



Research article

Biosorption of Hg (II) from aqueous solution using algal biomass: kinetics and isotherm studies

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ABSTRACT

The present work investigated the ability of algal biomass *Chlorella vulgaris* to remove mercury from aqueous solutions. The mercury biosorption process was studied through batch experiments 35 °C temperature with regard to the influence of contact time, initial mercury concentration, pH and desorption. The maximum adsorption capacity was registered at pH 6. The adsorption conduct of Hg(II) was defined by pseudo second order well rather pseudo first order as the experimental data (q_e) come to an agreement with the calculated value. The kinetics of adsorption was fast and a high capacity of adsorption occurred within only 90 min. The adsorption data were signified by many models but Langmuir ($q_{max} = 42. \text{ mg g}^{-1}$) & Freundlich fitted well having regression coefficients near to unity. The thermodynamic parameters were also suited well as negative value of free energy cope up to spontaneity, positive value of the randomness described by ΔS attributed to affinity of Hg^{+2} towards algal bioadsorbant and high positive value of heat of enthalpy designates that the adsorption process is expected due to robust interactions between the Hg(II) ions and various functional groups on surface of algal bioadsorbant. Field emission scanning electron microscopy integrated with energy dispersive X-ray spectroscopy analysis before and after adsorption of Hg(II) reveals the adsorption of metallic ions over the surface. FTIR study supported the existence of various functional groups (carboxylic, amines, hydroxyls, amides etc.) helped in adsorption. Continuous adsorption desorption experiments proved that algal cells was excellent biosorbents with potential for further development.

1. Introduction

Heavy metals are natural elements of the earth but negatively affect aquatic life as well as human beings if found more than a permissible limits (Sathe et al., 2020; Souri et al., 2019; Goswami et al., 2019a, b; Areco et al., 2012). They enter in plant, animals and human through inhalation and aqueous media. Industrial operations like mining, metallurgy, electroplating etc. are responsible to discharge these toxic metals extensively in aqueous medium and industrial effluents (Kushwaha et al., 2018, 2017; Bind et al., 2018; Liu et al., 2009). Heavy metals like cobalt (Co), chromium (Cr), cadmium (Cd), mercury (Hg) and lead (Pb) are known to be toxic on the ecosystem by accumulating in food chain at various tropic levels (Kushwaha et al., 2019, 2015; Hatamian et al., 2019; Souri et al., 2018). These elements are non biodegradable and once enter in our body they neither degrade nor destroyed, cause serious threat to our life (Goswami et al., 2018a; b; Kumar et al., 2016). EPA (Environmental Protection Agency) find mercury as highly threatening metal due to

its perpetual and bioaccumulating nature in the ecosystem. It is third most toxic metal decalored by International agency of 21st century. The elemental form of mercury (Hg) affect living system by its transport routes whereas the most toxic form is oxidized Hg (II) which binds to the cysteinein proteins causing mercury poisoning affecting neural system, cardiovascular system, bones and nephrons of the body (USEPA, 1997). LED's, CFL, thermometer, measuring, wiring and control devices, paper and pulp industry, oil refining and battery manufacturing industries are important sources of mercury pollution. Bureau of Indian standards set mercury permissible limit in drinking water as $1 \mu\text{g L}^{-1}$ (BIS, 2005).

The accumulation of the heavy metals in food chain demands attention to develop the sustainable techniques for its effective remove from the industrial effluents. Several techniques viz. adsorption, coagulation, advanced oxidation and membrane separation have been used for the removal of heavy metals from the aqueous system (Alyüz and Veli, 2009). Among these methods biosorption is the best and economical method as

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biosorbents are low cost materials, easily available and highly efficient (Barakat, 2011).

Extensive research are going on treating pollutants from liquid medium by various adsorbant viz., microorganisms (bacteria, fungi, algae), industrial wastes, lignocellulosic materials, biopolymers and nano-adsorbants etc. (Goswami et al., 2017a, b; Fu and Wang, 2011). Few of the well-known utilized adsorbents particularly for heavy metals contaminated wastewater are chitosans, nanoadsorbents, barks, wastes from olive oil industry, coconut based materials, agricultural peels, zeolites, clay soils and betonites and vermiculites (Wuana and Okieimen, 2011). Researchers have been recently published their work with primary goal of removal of toxic heavy metals from industrial effluents using adsorbent materials.

Algae have been widely studied for heavy metal removal because of their global occurrence. A number of microalgal strains (*Chlorella vulgaris*, *Chlorella fuscas*, *Spirogyra species*, *Spirulina sp.*, which are potentially suitable for heavy metals removal in aqueous solution, were used in several studies and showed varying removal efficiencies (Bailey et al., 1999). *Chlorella vulgaris* has recently gained greater attention for the treatment of heavy metal contamination in aqueous solutions. *Chlorella vulgaris* is a chlorophyll containing organism, autotrophic in nature size vary from microscopic to giant macroscopic play a significant role in food chain and in maintaining the oxygen supply on our planet, and can easily grow anywhere (Yadav et al., 2013). Many researchers have reported that algal cells and may have a very high capacity for binding with metals due to the presence of polysaccharides, proteins, or lipids on the surface of cell walls, possessing the functional groups viz. aminos, hydroxyls, carboxyls and sulfhydryl, which can act as binding sites for metals (Kumar et al., 2019; Soury and Hatamian, 2019).

