Hindawi Publishing Corporation
Journal of Chemistry
Volume 2015, Article ID 293054, 12 pages
http://dx.doi.org/10.1155/2015/293054

Research Article

Phragmites karka as a Biosorbent for the Removal of Mercury Metal Ions from Aqueous Solution: Effect of Modification

Muhammad Hamid Raza,[1] Aqsa Sadiq,[2] Umar Farooq,[1] Makshoof Athar,[1] Tajamal Hussain,[1] Adnan Mujahid,[1] and Muhammad Salman[1]

[1] *Institute of Chemistry, University of the Punjab, Lahore 54590, Pakistan*
[2] *College of Earth and Environmental Sciences, University of the Punjab, Lahore 54590, Pakistan*

Correspondence should be addressed to Umar Farooq; umar.chem@pu.edu.pk

Received 3 December 2014; Revised 3 February 2015; Accepted 3 February 2015

Academic Editor: Wenshan Guo

Batch scale studies for the adsorption potential of novel biosorbent *Phragmites karka* (Trin), in its natural and treated forms, were performed for removal of mercury ions from aqueous solution. The study was carried out at different parameters to obtain optimum conditions of pH, biosorbent dose, agitation speed, time of contact, temperature, and initial metal ion concentration. To analyze the suitability of the process and maximum amount of metal uptake, Dubinin-Radushkevich (D-R) model, Freundlich isotherm, and Langmuir isotherm were applied. The values of $q_{\max}$ for natural and treated biosorbents were found at 1.79 and 2.27 mg/g, respectively. The optimum values of contact time and agitation speed were found at 50 min and 150 rpm for natural biosorbent whereas 40 min and 100 rpm for treated biosorbent, respectively. The optimum biosorption capacities were observed at pH 4 and temperature 313 K for both natural *P. karka* and treated *P. karka*. R_L values indicate that comparatively treated *P. karka* was more feasible for mercury adsorption compared to natural *P. karka*. Both pseudo-first-order and pseudo-second-order kinetic models were applied and it was found that data fit best to the pseudo-second-order kinetic model. Thermodynamic studies indicate that adsorption process was spontaneous, feasible, and endothermic.

1. Introduction

The generic name *Phragmites* is attributed to Trinius as the earlier *Phragmites* Adans is considered a redundant name for *Saccharum* Linn. *Phragmites* represents a part of *Arundo Linn*. It is a cosmopolitan genus of four species: *P. karka* (Retz.), *Phragmites australis* (Cav.), *Phragmites japonicus* Steud, and *Phragmites mauritianus* Kunth. *Phragmites australis* Trin and *P. karka* Trin are allopatric and are found to be in temperate and tropic species, respectively [1, 2]. *P. karka* (Retz.) is also known as *Arundo karka* (Retz.), *Arundo roxburghii* Kunth, *Phragmites maxima*, *Phragmites nepalensis* and *Phragmites roxburghii* (Kunth) Steud. It is a perennial reed having creeping rhizomes. Culms are erect up to 1.5–3 m high. Length and width of leaf blades range as 20–60 cm or more 8–32 mm, respectively, which are pungent and sometimes stiff. Panicles are 6–10 cm wide and 20–30 cm long, and the lowest node is usually few branched. Spikelets are 12–18 mm long, and the rhachilla hairs are 6–10 mm long, abundant, and silky [3]. The fertile lemmas are narrowly lanceolate and 9–13 mm long. The middle and upper stem internodes of American reed are smooth, shiny, and red-brown to dark red-brown during the growing season, while in common reed (*Phragmites australis*) middle to upper stem internodes are dull, ridged, and tan colored during the growing season. It is a perennial grass, abundantly found across railway lines and roadsides, near streams, and in marshes, ponds, wetlands, barrages, swamps, and water head works in New Guinea, Africa, Northern Australia, and Asia and is also widely distributed in Pakistan. In Pakistan, it is distributed in Punjab and Kashmir regions and temperate regions of both hemispheres. It is said to be poisonous to cattle (Duthie) and is not used as fodder. *P. karka* is mostly used as weaving material and decoration and for making musical instruments. It is also an excellent stabilizer of eroding river banks [1–3].

In this study, biosorption potential of *P. karka* (Trin Retz.) Steud, locally known as Khagra reed, was studied for heavy-metals uptake from aqueous solution, in single metal ion system as novel application. Heavy-metals pollution is a worldwide problem as they are nonbiodegradable and hazardous to human health and environment due to high bioaccumulation and magnification potential [2–7]. Lead, mercury, and cadmium are known as the three famous pollutants due to their high impact on the environment [8]. Natural sources of mercury include volcanic action, weathering of mercuriferrous rocks, degassing from surface water, biogenic emissions, and natural forest fires [9], while anthropogenic sources include chemical manufacturing, metallurgical and metal finishing industries, pulp and paper industry, pharmaceuticals, seed dressings, fungicides, dental preparations, thermometers, paints, and fluorescent and ultraviolet lamps [9, 10]. In humans, symptoms of mercury poisoning are malfunctioning of central nervous system, visual constriction, loss of memory hearing, and renal disturbance [11, 12]. Due to its high toxicity, European Union recommended maximum permissible limit of Hg in drinking and wastewater as 0.001 and 0.005 $\mathrm{mgL^{-1}}$, respectively [13, 14]. According to World Health Organization and China guidelines, permissible level of inorganic mercury in drinking water is 1.0 $\mu\mathrm{g\,L^{-1}}$ [15].

The term "Biosorption" describes the removal of the heavy metals from a solution by nonmetabolically mediated passive binding to living or dead biomass [1, 16]. This process is based on the fact that certain natural materials of biological origin have property of metal sequestering [17]. Depending on origin and physicochemical conditions, biosorption involves different processes which include metal ion exchange, coordination complexes, covalent linkage to biomass components, and physiologically mediated intracellular uptake [18, 19]. From last two decades, it is being considered as one of the most suitable economic and green technologies. The material reusability, no toxic sludge production, low operating cost, improved selectivity, and compressed operation time for certain metals are some of its advantages over conventional techniques [11, 20]. Microorganisms, fungi, algae, lichens, aquatic macrophytes and animals, waste materials and terrestrial plants in natural, and treated and modified forms are now being used to check their sorption potential by many researchers of the world. Furthermore, chemically treated biosorbents including orange peels, bagasse pith, coconut husks, and polyacrylamide-grafted banana stalks have been used for the biosorption of mercury ions [21].

The effects of agitation speed, biosorbent dose, pH, initial metal ion concentration, and temperature and contact time on adsorption potential were studied in this research. Characteristics of biosorbent were also studied by Fourier transform infrared spectroscopy. In addition, equilibrium studies were performed by applying Langmuir isotherm, Freundlich isotherms, and D-R model to calculate $q_{\max}$ values and suitability of the sorption process. Kinetic studies were performed by applying pseudo-first-order and pseudo-second-order kinetics. Thermodynamics studies were also performed to analyze spontaneity of the biosorption process.

2. Material and Methods

2.1. Raw Biomass. Plant biomass selected for biosorption studies (*P. karka*, Trin) was collected from railway headquarters, Mughalpura, Lahore (25°58′25″N, 68°38′15″E). Leaves and stems of the plants were used for sorption studies because they are waste materials while its rhizome is used in herbal medicines.

2.2. Preparation of Biosorbent. *P. karka* (Trin) is a long plant with length about two meters. So, for ease of washing and handling it was first manually broken down into four to five pieces per plant. Those pieces were then washed with distilled water twice in the laboratory to remove all the litter. Washed plant biomass was first air dried for one day and then manually chopped with Chinese axe to convert into small size pieces for ease of oven drying. Oven drying was done for 14 hours at 90°C till constant mass was obtained. Oven dried plant biomass was ground in a shredder and then passed through mesh number 50 of US standard sieves to get biosorbent of same particle size, that is, 297 μm.

2.3. Chemical Treatment of Biosorbent. Powdered biosorbent was divided into two parts; one was kept in air tight glass container as such in natural form and used for further experimentation (named as natural *P. karka*), while second part was treated according to the method described elsewhere [1]. For treatment purpose, 200 g of powdered biosorbent was soaked in solution containing 1000 ml ethanol, 500 mL NaOH (0.5 mol/L), and 500 mL $CaCl_2$ (1.5 mol/L) for 24 hours [1, 11–14]. After repeated filtration and decantation of biosorbent, it was first dried in open air and then oven dried to get its constant mass. The material was stored in airtight plastic container and named as treated *P. karka*.

