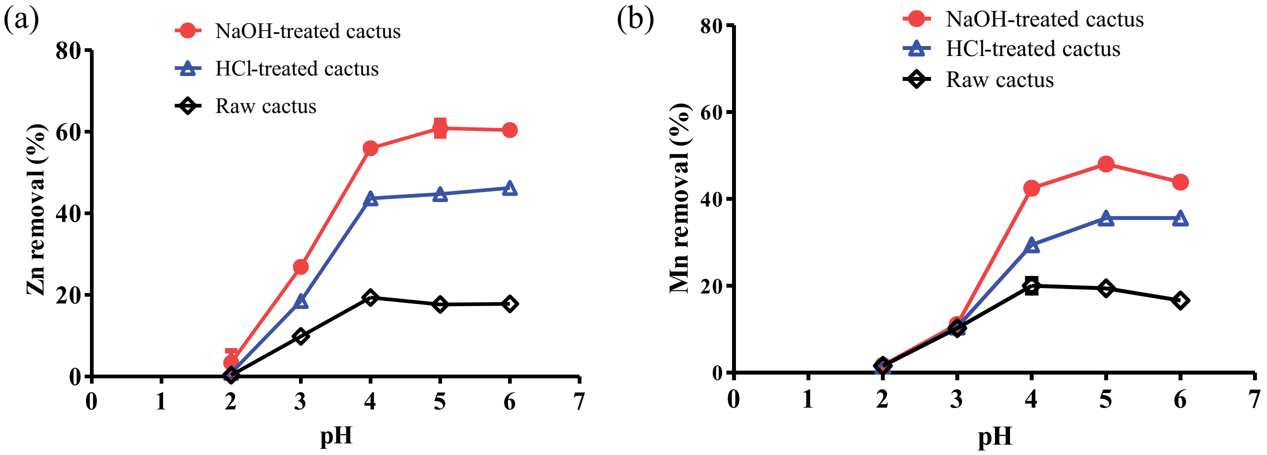


Fig. 5. Effect of initial solution pH on (a) Zn^{2+} and (b) Mn^{2+} biosorption (dose: 0.5 g/L; initial metal ion concentration: 10 mg/L; temperature: 25°C; pH: 2–6; contact time: 24 h).

the biosorbent surfaces, as confirmed by the FTIR and XPS analyses. Moreover, the removal efficiency of Zn^{2+} and Mn^{2+} by the NaOH-treated cactus was greater than that of the HCl-treated cactus and raw cactus. Therefore, a pH of 5 was considered the optimum pH and was used for the remainder of the biosorption experiments.

3.2.3. Kinetics study

Biosorption kinetics of Zn^{2+} and Mn^{2+} by the raw cactus, HCl-treated cactus, and NaOH-treated cactus biosorbents were examined for contact times ranging between 0.5 and 24 h in order to understand the rate of reaction in terms of order dynamics and rate constant. To elucidate the mechanisms involved in the biosorption kinetics, pseudo-first-order and pseudo-second-order equations were used to fit the biosorption data. The pseudo-first-order kinetics for adsorption of Zn^{2+} and Mn^{2+} onto the raw cactus, HCl-treated cactus, and NaOH-treated cactus adsorbents were calculated using the Lagergren model, which can be expressed as follows [36,37]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303} \times t \tag{3}$$

where q_e is the amount of Zn^{2+} or Mn^{2+} adsorbed (mg/g), t is the time (min), and K_1 is the adsorption rate constant.

The pseudo-second-order kinetics for the adsorption of Zn^{2+} and Mn^{2+} onto the raw cactus, HCl-treated cactus, and NaOH-treated cactus were calculated using the Ho model [38], as follows:

$$\frac{t}{q_t} = \frac{t}{K_2\left(q_e\right)^2} + \frac{t}{qe^2} \tag{4}$$

where K_2 is the adsorption rate constant.

Fig. 6 shows the adsorption capacity of Zn^{2+} and Mn^{2+} versus contact time at a concentration of 10 mg/L and a pH of 5. The results indicated that rapid biosorption kinetics were observed for 2 h for both Zn^{2+} and Mn^{2+}, after which the rates decreased gradually until equilibrium was reached. This trend indicated that all the adsorbent sites were initially vacant and the solute concentration gradient was high.