The aim of this work is to study the ability of *Chlorella vulgaris* to remove mercury from aqueous solutions. It identifies the functional groups involved in the interaction between algae and metal (Hg (II)). The purpose of this study is to develop a low cost adsorbent for treatment of toxic heavy metal (Hg) from industrial effluents. Algal biomass (*Chlorella vulgaris*) as a potential bioadsorbant was characterized by FTIR (Fourier transform infrared spectroscopy) for various functional groups, SEM (Scanning electron microscope) equipped with EDX (Energy dispersive spectroscopy) for morphological characters and elemental analysis along with physical, chemical and thermal parameters. The effects of several operating parameters such as pH, initial Hg (II) ion concentration, contact time, and adsorbent dosage were investigated in batch system. Adsorption isotherms and different kinetic models were examined to correlate the experimental data. The results of this work would contribute to a better understanding of the metal uptake by *Chlorella vulgaris* and can be beneficial in the development of potential biosorbents with high capacity for heavy-metal (mercury) uptake from aqueous environment. Investigation study of regeneration also have performed.

2. Materials and methods

2.1. Materials

All the chemicals and reagents used were procured from Merck (Mumbai, India). A stock solution (1000 ppm) of Hg (II) was prepared by dissolving approximately 1.35 g of mercury (II) chloride in 1.0 L of Milli-Q deionized water. Aqueous solutions of various concentrations were prepared from HgCl₂ and used as a source for Hg (II). The solutions were then diluted to the desired concentrations and analyzed.

2.2. Microalgae strain

The microalga *Chlorella vulgaris* UTEX 2714 was used for this study. The strain was obtained through the Culture Collection of Algae of IARI New Delhi and was revived in 10 ml Fog's Medium suitable for *Chlorella vulgaris*.

2.3. Preparation of adsorbent biomass

The algal biomass was deactivated by heating in an autoclave at 121 °C for 10 min (Gupta et al., 2015). Biomass was then harvested by filtering the cultured medium through cellulose nitrate Whatman membrane filters with pore size of 45 µm, and washed with deionized water. The biomass was then sun dried for 3 days, followed by oven drying at 55 °C for 24 h, and ground in a stone mortar pestle to get uniform particle size. The sieved material (195-148, 148-132, and 132-98 µm) was stored in air tight container for further use.

2.4. Adsorption experiments

Adsorption experiments were conducted at various solutions pH (1-8), dose (0.5–2.0 g), contact time (10 - 120 min) and initial concentration (10-200 mg/L) under batch mode. The solution pH was maintained using 0.1 M NaOH and 0.1 M H₂SO₄ before adsorption experiment using Labman digital pH meter (LBPH-10, India). Adsorption experiment were performed in 250 ml volumetric flask using 100 ml Hg (II) solution at room temperature i.e., 35 °C. The equilibrium time was maintained at 90 min in a rotary incubator at an agitation speed of 120 rpm. After completing the experiment the bioadsorbent was filtered and analyzed by spectrophotometric method using 2-Acetylpyridine thiosemicarbazone (APT) (Admasu et al., 2016). Double beam spectrophotometer (2375, Electronics India, India) was used for absorbance measurement. Experiments were carried out in triplicate and for data analysis, mean values were used.

The mercury (Hg⁺²) adsorbed by the adsorbent was calculate using the equations (Supplementary file).

2.5. Elemental analysis

The elemental compositions of the algal bioadsorbant were examined by ELTRA AD 2400 elemental analyzer, Germany. The percentage (%) of carbon (C), Hydrogen (H), Nitrogen (N) and oxygen (O) in the sample was determined accordingly.

2.6. Total ash content, density and surface area analysis of algal bioadsorbant

The ash content was determined by putting the algal bioadsorbant in the muffle furnace at 500 °C for 10 h. The Bulk density (weight per unit volume of algal bioadsorbant) was calculated by filling known weight of algal adsorbant in the calibrated glass cylinder. To determine surface area measurements, Brunauer-Emmet-Teller (BET) analysis was performed using BET surface analyzer (Horiba scientific SA-9600 series) (Goswami et al., 2019c).

2.7. FTIR and SEM analyses

To examine the functional groups of virgin algal bioadsorbant and Hg(II) loaded algal bioadsorbant were further recorded by using Fourier transform infrared (FTIR) spectrophotometer (Bruker Tensor 27, Germany) in the range of 400–4000 cm⁻¹. The morphological examination of algal bioadsorbant was performed by scanning electron (SEM) microscope (Zeiss, Sigma VP, Germany).

2.8. Desorption studies of algal bioadsorbant

Recycling of algal bioadsorbant is necessary to make the bioadsorbant industrially feasible. Repeated sorption-desorption experiments were carried out using the same bioadsorbant to examine the extent of sorption. It was studied in batch system in which algae (1 g) loaded with mercury (100 ppm) were employed in desorption medium of 100 ml in 150 ml conical flask for one hour at 35 °C and was stirred at 120 rpm. All glasswares were dunked in 0.1 N HNO₃ and cleaned with water to

Table 1. Percentage of Major Elements in powered form of algal bioadsorbant.