2.4. Analytical Instruments and Reagents. All chemicals used were of pure analytical grade purchased from Sigma Aldrich Inc. Glassware was soaked in 20% (v/v) nitric acid for 24 hours and then rinsed two to three times using double distilled water. Mercury stock solution (1000 mg/L) was prepared by dissolving specific quantity of mercuric chloride $HgCl_2$ salt in doubly distilled water. Working and standard solutions of mercury were prepared just before use by required dilutions of stock solution. NaOH (0.1 M) and HCl (0.1 M) solutions were used for pH adjustment of solutions by digital pH meter (Iono Lab pH 720). Oven used was of Memmert (Germany) and solutions were agitated after addition of biosorbent on orbital shaker (IKA Germany Yellow line OS 10 basic). Filtrates were analyzed by AAS (Perkin Elmer Analyst 700 equipped with MHS 15 CVAAS system). The bandwidth of spectrum was 0.7 nm for mercury ions isolation, while 6 mA operating hollow cathode lamp was used. Sodium borohydride (2% w/v) in sodium hydroxide was used as reducing agent.

2.5. Batch Biosorption Procedure. Biosorption of mercury, Hg(II) metal ions, on natural and treated plant biomass

(*P. karka*) was studied in batch fashion. The effects of temperature, pH, initial metal ion concentration, contact time, biosorbent dose, and agitation speed on adsorption capacity of biomass were investigated.

Batch pH experiments were performed for 200 mL solution of Hg(II) ions (10 mg/L) in Erlenmeyer flask (250 mL) with 2 g biosorbent, while the pH was varied from 2 to 8. The pH of solutions was adjusted initially and not thereafter. The flasks were agitated on orbital shaker at 150 rpm speed for 30 minutes at 298 K temperature. After each experiment, solutions were immediately filtered by using Whatman filter papers of grade 40 and filtrates were analyzed using CVAAS. Same process was done for other conditions by changing one parameter and keeping the rest constant.

The effect of biosorbent dose on sorption capacity was determined at six different doses in range of 1.0–6.0 g by keeping rest of parameters constant. The effect of temperature on the adsorption capacity of the biosorbent was determined at different temperatures (i.e., 20, 30, 40, and 50°C). Effect of agitation speed on sorption was studied at 100, 150, 200, 250, and 300 rpm. For determination of optimum contact time samples were drawn at regular intervals at 20, 30, 40, 50, and 60 min. Effect of initial metal ion concentration on biosorption was also studied at six different concentrations in range of 10–60 ppm. All experiments were performed in triplicate fashion and their average values were considered in analysis. Percent biosorptive removal and metal uptake capacity were calculated by the following equations:

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

$$\text{Amount of metal ions adsorbed }\left(q_e\right) = \left(C_i - C_f\right) \times \frac{V}{m}, \tag{1}$$

where C_i (mg/L) and C_f (mg/L) are the initial and final metal ion concentrations of solution, respectively, V is the volume of metal ion solution (L), and m is the mass of the biosorbent (g).

3. Results and Discussion

3.1. FTIR. FTIR spectroscopy is used to analyze the chemical functional groups on the biosorbent. FTIR spectra of the natural as well as treated biosorbent were recorded in 600–4000 cm^{-1} range and are shown in Figure 1.

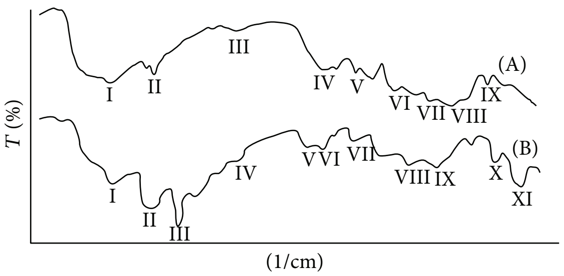


Figure 1: FTIR of natural *P. karka* and treated *P. karka* (biosorbents).

The two peaks A and B represent FTIR spectra of natural *P. karka* and treated *P. karka*, respectively. Peak (I) of natural biosorbent sample at 3370.56 cm^{-1} indicates presence of (O-H) hydroxyl group in cellulose, hemicellulose, pectin, and lignin; it is shifted after treatment to 3290.56 cm^{-1} peak (I). Peak (II) at 2900.94 cm^{-1} in natural biosorbent is representative of stretching vibration of alkanes (C-H), that is, methyl, methylene, or methoxy group. This peak is shifted to 2947.23 cm^{-1} in treated biosorbent with greater intensity. Peak (III) represents presence of aldehydes group in natural *P. karka* at 2885.51 cm^{-1}, whereas in treated biosorbent peak (III) is observed at 2885 cm^{-1} representing nitriles and alkyne groups. Peak (IV) at 1730.15 cm^{-1} represents carbonyl group (C=O) of aldehydes, whereas peak (IV) at treated biosorbent is at 2133 cm^{-1} representing carbonyl group of aldehydes and ketones. Peak (V) at 1633.71 cm^{-1} indicates presence of carboxylate group (COO^-) and it is shifted to 1595.13 cm^{-1} in treated biosorbent. Peak (VI) for both biosorbents is at 1506 cm^{-1} representing N-O (nitro groups). Peak VII is at 1425.4 cm^{-1} which is shifted to 1435.04 cm^{-1} in treated biosorbent and represents presence of (C-H) group of aliphatic or aromatic hydrocarbons. Peaks (IX) in range of 1300–1000 cm^{-1} (1240.3 and 1163 cm^{-1} for natural and treated biosorbents, resp.) are representative of (C-O) stretching of alcohols (R-OH) and carboxylic acids (RCOOH). The appearance of peak (IX) at 1163 cm^{-1} in treated biosorbent shows presence of aldehydes and aliphatic amines specifically. The addition of two more peaks (X, XI) in treated biosorbent at 1064 cm^{-1} and 896 cm^{-1} again shows the presence of nitrile and unsaturation in the carbon chain. Results confirmed the changes in some functional groups of treated biosorbent.

3.2. Effect of pH on Biosorption Determination of pH_{pzc}. Heavy metal ions sorption on the surface of biosorbent is a pH dependent process, which affects the functional groups of biosorbent and the metal ions chemistry in solution [22–27]. As a result, pH affects the availability of metal ions in solution and metal binding sites on biosorbent surfaces. As shown in Figure 3, Hg(II) adsorption capacity at pH 3 was 0.3055 mg g^{-1} and 0.338 mg g^{-1} for natural *P. karka* and treated *P. karka*, respectively. At low pH values below 4, competition between protons and metal ions exists for same binding sites; hence, metal binding capacity decreases [28, 29]. Different functional groups on plant surface are important for the sorption of mercury. A previous work on parsley stated that carboxylate groups of plants play a major role in mercury ions bindings [29]. At lower value of pH (pH < 4), H^+ ions may bind with negatively charged hydroxyl groups on plant surfaces or other lone pair carriers groups such as carbonyl. Hence, there arises a competition between H^+ ions and metal ions in the solution. The researchers found a similar situation that occurs in case of caster leaves, where the carboxylate groups are considered as attracting sites on leaves [9]. Adsorption capacity increased with further increase in pH and reached optimum values of 0.510 mg g^{-1} (80.1%) and 0.579 mg g^{-1} (95.8%) at pH 6 and pH 7 for natural *P. karka* and treated *P. karka*, respectively. This value is in agreement

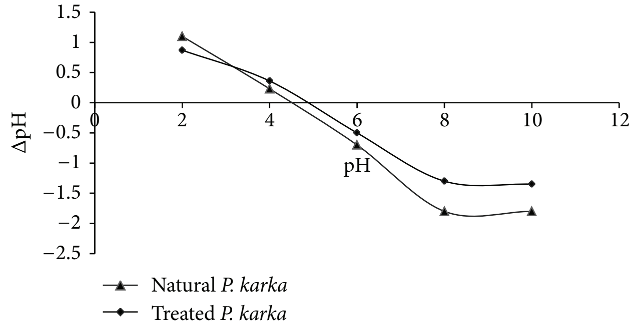


Figure 2: Point zero charge (pH_{pzc}) values for the biosorption of mercury ions on natural *P. karka* and treated *P. karka* (concentration = 10 mg/L, time = 30 minutes, T = 298 K, agitation speed = 150 rpm, dose of biosorbent = 2 g/100 mL, and pH = 2–8).