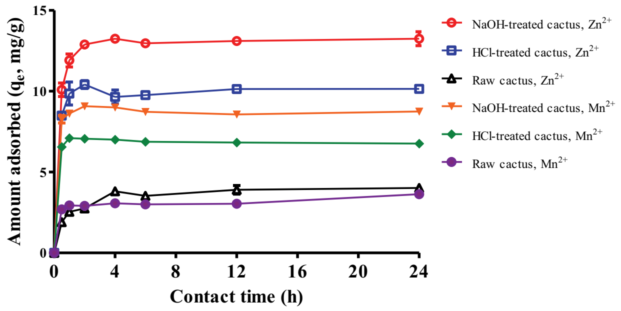


Fig. 6. Effect of contact time on the adsorption of Zn^{2+} and Mn^{2+} onto the raw cactus, HCl-treated cactus, and NaOH-treated cactus adsorbents(adsorbent dose: 0.5 g/L; initial metal ion concentration: 10 mg/L; temperature: 25°C; pH: 5; contact time: 0.5–24 h).

The straight line plots (not shown) of the pseudo-first-order [log(q_e–q_t) versus t] and pseudo-second-order (t/q_t vs. t) models indicated that the pseudo-second order was more relevant to the biosorption of Zn^{2+} and Mn^{2+} onto the raw cactus, HCl-treated cactus, and NaOH-treated cactus biosorbents. Table 4 shows the kinetic parameter data for the biosorption of Zn^{2+} and Mn^{2+}. The high equilibrium values (q_e) and higher correlation coefficient (R^2) results revealed that the pseudo-second-order model was the best fit and more appropriate for explaining the biosorption process. This result implied that the biosorption of Zn^{2+} and Mn^{2+} was controlled by the availability of biosorption sites on the biosorbents.

3.2.4. Isotherm study

The adsorption isotherm is an important parameter for understanding the biosorption process. Because of the high removal efficiency of the modified cactus, the adsorption of Zn^{2+} and Mn^{2+} onto the HCl-treated cactus and NaOH-treated cactus biosorbents was further investigated via

Table 4
Kinetic parameters for the biosorption of Zn^{2+} and Mn^{2+}

Metal	Biosorbent	q_e (mg/g)	Pseudo-first order			Pseudo-second order		
			q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/(mg min))	R^2
Zn^{2+}	Raw cactus	4.016	1.001	0.0012	0.546	4.016	0.2422	0.999
	HCl-treated cactus	10.415	0.632	0.0012	0.632	10.415	0.0983	0.999
	NaOH-treated cactus	13.249	1.269	0.0018	0.734	13.249	0.0774	0.970
Mn^{2+}	Raw cactus	3.630	7.587	0.0007	0.840	3.630	0.5520	0.986
	HCl-treated cactus	7.103	5.077	0.0005	0.795	7.103	0.2975	0.991
	NaOH-treated cactus	9.074	1.074	0.1082	0.989	9.074	0.1148	0.999

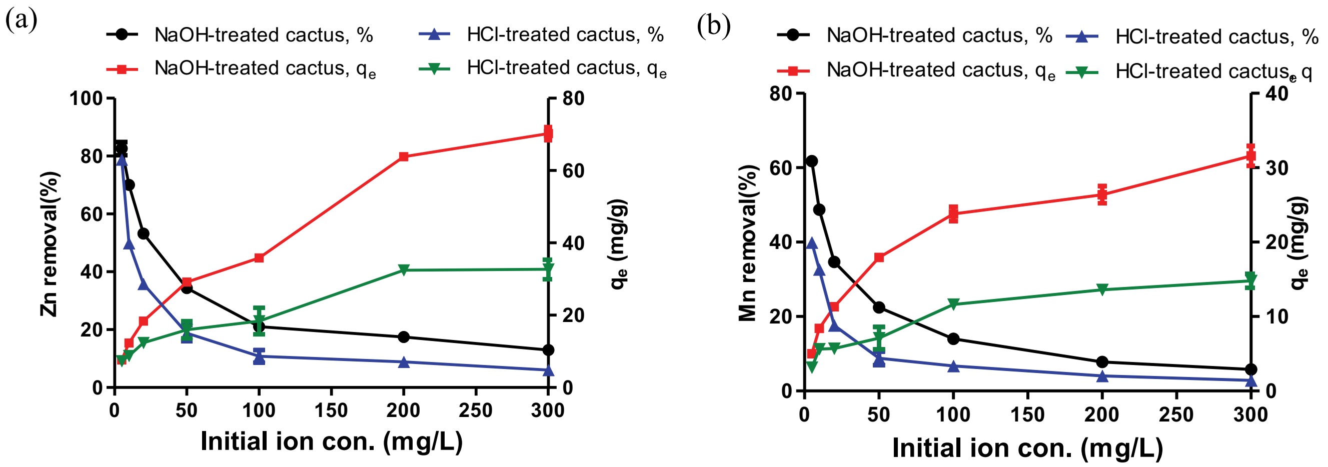


Fig. 7. Effect of initial metal ion concentration on the removal efficiency of (a) Zn^{2+} and (b) Mn^{2+} by the NaOH-treated cactus and HCl-treated cactus (adsorbent dose: 0.5 g/L; initial metal ion concentration: 5–300 mg/L; temperature: 25°C; pH: 5; contact time: 24 h).