Element	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
Percentage	48.94	7.89	5.76	.93	36.93

remove metal salt residue if any for highly sensitive experiments with metals. Desorption ratio was calculated as:

$$\text{Desorption ratio} = \left(\frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \right) \times 100$$

3. Results and discussion

3.1. Characterization of the algal bioadsorbant

3.1.1. BET surface area and elemental analyses

The accessibility of surface of organic materials is a key factor in heavy metal adsorption. The mean surface area of algal bioadsorbant was analysed $12.03 \text{ m}^2 \text{ g}^{-1}$ which is far better than many bioadsorbant recorded in the studies till now. It has good porosity of surface, pore structure, pore volume (0.197 cc g^{-1}), pore size ($107\text{--}186 \text{ \AA}$). These

factors provide significant insight for adsorption of Hg (II) over algal bioadsorbant. The ionic radii of Hg (II) in the present study was 0.3 \AA , very much suits the adsorption process with mean pore size (147 \AA) of algal adsorbant.

The major elements (Carbon (C): Hydrogen (H): Nitrogen (N): Sulphur (S): Oxygen (O)) in the powered algal bioadsorbant by percentage basis were presented in Table 1. The percentage of important contributed elements showed the various type of functional groups present on the algal bioadsorbant surface viz: carboxyl, amines, alcohol, phenol etc. responsible for Hg (II) adsorption.

3.1.2. Scanning electron microscopy

The surface morphology of plain algal and mercury loaded algal biomass and image with EDX graph was showing in (Figure 1 (a) & (b)) and (Figure 2), respectively. Presence of heterogeneous pores structure, its previous structures with rough cavities which are essential for prospective adsorbent were seen in unloaded SEM (Figure 1(a)) micrograph (Manikandan et al., 2016; Yadav et al., 2015). Loaded particles (Figure 1 (b)) are visually assume throughout the image with close, compact and smoother structure due to hostage of Hg (II). Emergence of new peak of Hg (II) along with peaks of virgin biomass in the EDX graph (Figure 2) confirm the presence of metal ions Hg (II). EDS layered and

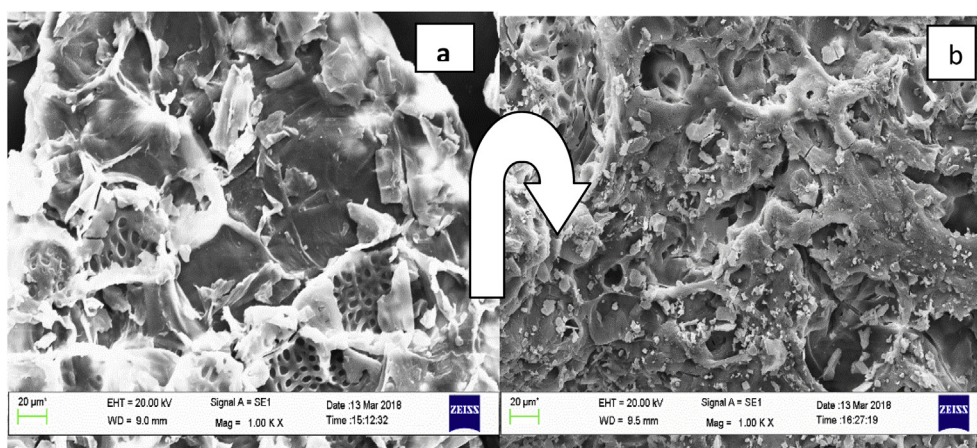


Figure 1. SEM micrographs of (a) Raw algal biomass and (b) Mercury loaded biomass.