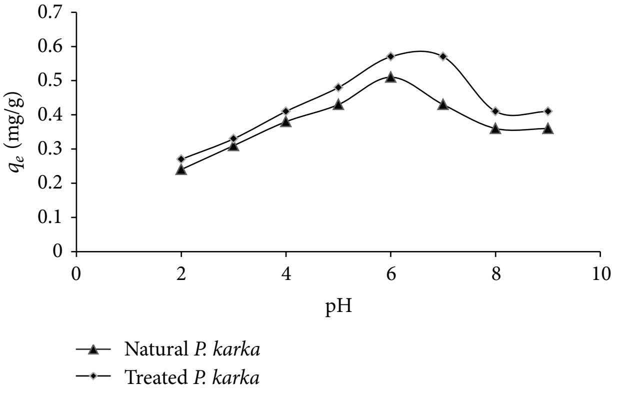


Figure 3: Effect of pH change on biosorption capacity of natural *P. karka* and treated *P. karka* (concentration = 10 mg/L, time = 30 minutes, T = 298 K, agitation speed = 150 rpm, dose of biosorbent = 2 g/100 mL, and pH = 2–8).

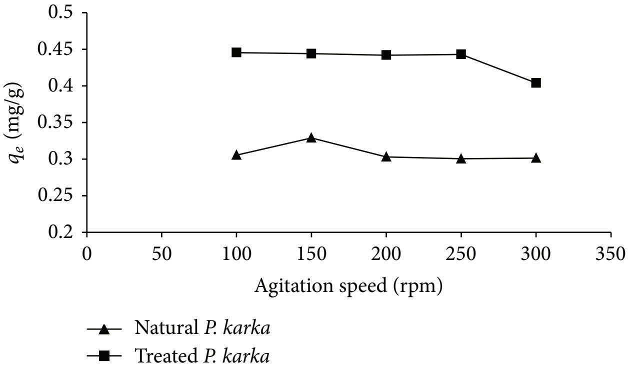


Figure 4: Effect of agitation speed on adsorption capacity of natural *P. karka* and treated *P. karka* (concentration = 10 mg/L, time = 30 minutes, T = 298 K, agitation speed = 100–300 rpm, dose of biosorbent = 2 g/100 mL, and pH = 6 and 7 for natural *P. karka* and treated *p. karka*, resp.).

with many previous researchers who have reported optimum biosorption of mercury by different biomasses at pH 6 or near values [17, 30–32]. An increase in biosorption levels with increasing pH can also be explained by relating the biosorption to the number of available negative charges on the surfaces. Beyond optimum pH values, decrease in adsorption capacities was observed. This is because at high pH, solution has excess number of OH^- ions, which enhance the probability of salt or hydroxide formation with metal ions in the solution. In case of alkali and alkaline earth metal ions, this probability can be ignored as their hydroxides are soluble but for heavy metal ions like mercury and so forth, it contributes significantly. Hence, there is a decrease in metal removal efficiency (Figure 2).

In point of zero charge, pH_{pzc} represents the pH where adsorbent surface becomes electrically neutral. Above the pH_{pzc} value, surface of biosorbent acquired negative charge, whereas below the pH_{pzc} point surface acquired positive charge. Hence, cationic biosorption will be favorable above the pH_{pzc} point and anionic biosorption will be optimum below the pH_{pzc} point. pH_{pzc} was determined for the biosorption of mercury ions on the natural *P. karka* and treated *P. karka* using the method described in [28, 33], Figure 2. The values of pH_{pzc} were found at 4.5 and 5 for natural *P. karka* and treated *P. karka*, respectively (Figure 3). The results are in agreement with the pH values obtained for the same experiment showing maximum biosorption at pH 6 and 7 for natural *P. karka* and treated *P. karka*, respectively (above pH_{pzc} values, adsorption of mercury ions is cationic adsorption, Figure 3).

3.3. Effect of Agitation Speed on Biosorption. Shaking speed is important in biosorption process because it increases the chances of interaction between metal ions and biomass. Adsorption increases with increase in shaking speed. At slow speed, biosorbent settles down and buries many active sites under its top layers. So, only top layer takes part in adsorption process because the under buried layers do not have contact with metal ions. Figure 4 indicates that maximum adsorption of Hg(II) ions for natural *P. karka* was 0.329 mg g^{-1} (65.8%) at 150 rpm, while for treated *P. karka* maximum adsorption of Hg(II) attained was 0.446 mg g^{-1} (89.1%) at 100 rpm. Treated *P. karka* has 23.3% more biosorptive removal capacity than natural *P. karka*. A decrease in adsorption was observed by further increase in shaking speed because at high agitation speed, random collisions between particles (adsorbate-adsorbate, adsorbent-adsorbate, and adsorbent-adsorbent) do not provide enough time to heavy metal ions to bind with surface of the biosorbent [33]. Moreover, increase in biosorption capacity in treated biosorbent is due to the addition of some functional groups, which cause increase in the binding capacity of the material.

3.4. Effect of Dose on Biosorption. The effect of biosorbent dose on biosorption efficiency for Hg(II) ions was investigated. As shown in Figure 5, the maximum metal uptake was found to be 0.107 mg/g (89.3%) for natural biomass at concentration of 1 g/100 mL and for treated biomass was 0.398 mg/g (93.2%) at 1 g/100 mL. The uptake capacities decreased at higher dosages. The above facts can be illustrated as a

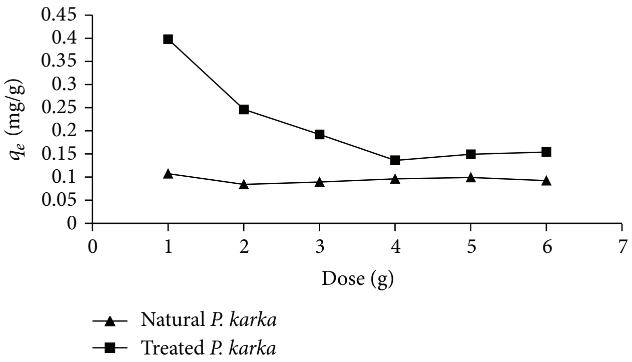


Figure 5: Effect of biosorbent dose on adsorption capacity of natural *P. karka* and treated *P. karka* (concentration = 10 mg/L, time = 30 minutes, $T = 298$ K, agitation speed = 150 and 100 rpm natural *P. karka* and treated *p. karka* resp., dose of biosorbent = 1–6 g/100 mL, and pH = 6 and 7 for natural *P. karka* and treated *p. karka*, resp.).

result of partial aggregation that occurs at high doses of biomass, resulting in decreasing the number of active sites on the surfaces of biomass [22, 23]. A further increase in biomass concentration over optimum dose does not lead to appreciable improvement in biosorptive metal removal due to the saturation of the adsorbent surface with metal ions and the establishment of equilibrium between the ions remaining nonadsorbed in the solution and which bound to the adsorbent.

3.5. Effect of Contact Time on Biosorption. Time of contact is also one of the most important parameters that helps to use biosorbent successfully in practical and the rapid biosorption application [27–32, 34, 35]. Time needed for metal sorption helps to determine the amount of solutions that can be treated and impacts on the process selection and its design [26]. Figure 6 indicates the biosorption capacity of natural *P. karka* and treated *P. karka* versus time for Hg(II) ions removal from aqueous solution. The maximum sorption capacity of Hg(II) was attained in first 20 min for both natural *P. karka* and treated *P. karka*. After that, there was slight increase in sorption with time and sorption equilibrium was reached in 50 min (0.4365 mg g^{-1}, 87.3%) and 40 min (0.4545 mg g^{-1}, 90.9%) for natural *P. karka* and treated *P. karka*, respectively. Most of the mercury ions sorption was attained in first 20 min that may be due to availability of more sorption sites in the beginning of experiment. Initially, with increase in time, metal ions find more adsorption/binding sites; hence, metal adsorption amount of metal ions increased. The maximum amount of metal ions adsorbed at 50 min and system reached equilibrium. At equilibrium state, maximum adsorption of metal ions illustrated the covering of maximum binding sites with metal ions. Hence, rate of adsorption may decrease to a constant value with further increase in time as in case of natural *P. karka* which is due to complete coverage of active sites to the surface of biosorbent and increase in rate of desorption with respect to time as well, which is in agreement with some previous researches on different biosorbents [3–5, 27–32, 34].