isotherms, as presented in Figs. 7(a) and (b). All the isotherm curves showed that the adsorbed amount increased with the initial concentration of Zn^{2+} and Mn^{2+}. The high driving force for mass transfer at higher concentrations of the biosorbent could explain this result. In addition, the highest adsorption capacities for Zn^{2+} and Mn^{2+} were with the NaOH-treated cactus biosorbent. The NaOH-treated cactus adsorbed approximately 72.1 mg/g of Zn^{2+} and 31.6 mg/g of Mn^{2+}. Moreover, the NaOH-treated cactus performed better than the HCl-treated cactus, with approximately 50% more sorption capacity (q_e) for Zn^{2+} and Mn^{2+} at an initial metal ion concentration of 300 mg/L.

The experimental data were fitted to the most commonly used isotherm models (Langmuir and Freundlich models) to examine adsorbate and adsorbent interactions [39–41]. The Langmuir isotherms for the biosorption of Zn^{2+} and Mn^{2+} onto the HCl-treated cactus and NaOH-treated cactus biosorbents were calculated using the following equation [42]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{5}$$

where q_e is the biosorption capacity at equilibrium (mg/g), $q_{\max}$ is the maximum adsorption capacity (mg/g) based on the Langmuir isotherm, and b is a constant (L/mg) related to the energy of adsorption that quantitatively reflects the affinity between the adsorbent and adsorbate [5].

The Freundlich isotherms for the biosorption of Zn^{2+} and Mn^{2+} onto the HCl-treated cactus and NaOH-treated cactus biosorbents were calculated using the following equation [43]:

$$\ln q_e = \ln K + \left(\frac{1}{n}\right)\ln C_e \tag{6}$$

where K is the maximum adsorption capacity (mg/g) based on the Freundlich model and n is related to adsorption intensity.

The Langmuir isotherm assumes several factors, namely, monolayer coverage, equilibrium model use, that adsorption sites are equally probable, and that second-order reactions occur, whereas the Freundlich isotherm is used to describe adsorption on heterogeneous surfaces [5].

Table 5 shows the results obtained from the Langmuir and Freundlich equations for the HCl-treated cactus and NaOH-treated cactus biosorbents. As shown, both isotherm models had good correlation coefficients with $R^2 > 0.91$. The $q_{\max}$ for Zn^{2+} (49.75 mg/g) was higher than that for Mn^{2+}, thereby indicating that the NaOH-treated cactus and HCl-treated cactus biosorbents had higher affinity toward Zn^{2+}. In addition, the $q_{\max}$ obtained for the NaOH-treated cactus was

Table 5
Isotherm parameters for the biosorption of Zn^{2+} and Mn^{2+}

Metal	Biosorbent	Langmuir			Freundlich		
		q_{max} (mg/g)	b (L/min)	R^2	$1/n$	K (mg/g)	R^2
Zn^{2+}	HCl-treated cactus	21.28	0.102	0.907	0.381	3.995	0.970
	NaOH-treated cactus	49.75	0.039	0.991	0.546	3.589	0.988
Mn^{2+}	HCl-treated cactus	10.96	0.102	0.930	0.364	2.120	0.945
	NaOH-treated cactus	25.58	0.599	0.989	0.447	3.075	0.968

Table 6
Zn^{2+} and Mn^{2+} adsorption capacities of various plant-based adsorbents

Biosorbent	Modifying agent	q_{max} (mg/g)		Reference
		Zn^{2+}	Mn^{2+}	
Cactus	Hydrochloric acid	25.58	10.96	Present study
Cactus	Sodium hydroxide	49.75	21.28	Present study
Sawdust (poplar tree)	Sodium hydroxide	13.40	–	[45]
Sugar beet pulp	Hydrochloric acid	0.18	–	[46]
Chitosan	Acetic acid	–	71.40	[47]
Carrot residues	Hydrochloric acid	29.61	–	[48]
Corn cob biomass	Oxalic acid	–	7.87	[49]
Cotton stalks	Sodium hydroxide	4.35	12.45	[50]
Maize husk	Oxalic acid	–	9.00	[51]

superior to that of the HCl-treated cactus biosorbent, thereby implying that treatment with NaOH increased the dissociated groups on the biosorbent surface. The R^2 values obtained from the Freundlich model were also higher, and the n values obtained from this model were greater than unity, thereby indicating a favorable biosorption process for both metals on the NaOH-treated cactus and HCl-treated cactus biosorbents under the experimental conditions.