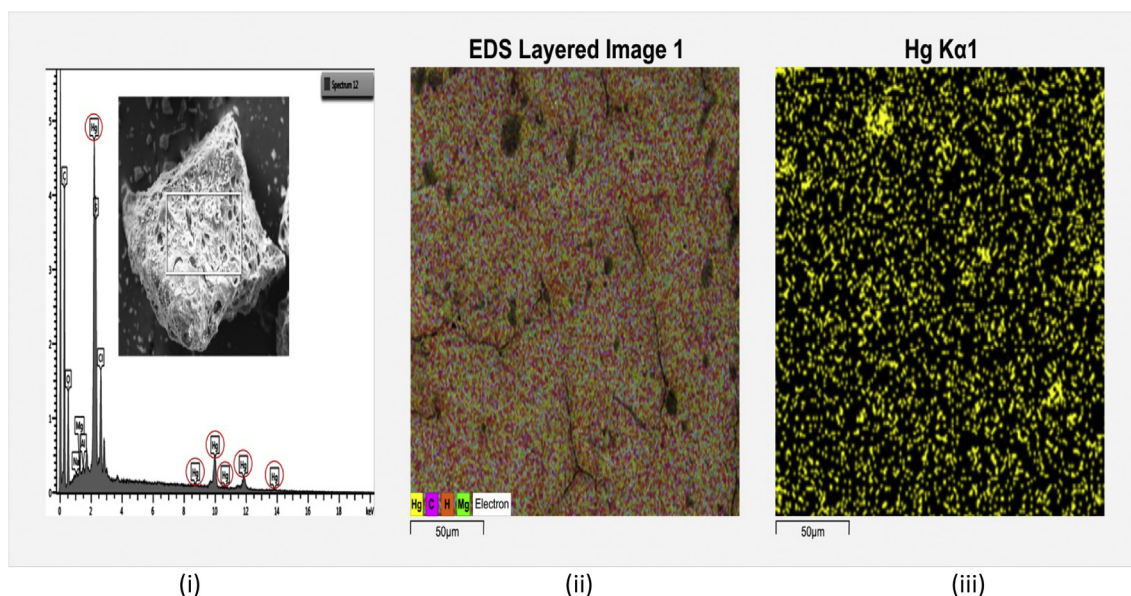


Figure 2. EDX graph and mapping of Hg(II) adsorbed algal biomass; (i) EDX spectra of the Hg-loaded biomass, (ii) elemental mapping of the biomass and (iii) Hg-mapping on to the adsorbed biomass.

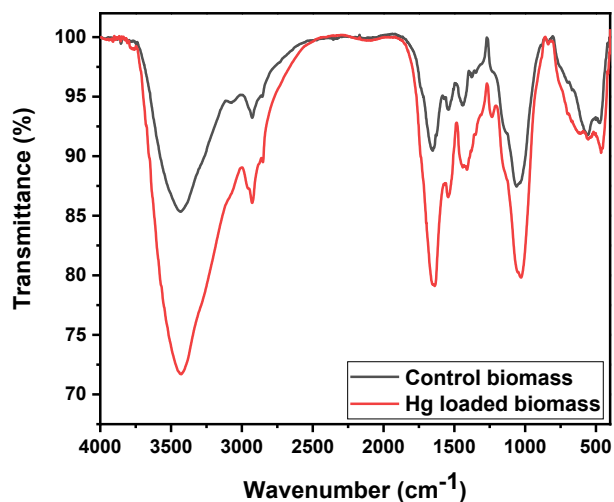


Figure 3. FTIR spectra of *Chlorella* biomass & Hg(II) loaded biomass.

compositional images showed the presence of Hg (II) along with other elements validate the adsorption of metal ions strongly.

3.1.3. FTIR analysis

Different types of vibrational frequencies because of different functional groups were shown in FTIR spectra of the algal bioadsorbant and is presented in Figure 3. The strong, extended (2934 cm^{-1}) and broad adsorption peak belong to N-H stretching and bending vibrations (Goswami et al., 2017c). The alcohol group (-OH) also come in this range. The stretched peak seen to be shifted in loaded biomass compared to unloaded algal biomass (Gupta et al., 2014). The peak at 1614.8 cm^{-1} attributed to (C=O) carbonyl group shifted to 1770 cm^{-1} . Larger shifting clarify the strong bonding of metal ions (Hg(II)) to the algal surface. The shifting of band from 1498 cm^{-1} to 1400 cm^{-1} corresponds to -CH stretching vibrations (Bhasney et al., 2019). The peak at 1210.10 cm^{-1} attributed to -SO₃ with stretching of aliphatic amines (C-N) (Plazinski et al., 2009).

3.2. Effect of various process parameters on adsorption of Hg (II) on algal bioadsorbant

3.2.1. Role of pH on adsorption of Hg (II) on algal bioadsorbant

The effect of pH on Hg (II) removal was examined by batch sorption studies. The study was performed using algal biomass at the initial concentration was $100\text{ }\mu\text{g/L}$, biomass dose of 1 g and contact time of 120

min. Hydrogen ion concentration plays important task in affecting the adsorption of heavy metals over adsorbant because it itself compete to the metal ions while adsorption. Degree of ionization of H⁺ and surface charge ratio of adsorbant affect the binding of metal ions (Mason et al., 1996). It is evidenced from Figure 4 that Hg (II) adsorption was maximum at pH 6, study was conducted between pH 3 to 8. The inference of this result suggested that at lower pH (<6) hydrogen ion concentrations were busy with the negative ligands of the adsorbant causing low adsorption as less number of vacant sites were available for heavy metal ions (Gupta et al., 2011). pH around 6 facilitate deprotonation of negative ligands which created vacant sites to promote adsorption. Thus, in further experiments the initial pH was maintained at pH 6. This study is similar to the work reported earlier by Gupta et al. (2011). Efforts were not taken to maintain the pH during the course of the experiment.

3.2.2. Role of adsorbant dosage on adsorption of Hg(II) on algal bioadsorbant

Increase of percentage removal of Hg (II) was seen with increasing adsorbant dose. Sharp increase in removal of Hg (II) was observed when we increased the algal adsorbant dose from 0.5 g to 1.5 g and beyond 2 g of adsorbant dose, no significant percentage removal was observed in Figure 5 (a) that probably because of increase in adsorbant dose, provide large number of available active sites at the surface of algal bioadsorbant which recognized as various functional groups leads to adsorption of Hg (II) ions. However further increase in adsorbant dose does not affect the sorption due to constant initial concentration. It was noticed that the adsorption capacity (q_e) which attributed amount of metal adsorbed per unit of mass of the adsorbent (mg/g) decreases with increase in adsorbant dose because the fixed initial metal ion concentration do not meets need to extend over all the available sites on the adsorbant (Wilde and Benemann, 1993).