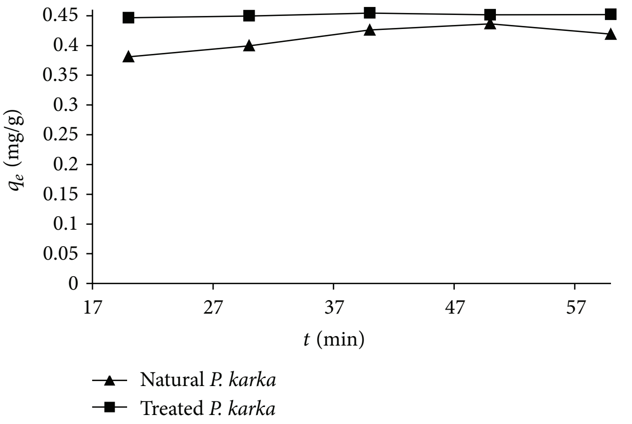


Figure 6: Effect of contact time on adsorption capacity of natural *P. karka* and treated *P. karka* (concentration = 10 mg/L, time = 20–60 minutes, $T = 298$ K, agitation speed = 150 and 100 rpm natural *P. karka* and treated *p. karka*, resp., dose of biosorbent = 1 g/100 mL, and pH = 6 and 7 for natural *P. karka* and treated *p. karka*, resp.).

3.6. Kinetic Studies of Adsorption. Rate of metal uptake by a particular adsorbent is calculated from kinetic studies and it is important for design of biosorption process [36]. Comparison of calculated and experimental uptake (q_e) data and shape of graph helps to find which model fits best to the biosorption process. Moreover, value of coefficient of determination (R^2) above 0.98 is an indication of model suitability [37]. The pseudo-first-order (Lagergren kinetic model) describes sorption of solid or liquid systems based on solid capacity:

$$\frac{\Delta q_t}{\Delta t} = K_1 \left(q_e - q_t\right), \tag{2}$$

where q_t and q_e (mg/g) are adsorption capacities at time t and at equilibrium, respectively, and k_1 is the first-order rate constant (min^{-1}). Linear form of pseudo-first-order kinetics model is written by the following equations:

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t. \tag{3}$$

Consider pseudo-second-order rate kinetics by

$$\frac{\Delta q_t}{\Delta t} = K_2 \left(q_e - q_t\right)^2, \tag{4}$$

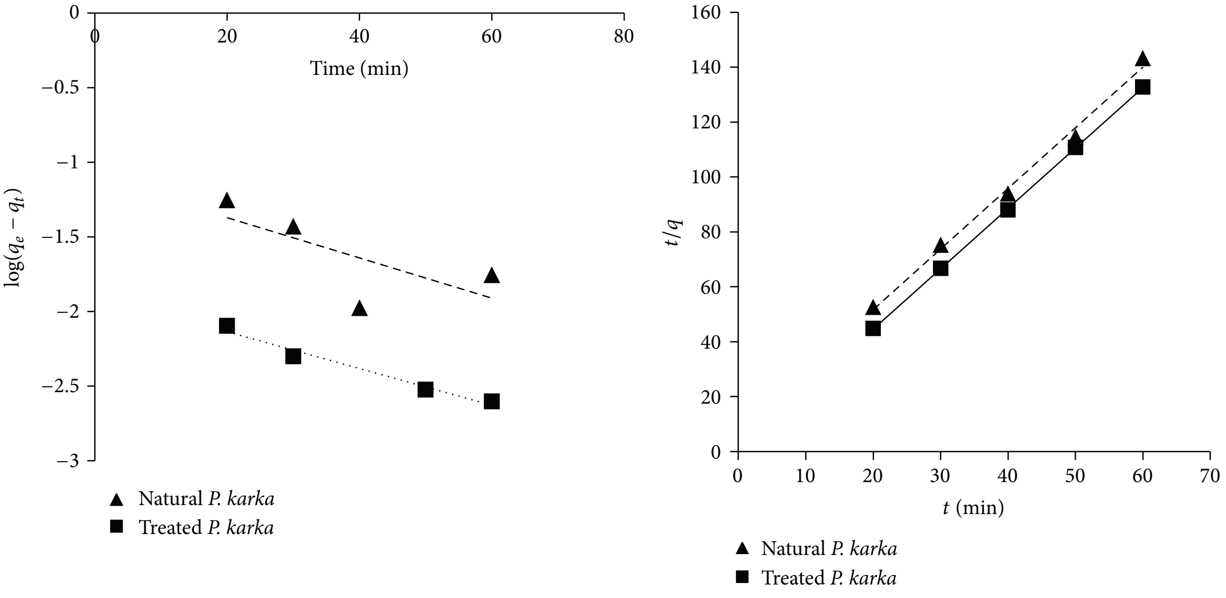
where k_2 is constant for second-order rate (mg g^{-1} min^{-1}). Its linear form is written by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e}. \tag{5}$$

The rate-controlling mechanism may be varying during the adsorption process. There are three possible mechanisms that may be cropping up. Diffusion process or mass transfer through external surfaces controls the early stage of this process. Then there is a reaction or a stage of constant rate and then it finally reached diffusion stage after that biosorption process slows down significantly [12]. Data shows R^2 values

TABLE 1: Parameters of pseudo-first-order and pseudo-second-order kinetic models for the biosorption of mercury ions on the surface of natural *P. karka* and treated *P. karka*.

Biosorbent type	q_{exp} (mg/g)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
		q_{cal} (mg/g)	k_1 (min^{-1})	R^2	q_{cal} (mg/g)	k_2 ($\mathrm{g\,mg^{-1}\,min^{-1}}$)	R^2
Natural *P. karka*	0.436	0.079	−0.0308	0.502	0.453	0.65	0.994
Treated *P. karka*	0.454	0.013	−0.0283	0.972	0.456	7.47	0.999



(a)

(b)

FIGURE 7: (a) Pseudo-first-order rate kinetics of Hg(II) for natural *P. karka* and treated *P. karka*. (b) Pseudo-second-order rate kinetics of Hg(II) for natural *P. karka* and treated *P. karka* (concentration = 10 mg/L, time = 20–60 minutes, $T = 298$ K, agitation speed = 150 and 100 rpm natural *P. karka* and treated *p. karka*, resp., dose of biosorbent = 1 g/100 mL, and pH = 6 and 7 for natural *P. karka* and treated *p. karka*, resp.).

for pseudo-first-order as 0.502 and 0.972, while for pseudo-second-order, R^2 values are 0.994 and 0.999 for natural *P. karka* and treated *P. karka*, respectively (Table 1). So, for pseudo-second-order kinetic values of R^2 for both natural *p. karka* and treated *P. karka* are in agreement as $R^2 > 0.98$. The experimental metal uptake values are also much closer to the values calculated from pseudo-second-order model. Hence, the pseudo-first-order kinetics is more deviated from experimental values as compared to pseudo-second-order kinetics. These results revealed that the pseudo-second-order mechanism is overpowering and chemisorption might be the rate-limiting step that controls the biosorption process [38, 39]. The plots of pseudo-first-order and pseudo-second-order kinetic models are shown in Figure 7.

3.7. Effect of Initial Concentration of Hg(II) on Biosorption. Factor of initial metal ion concentration is important for determining the types of effluents that can be treated with biosorbent. Figure 8 shows that metal uptake capacity of the biosorbent increased with increase in initial metal ion concentration while it decreased in percentage removal of metal ions for both natural *P. karka* and treated *P. karka*. Adsorption capacity (q_e) ranged from 0.439 and 0.449 mg of Hg(II)/g of biosorbent for initial concentration 10 ppm to 1.7685 and 2.169 mg of Hg(II)/g of biosorbent for initial concentration 60 ppm for natural and treated biosorbents, respectively. The results gave evidence of the great ability of material to remove mercury ions from solutions [40, 41].