The effectiveness of the HCl-treated cactus and NaOH-treated cactus biosorbents was also compared with that of other biosorbents using the maximum adsorption capacity. As shown in Table 6, the maximum biosorption capacity of the different biomaterials differed, which could have been due to the nature and chemical composition of the materials used [33]. The adsorption capacity of modified cactus was found to be greater than that of biosorbents reported in previous studies [33,44].

4. Conclusion

The effects of acid and alkaline modification on the adsorption capacity of cactus were investigated in this study. The properties of the adsorbents were characterized systematically using FTIR spectroscopy, XPS, elemental, SEM, and BET analyses. The FTIR results indicated that chemical treatment changed the stretching vibration of the methyl and carbonyl groups on the surface of the biosorbents. After treatment with NaOH, an increase in oxygen of 56.91% was observed, while the amount of carbon decreased by 26.44%. These results revealed that the oxygen atoms in the biosorbents contributed to adsorbing the Zn^{2+} and Mn^{2+}, which correlated strongly with the results of the FTIR analysis. This study showed that the NaOH-treated cactus had greater adsorption capacity for both Zn^{2+} and Mn^{2+} than either the HCl-treated cactus or the raw cactus. Significant differences were observed between the basic treated biosorbent and the untreated biomaterial. The maximum adsorption capacities of the NaOH-treated cactus obtained from the Langmuir isotherms were 49.75 and 25.58 mg/g of Zn^{2+} and Mn^{2+}, respectively, whereas they were 21.28 and 10.96 mg/g of Zn^{2+} and Mn^{2+}, respectively, for the HCl-treated cactus. From this study, it can be concluded that chemical pretreatment of raw cactus with NaOH strongly enhanced its biosorption potential for the studied metals.

Acknowledgment

This work was supported by the National Research Foundation of Korea (NRF-2018K1A3A9A01000015).

References

[1] S. Rengaraj, Y. Kim, C.K. Joo, J. Yi, Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: kinetics and equilibrium, J. Colloid Interface Sci., 273 (2004) 14–21.
[2] N. Unlu, M. Ersoz, Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions, J. Hazard. Mater., 136 (2006) 272–280.
[3] I. Ali, V. Gupta, Advances in water treatment by adsorption technology, Nat. Protoc., 1 (20066) 2661–2667.

[4] V.O. Arief, K. Trilestari, J. Sunarso, N. Indraswati, S. Ismadji, Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies, Clean, 36 (2008) 937–962.

[5] M. Hanafiah, H. Zakaria, W.W. Ngah, Preparation, characterization and adsorption behavior of Cu (II) ions onto alkali-treated weed (*Imperata cylindrica*) leaf powder, Water Air Soil Pollut., 201 (2009) 43–53.

[6] D. Park, Y.S. Yun, J.M. Park, The past, present, and future trends of biosorption, Biotechnol. Bioprocess Eng., 15 (2010) 86–102.

[7] W.W. Ngah, M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, Bioresour. Technol., 99 (2008) 3935–3948.

[8] K. Vijayaraghavan, Y.S. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv., 26 (2008) 266–291.

[9] A. Trejo-Gonzalez, G. Gabriel-Ortiz, A.M. Puebla-Perez, M.D. Huizar-Contreras, M.R. Munguia-Mazariegos, S. Mejia-Arreguin, E. Calva, A purified extract from prickly pear cactus (*Opuntia fuliginosa*) controls experimentally induced diabetes in rats, J. Ethnopharmacol., 55 (1996) 27–33.

[10] P. Inglese, F. Basile, M. Schirra, Cactus Pear Fruit Production, Cacti: Biology and Uses, University of California Press, Berkley, CA, 2002.

[11] L.Y. Zhao, W. Huang, Q.X. Yuan, J. Cheng, Z.C. Huang, L.J. Ouyang, Hypolipidaemic effects and mechanisms of the main component of *Opuntia dillenii* Haw. polysaccharides in high-fat emulsion-induced hyperlipidaemic rats, Food Chem., 134 (2012) 964–971.