3.2.3. Role of contact time on adsorption of Hg(II) on algal bioadsorbant

The effect of contact time for the adsorption of Hg (II), onto algal biomass was investigated. Initially, the amount of heavy metal ions adsorbed rapidly within one hour due to presence of extended surface area. After this adsorption followed with constant rate, reached equilibrium at 90 min for Hg (II) on to algal biomass (Figure 5b). Fast adsorption rate followed by slower rate and then equilibrium is characteristic results obtained by most of studies (Veglio and Beolchini, 1997). The rate of adsorption of heavy metal occurred from outer side of the adsorbant to inner side of the adsorbant and in that event became insignificant afterwards (Kapoor and Viraraghavan, 1998). The curve having plateau portion relates to pore diffusion and the linear portion of the curve reveals surface layer diffusion (Saifuddin and Kumaran, 2005) Equilibrium stage attributed saturation of vacant sites. Thus, all the experiments were carried out at 90 min equilibration time.

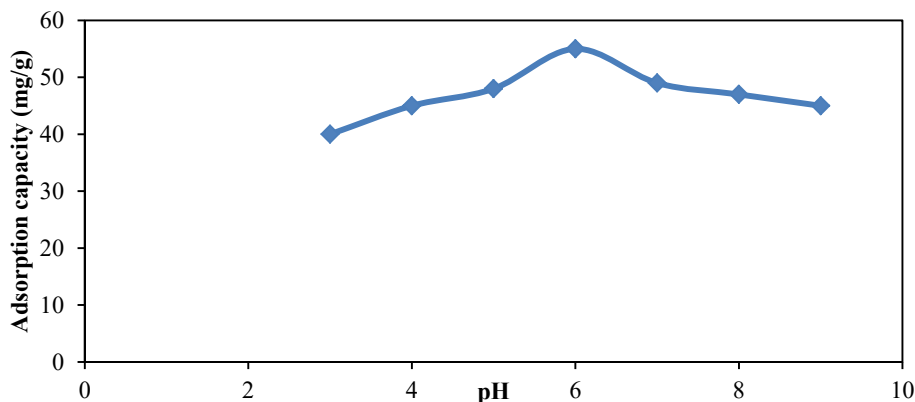


Figure 4. Effect of pH on adsorption study of Hg(II) ions on algal bioadsorbant: pH = 6, $C_i = 100\text{ }\mu\text{g/L}$, dose = 1 g/L , contact time = 2 h at $35\text{ }^\circ\text{C}$.