3.8. Adsorption Study of Isotherms. Adsorption isotherms are important for developing an equation which is true representative of the adsorption data and help to design the adsorption process. Mostly Langmuir isotherm, Freundlich isotherm, and D-R model were applied to the data. According to Langmuir isotherm, monolayer adsorption occurs on a homogeneous surface of adsorbent and no interaction is found between adsorbed molecules on surface of sorbent [42]:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e}, \tag{6}$$

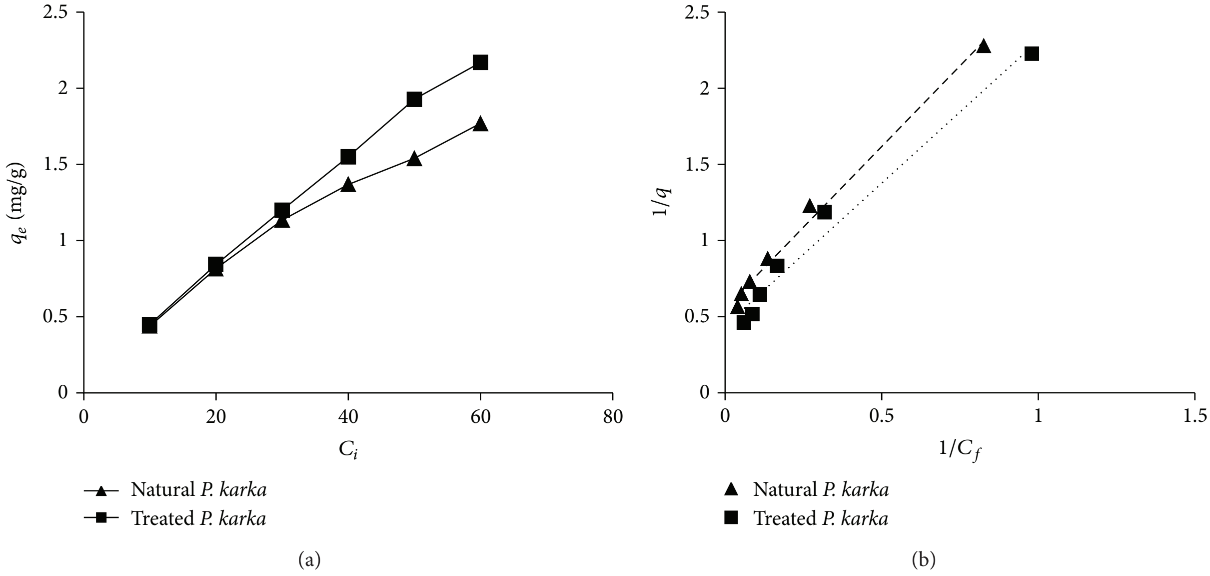


FIGURE 8: (a) Effect of initial metal ion concentration on adsorption capacity of natural *P. karka* and treated *P. karka*. (b) Langmuir adsorption isotherm for natural *P. karka* and treated *P. karka* (concentration = 10–60 mg/L, time = 50 and 40 minutes for natural *P. karka* and treated *p. karka* resp., $T = 298$ K, agitation speed = 150 and 100 rpm natural *P. karka* and treated *p. karka*, resp., dose of biosorbent = 1 g/100 mL, and pH = 6 and 7 for natural *P. karka* and treated *p. karka*, resp.).

where q_e (mg/g) is metal uptake capacity at equilibrium, $q_{\max}$ (mg/g) is maximum uptake capacity, b (L/mg) is Langmuir constant, and C_e (mg/L) is concentration of adsorbate at equilibrium. The linear form of the Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}}. \tag{7}$$

Feasibility and shape of Langmuir isotherm are calculated by following equation of equilibrium parameter [43]:

$$R_L = \frac{1}{1 + bC_e}. \tag{8}$$

Values of R_L show that Langmuir isotherm is not favorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$, and irreversible if $R_L = 0$ [44]. All values of R_L for natural *P. karka* and treated *P. karka* lie between 0 and 1, which means Langmuir isotherm is favourable for both types of biomass.

According to the Freundlich isotherm, adsorption is a multilayer process and occurs on heterogeneous surfaces [42] (10):

$$q_e = K_f {C_e}^{1/n}, \tag{9}$$

where k and $1/n$ are Freundlich constants. Linear form of Freundlich equation is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e. \tag{10}$$

Dubinin-Radushkevich model is used for estimation of porosity of the biomass and adsorption mechanism based on the potential theory assuming heterogeneous surface. The linear form of (D-R) isotherm model is

$$\ln q_e = \ln q_{\max} - \beta\epsilon^2, \tag{11}$$

where β is a constant representing the mean free energy of biosorption per mole of the biosorbate (mol^2/ kJ^2), $q_{\max}$ is the theoretical saturation capacity of biosorbent (mg g^{-1}), and ϵ is the Polanyi potential, which can be calculated by

$$\epsilon = RT \ln\left(1 + \frac{1}{C_e}\right), \tag{12}$$

where T (K) is the absolute temperature and R (J mol^{-1} K^{-1}) is the gas constant. Hence, by plotting $\ln q_e$ versus ϵ^2, it is possible to calculate the value of $q_{\max}$ from the intercept and the value of β by the slope. The plots of Langmuir, Freundlich, and D-R models are shown in Figures 8(b), 9(a), and 9(b), respectively. The biosorption mean free energy E_s (kJ/mol) is calculated as follows [45]:

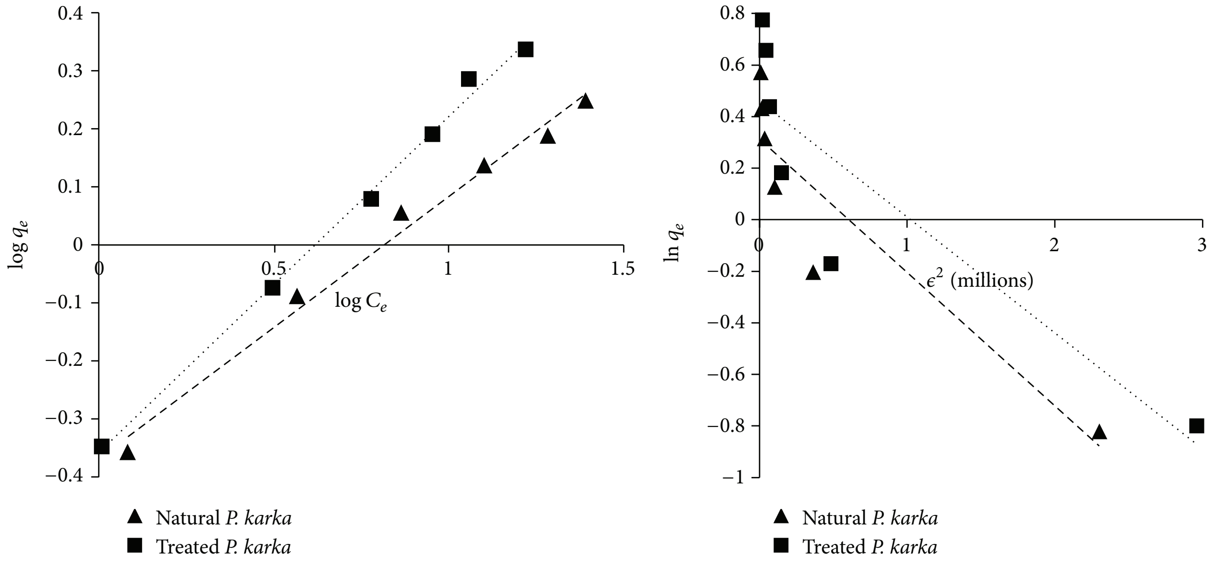
$$E_s = \frac{1}{\sqrt{2\beta}}. \tag{13}$$

Table 2 shows the different parameters calculated from Langmuir, Freundlich, and D-R equations for both natural *P. karka* and treated *P. karka* biomass. The values of $q_{\max}$ are calculated as 1.787 and 2.268 mg/g for natural *P. karka* and treated *P. karka*, respectively. The values of correlation factor (R^2) values for Langmuir isotherm are 0.978 and 0.991, which shows good fit of the model to both types of biosorbents. Hence, it shows homogeneous distribution of active sites on the surface of biosorbent [22–27]. The $q_{\max}$ value is greater than a number of reported materials (Table 4).

The slope and intercept of Freundlich model were used to calculate the constant indicative of relative adsorption capacity, k_f and factor n, and that indicative of adsorption intensity. The value of n tells about favorability of adsorption process. Adsorption is said to be better if n is in the range of 2–10,

Table 2: Langmuir isotherm, Freundlich isotherm, and D-R model parameters for the biosorption of mercury ions on the surface of natural *P. karka* and treated *P. karka*.