[12] E.H. Park, J.H. Kahng, S.H. Lee, K.H. Shin, An anti-inflammatory principle from cactus, Fitoterapia, 72 (2001) 288–290.

[13] D. Palevitch, G. Earon, I. Levin, Treatment of benign prostatic hypertrophy with *Opuntia ficus-indica* (L.) Miller, J. Herbs Spices Med. Plants, 2 (1998) 45–49.

[14] S.M. Miller, E.J. Fugate, V.O. Craver, J.A. Smith, J.B. Zimmerman, Toward understanding the efficacy and mechanism of *Opuntia* spp. as a natural coagulant for potential application in water treatment, Environ. Sci. Technol., 42 (2008) 4274–4279.

[15] G. Vijayaraghavan, T. Sivakumar, A.V. Kumar, Application of plant based coagulants for wastewater treatment, Int. J. Adv. Eng. Res. Stud., 1 (2011) 88–92.

[16] A. Belayneh, W. Batu, Application of biosorbent derived from Cactus peel for removal of colorful manganese ions from ground water, J. Water Resour. Ocean Sci., 4 (2015) 18–23.

[17] Y. Sun, P.A. Webley, Preparation of activated carbons from corncob with large specific surface area by a variety of chemical activators and their application in gas storage, Chem. Eng. J., 162 (2010) 883–892.

[18] Y.S. Yun, D. Park, J.M. Park, B. Volesky, Biosorption of trivalent chromium on the brown seaweed biomass, Environ. Sci. Technol., 35 (2001) 4353–4358.

[19] N. Yee, L.G. Benning, V.R. Phoenix, F.G. Ferris, Characterization of metal−cyanobacteria sorption reactions: a combined macroscopic and infrared spectroscopic investigation, Environ. Sci. Technol., 38 (2004) 775–782.

[20] R.S. Bai, T.E. Abraham, Studies on enhancement of Cr (VI) biosorption by chemically modified biomass of *Rhizopus nigricans*, Water Res., 36 (2002) 1224–1236.

[21] A. Kapoor, T. Viraraghavan, Heavy metal biosorption sites in *Aspergillus niger*, Bioresour. Technol., 61 (1997) 221–227.

[22] N.C. Feng, X.Y. Guo, S. Liang, Enhanced Cu(II) adsorption by orange peel modified with sodium hydroxide, Trans. Nonferrous Met. Soc. China, 20 (2010) 146–152.

[23] D. Feng, C. Aldrich, H. Tan, Treatment of acid mine water by use of heavy metal precipitation and ion exchange, Miner. Eng., 13 (2000) 623–642.

[24] A. Ronda, M.A. Martín-Lara, M. Calero, G. Blázquez, Analysis of the kinetics of lead biosorption using native and chemically treated olive tree pruning, Ecol. Eng., 58 (2013) 278–285.

[25] A. Chatterjee, S. Schiewer, Multi-resistance kinetic models for biosorption of Cd by raw and immobilized citrus peels in batch and packed-bed columns, Chem. Eng. J., 244 (2014) 105–116.

[26] R. Nadeem, T.M. Ansari, K. Akhtar, A.M. Khalid, Pb (II) sorption by pyrolysed *Pongamia pinnata* pods carbon (PPPC), Chem. Eng. J., 152 (2009) 54–63.

[27] D. Park, Y.S. Yun, H.Y. Cho, J.M. Park, Chromium biosorption by thermally treated biomass of the brown seaweed, *Ecklonia* sp., Ind. Eng. Chem. Res., 43 (2004) 8226–8232.

[28] Y.S. Yun, B. Volesky, Modeling of lithium interference in cadmium biosorption, Environ. Sci. Technol., 37 (2003) 3601–3608.

[29] P. Sarkar, E. Bosneaga, M. Auer, Plant cell walls throughout evolution: towards a molecular understanding of their design principles, J. Exp. Bot., 60 (2009) 3615–3635.

[30] S.L. Sun, A.Q. Wang, Adsorption properties and mechanism of cross-linked carboxymethyl-chitosan resin with Zn (II) as template ion, React. Funct. Polym., 66(2006) 819–826.

[31] R.S. Vieira, M.L.M. Oliveira, E. Guibal, E. Rodríguez-Castellón, M.M. Beppu, Copper, mercury and chromium adsorption on natural and crosslinked chitosan films: an XPS investigation of mechanism, Colloids Surf., A, 374 (2011) 108–114.