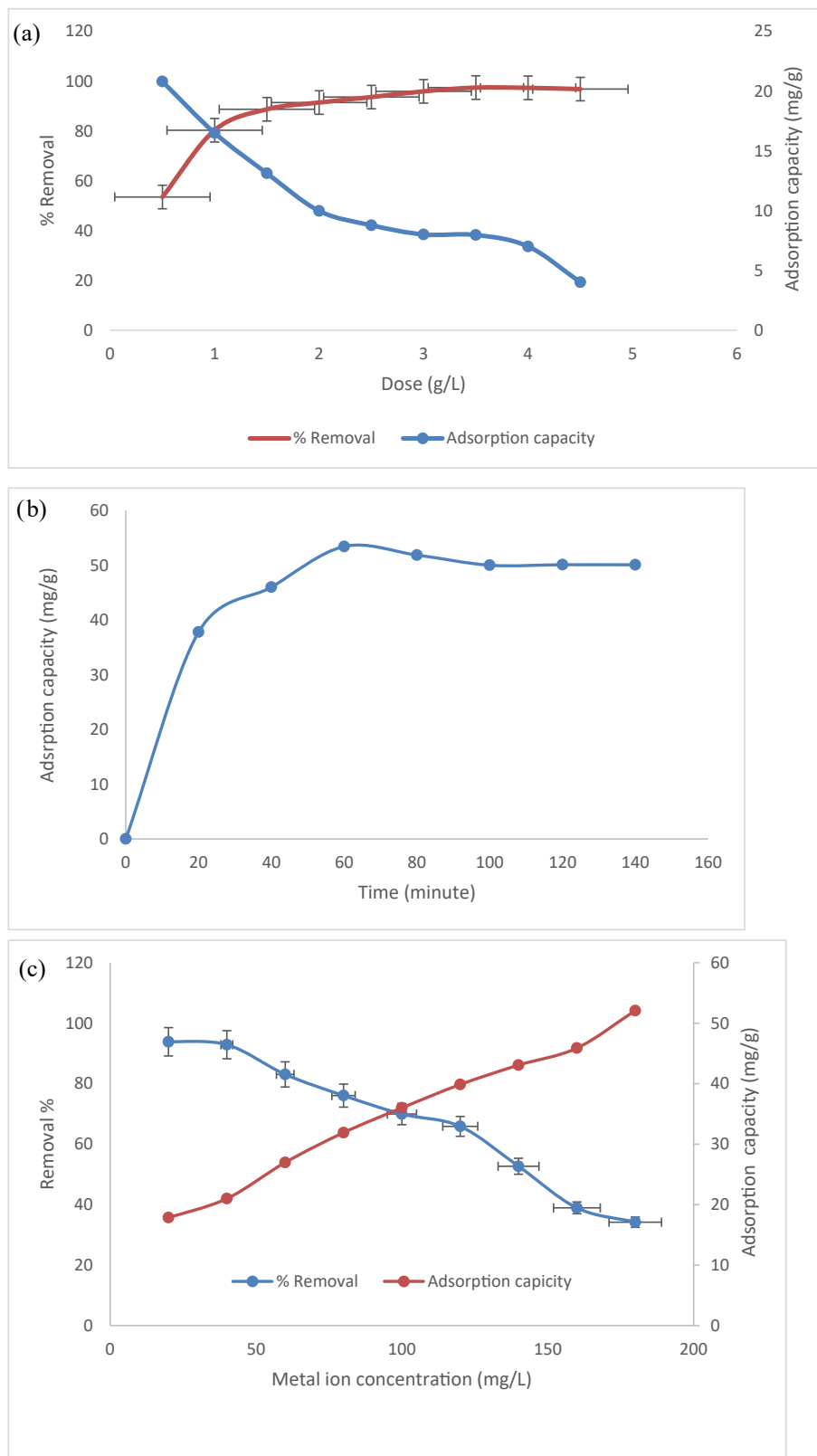


Figure 5. (a) Role of adsorbant dosage on the adsorption of Hg(II) on algal adsorbent: pH = 6, $C_i = 100$ mg/L, contact time = 2 hours at 35 °C (b) Role of contact time on the adsorption of Hg(II) on to algal bioadsorbent: pH = 6, $C_i = 100$ mg/L, dose = 1 g/L at 35 °C (c) Role of initial metal concentration on the adsorption on to algal bioadsorbent: pH = 6, dose = 1 g/L, contact time = 2 h at 35 °C.

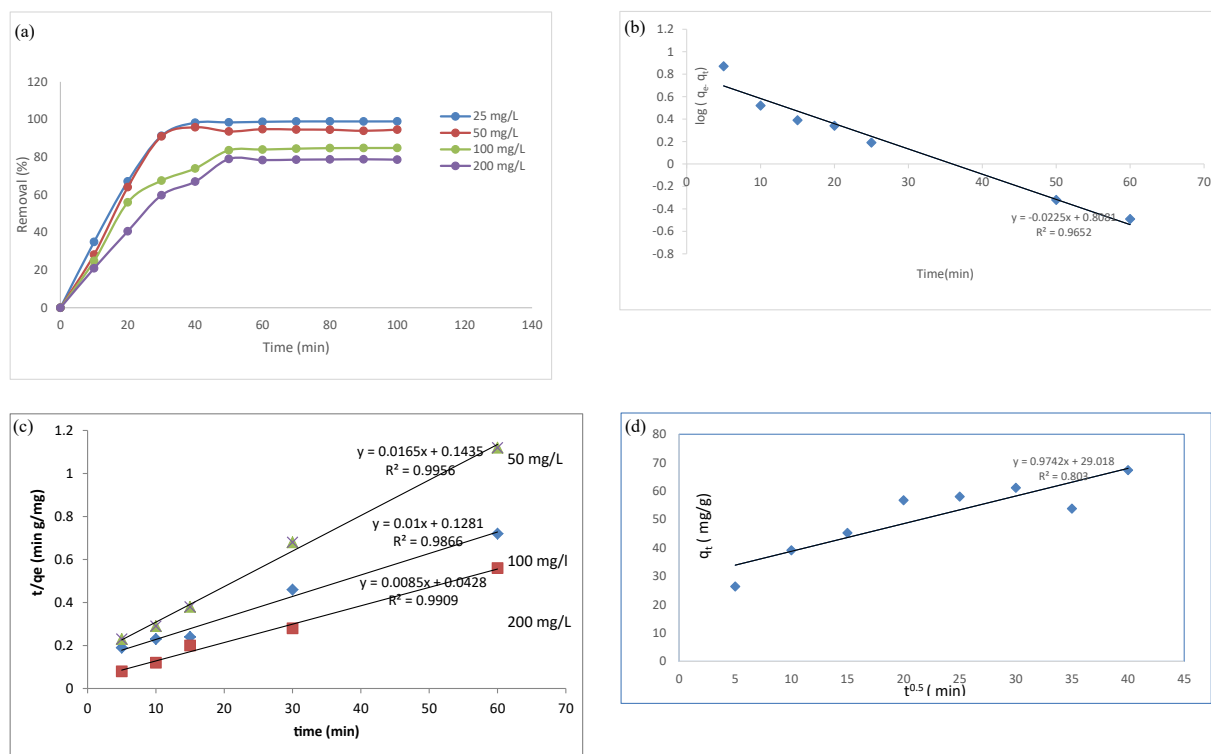


Figure 6. (a) Kinetic plot of the adsorption of Hg(II) on to algal bioadsorbant: pH = 6, C_i =(25,50,100,200) mg/L, dose = 1 g/L at 35 °C (b) Pseudo first order plot for the adsorption of Hg(II): pH = 6, 100 mg/L, dose = 1 g/L at 35 °C (c) Pseudo second order plot for the adsorption of Hg(II) on to algal bioadsorbant: pH = 6, C_i =(50,100,200) mg/L, dose = 1 g/L at 35 °C (d) Intra particle diffusion model for the adsorption of Hg(II) on to algal bioadsorbant: pH = 6, C_i = 100 mg/L, dose = 1 g/L at 35 °C.