Biosorbent material	Langmuir isotherm	Freundlich isotherm	D-R (Dubinin-Radushkevich) model
Natural *P. karka*	$y = 2.1175x + 0.5594$ $R^2 = 0.978$ b (L/mg) = 0.264 $q_{\max}$ (mg/g) = 1.787 $R_L = (0.274\text{–}0.059)$	$y = 0.4506x - 0.3675$ $R^2 = 0.987$ $n = 2.219$ $K_f = 0.429$ $1/n = 0.451$	$y = -5E - 07x + 0.3135$ $R^2 = 0.8373$ q_m (mg/g) = 1.36 E_s (kJ/mol) = 1.00
Treated *P. karka*	$y = 1.8715x + 0.4409$ $R^2 = 0.991$ b (L/mg) = 0.235 $q_{\max}$ (mg/g) = 2.268 $R_L = (0.298\text{–}0.066)$	$y = 0.5784x - 0.3573$ $R^2 = 0.996$ $n = 1.729$ $K_f = 0.439$ $1/n = 0.578$	$y = -4E - 07x + 0.4599$ $R^2 = 0.7853$ q_m (mg/g) = 1.58 E_s (kJ/mol) = 1.118



(a) (b)

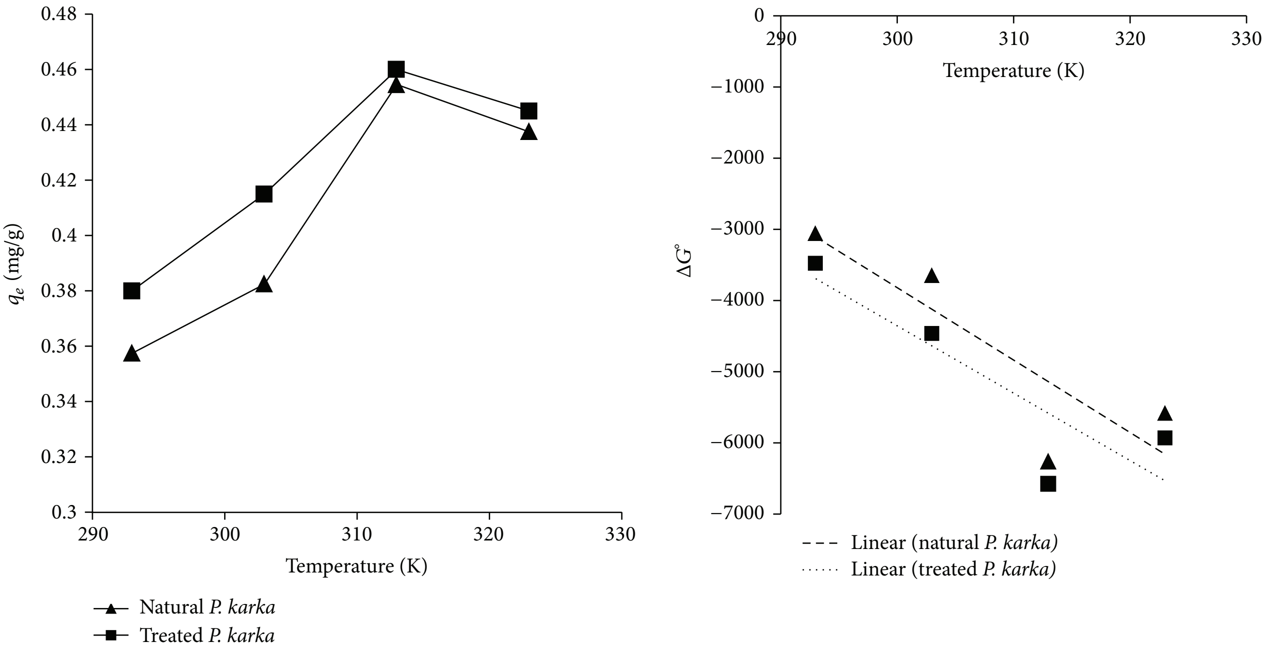
Figure 9: (a) Freundlich adsorption isotherm for natural *P. karka* and treated *P. karka*. (b) Dubinin-Radushkevish (D-R) model fornatural *P. karka* and treated *P. karka* (concentration = 10–60 mg/L, time = 50 and 40 minutes for natural *P. karka* and treated *p. karka*, resp., T = 298 K, agitation speed = 150 and 100 rpm natural *P. karka* and treated *p. karka*, resp., dose of biosorbent = 1 g/100 mL, and pH = 6 and 7 for natural *P. karka* and treated *p. karka*, resp.).

good if in range of 1-2, and average if below 1. Here natural and treated biosorbents have value of n, 2.219 and 1.729, respectively. This is an indication of better adsorption for natural biosorbent and good for treated biosorbent. The values of coefficient of approximation (R^2) were 0.991 and 0.996 for natural and treated biosorbents, respectively, that pointed out a good fit of Freundlich model [24, 27–29].

The slope and intercept of D-R model (Equation (12)) are used to calculate maximum adsorption capacity, and $q_{\max}$ (mg/g) was 1.36 mg/g and 1.58 mg/g, respectively, for natural *P. karka* and treated *P. karka*. These values are not comparable with experimental values. Moreover, the values of coefficient of approximation (R^2) are 0.8373 and 0.7853, respectively, for natural and treated biosorbents which indicate data is not fit to the D-R model for both types of biosorbents as compared to Langmuir and Freundlich isotherms. The values of adsorption energy are calculated to be 1.0 kJ/mol and 1.18 kJ/mol for natural and treated biosorbents, respectively. These values are below 8, which indicate physical nature of adsorption. Biosorption process may be chemisorption if $8 < E_s < 16$ and physisorption for $E_s < 8$ kJ/mol [27–32].

3.9. *Effect of Temperature on Adsorption of Hg(II).*

Study of temperature is an important parameter for all energy dependent mechanisms as in metal biosorption, which is mostly physicochemical in nature [31]. Economic suitability of any process is always based on energy efficient process.



(a)

(b)

FIGURE 10: (a) Effect of temperature on adsorption capacity of natural *P. karka* and treated *P. karka*. (b) Thermodynamics studies for natural *P. karka* and treated *P. karka* (concentration = 10 mg/L, time = 50 and 40 minutes for natural *P. karka* and treated *p. karka*, resp., T = 298–328 K, agitation speed = 150 and 100 rpm natural *P. karka* and treated *p. karka*, resp., dose of biosorbent = 1 g/100 mL, and pH = 6 and 7 for natural *P. karka* and treated *p. karka*, resp.).

Figure 10(a) shows effect of temperature on Hg(II) sorption capacity of natural *P. karka* and treated *P. karka* at a temperature range 293–323 K. Optimum removal capacity was obtained at 313 K for both types of biosorbents, that is, 0.4545 mg g^{-1} and 0.46 mg g^{-1}, respectively. Increase of temperature beyond optimum value, that is, 40°C, leads to a decreased in metal uptake.

3.10. Thermodynamics. Thermodynamics parameters of biosorption process are calculated by studying effect of temperature on the sorption process. Values of Gibbs free energy change (ΔG°), entropy change (ΔS°), and enthalpy change (ΔH°) change with temperature [46]. Gibbs free energy change is calculated to determine feasibility and spontaneity of the biosorption process by (12)

$$\Delta G^\circ = -RT \ln K_d, \tag{14}$$

where ΔG° (kJ/mol) is Gibbs free energy change, R is universal gas constant (8.3145 J/mol K), and K_d is equilibrium constant ($K_d = C_o - C_e/C_e$). The value of ΔH° (kJ/mol) gives information about the endothermic or exothermic nature of the process, while ΔS° (J/molK) indicates whether sorption process is ordered or random. Both parameters were calculated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \tag{15}$$

Energy and entropy factors are considered to determine which processes will occur spontaneously. Negative value of ΔG° indicates that the reaction is spontaneous. The linear plot between temperature and Gibb's free energy change (ΔG°) gives the enthalpy change (ΔH°) from intercept and entropy change (ΔS°) from slope of (13). The values of enthalpy change were found to be +26.688 and +24.034 kJ/mol and entropy change as +101.6 and +94.62 J/mol K, for natural *P. karka* and treated *P. karka*, respectively.