[32] F. Asadi, H. Shariatmadari, N. Mirghaffari, Modification of rice hull and sawdust sorptive characteristics for remove heavy metals from synthetic solutions and wastewater, J. Hazard. Mater., 154 (2008) 451–458.

[33] Y. Zhang, R. Zheng, J.Y. Zhao, Z. Jiang, D.X. Shan, Y. Lu, Biosorption of Fe (II) and Mn (II) ions from aqueous solution by rice husk ash, Biomed. Res. Int., 2014 (2014) 1–10.

[34] M. Farnanea, H. Tounsadia, R. Elmoubarkia, F.Z. Mahjoubia, A. Elhalila, S. Saqranea, M. Abdennouria, S. Qourzalb, N. Barka, Alkaline treated carob shells as sustainable biosorbent for clean recovery of heavy metals: kinetics, equilibrium, ions interference and process optimization, Ecol. Eng., 101 (2017) 9–20.

[35] E.K. Putra, R. Pranowo, J. Sunarso, N. Indraswati, S. Ismadji, Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: mechanisms, isotherms and kinetics, Water Res., 43 (2009) 2419–2430.

[36] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J., 70 (1998) 115–124.

[37] S. Lagergren, Zur theorie der sogenannten absorption gelöster stoffe, K. Sven. Vetensk. Akad. Handl., 24 (1898) 1–39.

[38] Y.S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater., 136 (2006) 681–689.

[39] L.P. Cheng, L. Sun, W.L. Xue, Z.X. Zeng, S.M.S. Li, Adsorption equilibrium and kinetics of Pb (II) from aqueous solution by modified walnut shell, Environ. Prog. Sustain. Energy, 35 (2016) 1724–1731.

[40] S. Deng, Y.P. Ting, Fungal biomass with grafted poly (acrylic acid) for enhancement of Cu (II) and Cd (II) biosorption, Langmuir, 21 (2005) 5940–5948.

[41] F. Deniz, Effective removal of maxilon red GRL from aqueous solutions by walnut shell: nonlinear kinetic and equilibrium models, Environ. Prog. Sustain. Energy, 33 (2014) 396–401.

[42] I. Langmuir, The constitution and fundamental properties of solids and liquids, II. Liquids[1], J. Am. Chem. Soc., 39 (1917) 1848–1906.

[43] H. Freundlich, Ueber die adsorbtion in loesungen, Z. Phys. Chem., 57 (1907) 385–470.

[44] B. Singha, S.K. Das, Removal of Pb (II) ions from aqueous solution and industrial effluent using natural biosorbents, Environ. Sci. Pollut. Res., 19 (2012) 2212–2226.

[45] M. Šćiban, M. Klašnja, B. Škrbić, Modified softwood sawdust as adsorbent of heavy metal ions from water, J. Hazard. Mater., 136 (2006) 266–271.

[46] E. Pehlivan, S. Cetin, B. Yanık, Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash, J. Hazard. Mater., 135 (2006) 193–199.

[47] R.M.S. Perez, A.R. Abalos, J.M.O.M. Gomez, D.M. Cantero, Biosorption of chromium, copper, manganese and zinc by *Pseudomonas aeruginosa* AT18 isolated from a site contaminated with petroleum, Bioresour. Technol., 100 (2009) 1533–1538.

[48] B. Nasernejad, T.E. Zadeh, B.B. Pour, M.E. Bygi, A. Zamani, Comparison for biosorption modeling of heavy metals (Cr (III), Cu (II), Zn (II)) adsorption from wastewater by carrot residues, Process Biochem., 40 (2005) 1319–1322.

[49] A.I. Adeogun, A.E. Ofudje, M.A. Idowu, S.O. Kareem, Equilibrium, kinetics and thermodynamic studies of the biosorption of Mn (II) ions from aqueous solution by raw and acid-treated corncob biomass, BioResources, 6 (2011) 4117–4134.

[50] A.A. Mosa, A. El-Ghamry, P. Trüby, Chemically modified crop residues as a low-cost technique for the removal of heavy metal ions from wastewater, Water Air Soil Pollut., 217 (2011) 637–647.

[51] A.I. Adeogun, M.A. Idowu, A.E. Ofudje, S.O. Kareem, S.A. Ahmed, Comparative biosorption of Mn (II) and Pb (II) ions on raw and oxalic acid modified maize husk: kinetic, thermodynamic and isothermal studies, Appl. Water Sci., 3 (2013) 167–179.