3.2.4. Role of initial metal concentration on adsorption of Hg(II) on algal bioadsorbant

Role of initial metal concentration over range of 20–180 mg/L fixing pH 6 and agitation time 90 min for removal of Hg (II) was studied (Figure 5c). The adsorption capacity showed increasing trend from 17.87 to 52.09 mg/g and removal percentage decreased from 93% to 34.21% with increase of initial metal concentration. At specific fixed dose with the low initial concentration adequate sites are available for adsorption of Hg (II) however at higher initial concentration, there is increase in number of mole of metal ions compared to available adsorption sites resulting in the decrease in removal percentage (Nassar, 2010).

3.2.5. Kinetics of biosorption of Hg(II) on algal bioadsorbant

Adsorption equilibria studies are vital to regulate the effectiveness of adsorption. In spite of this, it is also necessary to identify the adsorption mechanism type in a given system. The study of adsorption have two components viz., equilibrium and kinetic study. The rate of uptake in the adsorption process is related to adsorption equilibrium and is explained by various equilibrium isotherms whereas kinetic study provide insight to rate limiting mechanism & deduce operating conditions (Deng et al., 2007). These two factors facilitate to recognize operating conditions and marginalize resistance of mass transfer to forecast efficacy of adsorbant. For determining the biosorption mechanism and its potential rate-controlling steps that includes: mass transport and chemical reaction processes, kinetic models have been exploited to test the experimental data (Simons and van Beem, 1990). Kinetics studies were conducted at an initial concentration (25–200 mg/L) of Hg (II) in batch operation to investigate intrinsic kinetics. High agitation speed to reduce film thickness and small particle size for reduction of pore diffusion resistance were applied to ease mass transfer effect to ascertain the time required to attain the equilibrium between the adsorbent and the adsorbate. Figure 6 (a) illustrated Hg (II) percentage removal vs time sketched by *Chlorella vulgaris* at various initial Hg (II) concentrations. Initially the rapid removal

percentage reveals that the high initial concentration overcome the mass transfer resistance between the aqueous and solid phases (i.e., availability of large surface sites) are initially speed up the process and with course of time, remaining sites are tough to be employed due to repulsion between solute molecules of solid and bulk phases. Higher initial metal concentration showed less removal percentage due to higher number of surface sites accessible per mole of metal ions but increased number of moles can not access the required surface sites and hence the removal percentage decreases (Wilde and Benemann, 1993). Straight line plot for Hg(II) and correlation coefficient values ($R^2 = 0.9652$ for 100 mg/L initial concentration) showed in Figure 6 (b) suggest that the removal of metal ions by adsorption follows Pseudo first order kinetics in certain extent. The values of the adsorption parameters q_e and k_2 were determined from the slope and intercept of the plot shown in Figure 6 (c), respectively. The

Table 2. Pseudo first order, pseudo second order & intra-particle diffusion rate for adsorption of Hg(II) on algal Bioadsorbant.

Constants	Initial concentration (mg/L)		
	50	10	200
q_e exp. (mg/g)	38.02	76.39	132.98
Pseudo first order			
q_e cal. (mg/g)	21.71	46.75	81.49
k_1 (min^{-1})	0.024	0.034	0.028
R^2	0.9876	0.9652	0.9882
Pseudo second order			
q_e cal. (mg/g)	36.69	75.41	141.46
k_2 ($\text{g mg}^{-1}\text{min}^{-1}$)	0.094	0.083	0.068
R^2	0.9956	0.9866	0.9909
Intraparticle diffusion			
K_{id} ($\text{mg g}^{-1}\text{min}^{-1}$)	0.024	0.034	0.028
R^2	0.876	0.803	0.890