TABLE 3: Values of thermodynamic parameters for the biosorption of mercury ions on the surface of natural *P. karka* and treated *P. karka*.

Biosorbent type	Temperature (K)	ΔS ($\text{Jmol}^{-1}\,\text{K}^{-1}$)	ΔH (kJmol^{-1})	ΔG (kJmol^{-1})
Natural *P. karka*	293	+101.69	+26.688	−3.058
	303			−3.648
	313			−6.237
	323			−5.584
Treated *P. karka*	293	+94.62	+24.034	−3.476
	303			−4.464
	313			−6.573
	323			−5.927

Negative values of ΔG° indicate that sorption process of mercury is spontaneous and feasible for both natural biosorbent and treated biosorbent [47]. Increasing trend in feasibility of biosorption process is observed up to 40°C afterwards spontaneity and feasibility of process decreased by increasing temperature to 50°C. Positive values of ΔH°

Table 4: A comparison of mercury metal ions adsorbed by different biosorbents.

Serial number	Type of biosorbent	Amount of mercury ions absorbed	Reference
1	Spent rootlets	0.248 mmol/g	[48]
2	Saw dust	0.042 mmol/g	[49]
3	Bamboo pulp	0.046 mmol/g	[49]
4	Jute	0.038 mmol/g	[49]
5	Ground-up tree fern	0.132 mmol/g	[50]
6	Lemma minor	0.138 mmol/g	[16]
7	Garlic powder	0.650 mmol/g	[51]
8	Rasped pith sago residue	0.001 mmol/g	[52]
9	Natural *P. karka*	0.0089 mmol/g	Present study
10	Treated *P. karka*	0.113 mmol/g	Present study

indicate that reaction is endothermic while negative values of ΔS° means there is very less randomness in sorption process at solid/liquid interface (Table 3).

4. Conclusion

Current study on sorption and desorption behavior of natural *P. karka* and treated *P. karka* (Trin) indicates that its Hg(II) uptake capacity is 1.79 and 2.27 mg/g, respectively. Sorption process fits Langmuir and Freundlich models and follows pseudo-second-order rate kinetics. Thermodynamic studies show that the sorption process is spontaneous and endothermic. Studies indicate that *P. karaoke* can be used effectively for treatment of Hg(II) loaded effluents and treated absorbent effectively increases the metal sorption capacity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

[1] A. Zehra and M. A. Khan, "Comparative effect of NaCl and sea salt on germination of halophytic grass *Phragmites karka* at different temperature regimes," *Pakistan Journal of Botany*, vol. 39, no. 5, pp. 1681–1694, 2007.

[2] J.-Z. Chen, X.-C. Tao, J. Xu, T. Zhang, and Z.-L. Liu, "Biosorption of lead, cadmium and mercury by immobilized *Microcystis aeruginosa* in a column," *Process Biochemistry*, vol. 40, no. 12, pp. 3675–3679, 2005.

[3] M. Horsfall Jr. and A. I. Spiff, "Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wild cocoyam)," *African Journal of Biotechnology*, vol. 4, no. 2, pp. 191–196, 2005.

[4] J. C. Igwe and A. A. Abia, "Maize cob and husk as adsorbents for the removal of heavy metals from waste water," *The Physical Scientist*, vol. 2, no. 1, pp. 83–92, 2003.

[5] J. Plaza, M. Viera, E. Donati, and E. Guibal, "Biosorption of mercury by *Macrocystis pyrifera* and *Undaria pinnatifida*: influence of zinc, cadmium and nickel," *Journal of Environmental Sciences*, vol. 23, no. 11, pp. 1778–1786, 2011.

[6] S. W. Al Rmalli, A. A. Dahmani, M. M. Abuein, and A. A. Gleza, "Biosorption of mercury from aqueous solutions by powdered leaves of castor tree (*Ricinus communis* L.)," *Journal of Hazardous Materials*, vol. 152, no. 3, pp. 955–959, 2008.

[7] F. E. El-Nady and M. M. Atta, "Toxicity and bioaccumulation of heavy metals to some marine biota from the Egyptian coastal waters," *Journal of Environmental Science and Health, Part A*, vol. 31, no. 7, pp. 1529–1545, 1996.

[8] K. M. Paknikar, A. V. Pethkar, and P. R. Puranik, "Bioremediation of metalliferous wastes and products using inactivated microbial biomass," *Indian Journal of Biotechnology*, vol. 2, no. 3, pp. 426–443, 2003.

[9] B. Volesky, "Advances in biosorption of metals: selection of biomass types," *FEMS Microbiology Reviews*, vol. 14, no. 4, pp. 291–302, 1994.

[10] M. Tuzen, A. Sari, D. Mendil, and M. Soylak, "Biosorptive removal of mercury(II) from aqueous solution using lichen (*Xanthoparmelia conspersa*) biomass: kinetic and equilibrium studies," *Journal of Hazardous Materials*, vol. 169, no. 1–3, pp. 263–270, 2009.

[11] J. C. Igwe, E. C. Nwokennaya, and A. A. Abia, "The role of pH in heavy metal detoxification by biosorption from aqueous solutions containing chelating agents," *African Journal of Biotechnology*, vol. 4, no. 10, pp. 1109–1112, 2005.

[12] M. Tuzen, A. Sari, D. Mendil, and M. Soylak, "Biosorptive removal of mercury(II) from aqueous solution using lichen (*Xanthoparmelia conspersa*) biomass: kinetic and equilibrium studies," *Journal of Hazardous Materials*, vol. 169, no. 1–3, pp. 263–270, 2009.

[13] H. Yavuz, A. Denizli, H. Güngüneş, M. Safarikova, and I. Safarik, "Biosorption of mercury on magnetically modified yeast cells," *Separation and Purification Technology*, vol. 52, no. 2, pp. 253–260, 2006.

[14] I. B. Rae, S. W. Gibb, and S. Lu, "Biosorption of Hg from aqueous solutions by crab carapace," *Journal of Hazardous Materials*, vol. 164, no. 2-3, pp. 1601–1604, 2009.

[15] A. Sari and M. Tuzen, "Removal of mercury(II) from aqueous solution using moss (*Drepanocladus revolvens*) biomass: equilibrium, thermodynamic and kinetic studies," *Journal of Hazardous Materials*, vol. 171, no. 1–3, pp. 500–507, 2009.

[16] S.-X. Li, Z. Feng-Ying, H. Yang, and N. Jian-Cong, "Thorough removal of inorganic and organic mercury from aqueous solutions by adsorption on *Lemna minor* powder," *Journal of Hazardous Materials*, vol. 186, no. 1, pp. 423–429, 2011.

[17] Y. Kaçar, Ç. Arpa, S. Tan, A. Denizli, Ö. Genç, and M. Y. Arıca, "Biosorption of Hg(II) and Cd(II) from aqueous solutions: comparison of biosorptive capacity of alginate and immobilized

live and heat inactivated *Phanerochaete chrysosporium*," *Process Biochemistry*, vol. 37, no. 6, pp. 601–610, 2002.

[18] G. Bayramoğlu, I. Tuzun, G. Celik, M. Yilmaz, and M. Y. Arica, "Biosorption of mercury(II), cadmium(II) and lead(II) ions from aqueous system by microalgae *Chlamydomonas reinhardtii* immobilized in alginate beads," *International Journal of Mineral Processing*, vol. 81, no. 1, pp. 35–43, 2006.

[19] M. Y. Arıca, G. Bayramoğlu, M. Yılmaz, S. Bektas, and O. Genç, "Biosorption of Hg^{2+}, Cd^{2+}, and Zn^{2+} by Ca-alginate and immobilized wood-rotting fungus *Funalia trogii*," *Journal of Hazardous Materials*, vol. 109, no. 1–3, pp. 191–199, 2004.

[20] G. Bayramoglu and M. Y. Arıca, "Removal of heavy mercury(II), cadmium(II) and zinc(II) metal ions by live and heat inactivated *Lentinus edodes* pellets," *Chemical Engineering Journal*, vol. 143, no. 1–3, pp. 133–140, 2008.

[21] V. T. P. Vinod, R. B. Sashidhar, N. Sivaprasad et al., "Bioremediation of mercury (II) from aqueous solution by gum karaya (*Sterculia urens*): a natural hydrocolloid," *Desalination*, vol. 272, no. 1–3, pp. 270–277, 2011.

[22] U. Shafique, A. Ijaz, M. Salman et al., "Removal of arsenic from water using pine leaves," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 43, no. 2, pp. 256–263, 2012.

[23] Ö. Genç, Y. Yalçınkaya, E. Büyüktuncel, A. Denizli, M. Y. Arıca, and S. Bektaş, "Uranium recovery by immobilized and dried powdered biomass: characterization and comparison," *International Journal of Mineral Processing*, vol. 68, no. 1–4, pp. 93–107, 2003.

[24] E. W. Wilde and J. R. Benemann, "Bioremoval of heavy metals by the use of microalgae," *Biotechnology Advances*, vol. 11, no. 4, pp. 781–812, 1993.

[25] P. X. Sheng, Y. P. Ting, J. P. Chen, and L. Hong, "Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms," *Journal of Colloid and Interface Science*, vol. 275, no. 1, pp. 131–141, 2004.

[26] G. Bayramoğlu and M. Y. Arıca, "Ethylenediamine grafted poly(glycidylmethacrylate-co-methylmethacrylate) adsorbent for removal of chromate anions," *Separation and Purification Technology*, vol. 45, no. 3, pp. 192–199, 2005.

[27] J. Wase and C. F. Forster, *Biosorbents for Metal Ions*, Taylor & Francis, London, UK, 1995.

[28] M. F. Benedetti, C. J. Milne, D. G. Kinninburg, W. H. Van Riemsddijk, and L. K. Koopal, "Metal ion binding to humic substances: application of the non-ideal competitive adsorption model," *Environmental Science & Technology*, vol. 29, no. 2, pp. 446–457, 1995.

[29] E. Fourest and B. Volesky, "Alginate properties and heavy metal biosorption by marine algae," *Applied Biochemistry and Biotechnology*, vol. 67, no. 3, pp. 215–226, 1997.

[30] M. Amini, H. Younesi, N. Bahramifar et al., "Application of response surface methodology for optimization of lead biosorption in an aqueous solution by *Aspergillus niger*," *Journal of Hazardous Materials*, vol. 154, no. 1–3, pp. 694–702, 2008.

[31] B. S. Inbaraj and N. Sulochana, "Mercury adsorption on a carbon sorbent derived from fruit shell of *Terminalia catappa*," *Journal of Hazardous Materials*, vol. 133, no. 1–3, pp. 283–290, 2006.

[32] Y. Zeroual, A. Moutaouakkil, F. Z. Dzairi et al., "Biosorption of mercury from aqueous solution by Ulva lactuca biomass," *Bioresource Technology*, vol. 90, no. 3, pp. 349–351, 2003.

[33] N.-C. Feng and X.-Y. Guo, "Characterization of adsorptive capacity and mechanisms on adsorption of copper, lead and zinc by modified orange peel," *Transactions of Nonferrous Metals Society of China*, vol. 22, no. 5, pp. 1224–1231, 2012.

[34] S. Ilhan, C. F. Iscen, N. Caner, and I. Kiran, "Biosorption potential of dried Penicillium restrictum for Reactive Orange 122: isotherm, kinetic and thermodynamic studies," *Journal of Chemical Technology and Biotechnology*, vol. 83, no. 4, pp. 569–575, 2008.

[35] F. Kargi and S. Cikla, "Zinc (II) ion recovery by biosorption onto powdered waste sludge (PWS): effects of operating conditions," *Journal of Chemical Technology and Biotechnology*, vol. 81, no. 10, pp. 1661–1668, 2006.

[36] B. Volesky and Z. R. Holan, "Biosorption of heavy metals," *Biotechnology Progress*, vol. 11, no. 3, pp. 235–250, 1995.

[37] S. M. Al-Garni, "Biosorption of lead by Gram-ve capsulated and non-capsulated bacteria," *Water SA*, vol. 31, no. 3, pp. 345–350, 2005.

[38] S. J. Allen, Q. Gan, R. Matthews, and P. A. Johnson, "Kinetic modeling of the adsorption of basic dyes by kudzu," *Journal of Colloid and Interface Science*, vol. 286, no. 1, pp. 101–109, 2005.

[39] S. Tunali, T. Akar, A. S. Özcan, I. Kiran, and A. Özcan, "Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by *Cephalosporium aphidicola*," *Separation and Purification Technology*, vol. 47, no. 3, pp. 105–112, 2006.

[40] D. Karunasagar, J. Arunachalam, K. Rashmi, J. Naveena Lavanya Latha, and P. M. Mohan, "Biosorption of inorganic and methyl mercury by a biosorbent from *Aspergillus niger*," *World Journal of Microbiology and Biotechnology*, vol. 19, no. 3, pp. 291–295, 2003.

[41] C. Green-Ruiz, "Mercury(II) removal from aqueous solutions by nonviable *Bacillus* sp. from a tropical estuary," *Bioresource Technology*, vol. 97, no. 15, pp. 1907–1911, 2006.

[42] U. Farooq, J. A. Kozinski, M. A. Khan, and M. Athar, "Biosorption of heavy metal ions using wheat based biosorbents—a review of the recent literature," *Bioresource Technology*, vol. 101, no. 14, pp. 5043–5053, 2010.

[43] G. McKay, H. S. Blair, and J. R. Gardner, "Adsorption of dyes on chitin. I. Equilibrium studies," *Journal of Applied Polymer Science*, vol. 27, no. 8, pp. 3043–3057, 1982.

[44] K. R. Hall, L. C. Eagleton, A. Acrivos, and T. Vermeulen, "Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions," *Industrial and Engineering Chemistry Fundamentals*, vol. 5, no. 2, pp. 212–219, 1966.

[45] Y. Khambhaty, K. Mody, S. Basha, and B. Jha, "Pseudo-second-order kinetic models for the sorption of Hg(II) onto dead biomass of marine *Aspergillus niger*. Comparison of linear and non-linear methods," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 328, no. 1–3, pp. 40–43, 2008.

[46] S. Karthikeyan, R. Balasubramanian, and C. S. P. Iyer, "Evaluation of the marine algae *Ulva fasciata* and *Sargassum* sp. for the biosorption of Cu(II) from aqueous solutions," *Bioresource Technology*, vol. 98, no. 2, pp. 452–455, 2007.

[47] W. Zou, H. Bai, S. Gao, and K. Li, "Characterization of modified sawdust, kinetic and equilibrium study about methylene blue adsorption in batch mode," *Korean Journal of Chemical Engineering*, vol. 30, no. 1, pp. 111–122, 2013.

[48] Y. Zeroual, A. Moutaouakkil, F. Z. Dzairi et al., "Biosorption of mercury from aqueous solution by *Ulva lactuca* biomass," *Bioresource Technology*, vol. 90, no. 3, pp. 349–351, 2003.

[49] S. R. Shukla and V. D. Sakhardande, “Column studies on metal ion removal by dyed cellulosic materials,” *Journal of Applied Polymer Science*, vol. 44, no. 5, pp. 903–910, 1992.

[50] Y. S. Ho and C.-C. Wang, “Sorption equilibrium of mercury onto ground-up tree fern,” *Journal of Hazardous Materials*, vol. 156, no. 1–3, pp. 398–404, 2008.

[51] Y. Eom, J. H. Won, J.-Y. Ryu, and T. G. Lee, “Biosorption of mercury(II) ions from aqueous solution by garlic (*Allium sativum* L.) powder,” *Korean Journal of Chemical Engineering*, vol. 28, no. 6, pp. 1439–1443, 2011.

[52] N. Saman, K. Johari, S. S. Tien, and H. Mat, “Removal of Hg(II) and $CH_3Hg(I)$ using rasped pith sago residue biosorbent,” *CLEAN—Soil, Air, Water*, vol. 42, no. 11, pp. 1541–1548, 2014.


International Journal of Medicinal Chemistry
Organic Chemistry International
International Journal of Photoenergy
International Journal of Analytical Chemistry
Advances in Physical Chemistry
International Journal of Carbohydrate Chemistry
Journal of Quantum Chemistry
The Scientific World Journal
Journal of Analytical Methods in Chemistry
Journal of Spectroscopy
International Journal of Inorganic Chemistry
International Journal of Electrochemistry
Journal of Applied Chemistry
Bioinorganic Chemistry and Applications
Journal of Theoretical Chemistry
Chromatography Research International
Journal of Catalysts
Journal of Chemistry
International Journal of Spectroscopy