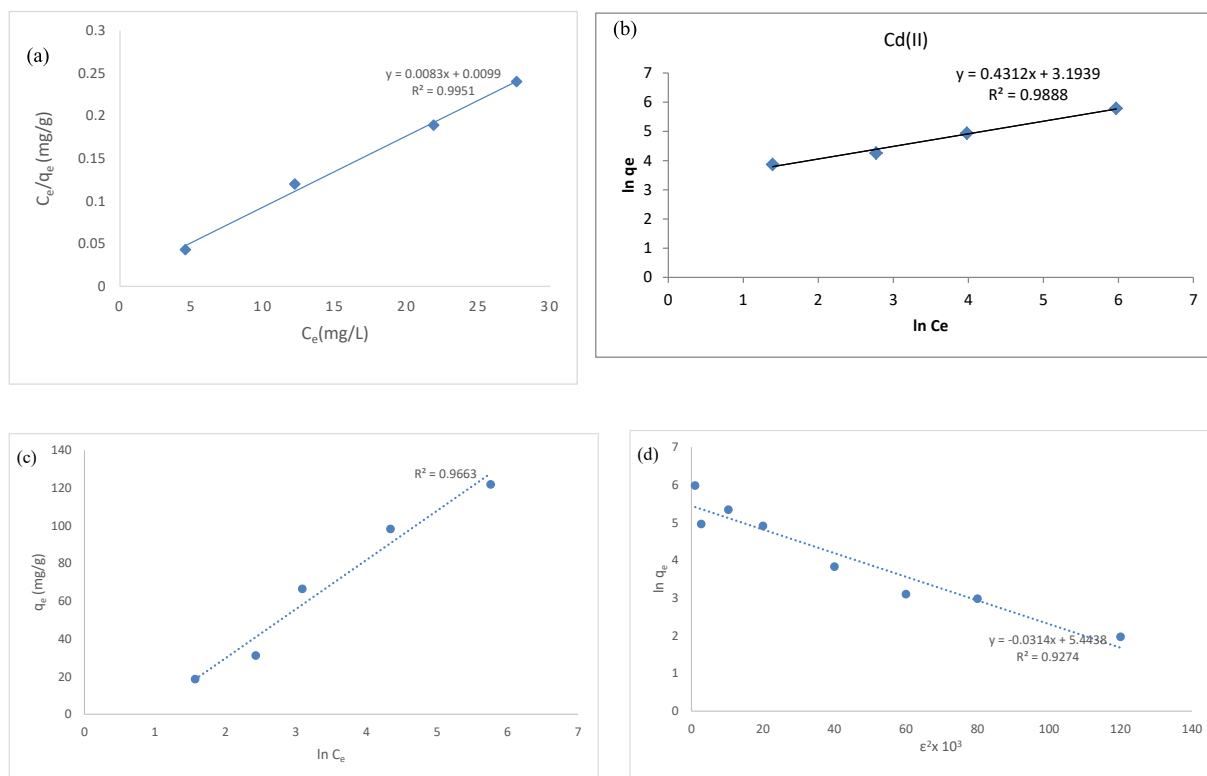


Figure 7. (a) Langmuir isotherm plot for the adsorption of Hg(II) on to algal biomass: pH = 6, $C_i = 25\text{--}200$ mg/L, dose = 1 g/L, contact time = 90 min at 35 °C (b) Freundlich isotherm plot for the adsorption of Hg(II) on to algal biomass: pH = 6, $C_i = 25\text{--}200$ mg/L, dose = 1 g/L, contact time = 90 min at 35 °C (c) Temkin Isotherm plot for adsorption of Hg(II) on to algal biomass: pH = 6, $C_i = 25\text{--}200$ mg/L, dose = 1 g/L, contact time = 90 min at 35 °C (d) D-R isotherm plot for adsorption of Hg(II) on to algal biomass: pH = 6, $C_i = 25\text{--}200$ mg/L, dose = 1 g/L, contact time = 90 min at 35 °C.

regression coefficients (R^2) at different initial metal concentrations indicate very close proximity to unity, illustrated better fit to experimental data (Table 2). The value of k_i was calculated from slope of plot q_t vs $t^{0.5}$ (Figure 6 (d)) and are presented in Table 2. Larger the intercept, greater the involvement of surface sorption in controlling the rate of adsorption.

To determine which model to use to describe the adsorption for a particular adsorbent/adsorbate isotherms experiments are usually run. Data from these isotherm experiments are then analyzed based on linearization of the models (Figure 7). A comparison of adsorption capacity by various algal species were shown in Table 4. The data obtained in determining the kinetics and equilibrium studies of the Hg(II) adsorption

are tabulated in Tables 3 & 4. To investigate the kinetics of heavy metal biosorption, many models have been developed. In spite of many alternative models, Pseudo first order, Pseudo second order and intraparticle diffusion model stay the most prevalent models for batch process to evaluate controlling mechanism in bioadsorption system (Supplementary file).

3.2.6. Role of temperature and thermodynamics of adsorption of Hg(II) on algal bioadsorbant

The data obtained from Figure 8 were presented in Table 5. The normal range of free energy for the physical adsorption ranges from -20 KJ/mol to 0 KJ/mol and for chemical adsorption range varies from -80 KJ/mol to -400 KJ/mol [102]. The negative free energies calculated in this study were -0.0268 KJ/mol, -0.0214 KJ/mol, -0.01644 KJ/mol respectively at temperature 293, 303, 313 K indicate the feasibility and

Table 3. Isotherm models and their calculated constants for sorption of Hg(II) on algal bioadsorbant.

Model	Parameters	
Langmuir	q_{max} (mg g ⁻¹)	42.1
	b (L mg ⁻¹)	0.01852
	R^2	0.9951
	R_L	0.231–0.973
Freundlich	k_f (mg/g)	3.792
	R^2	0.9888
	n	2.43
Temkin	B	32.76
	b (J/mol)	24.09
	A (L/g)	2.12
	R^2	0.9663
Dubinin-Radushkevich (D-R)	q_{max} (mg g ⁻¹)	38.76
	β (mol ² J ⁻²)	4.21×10^{-6}
	E (KJ/mol)	8.87
	R^2	0.9274

Table 4. Comparison of adsorption capacities of adsorbents towards heavy metal removal.

Algae	Metals	Capacity (mg/g)	References
<i>Spirulina plantensis</i>	Cu ²⁺	1.64–1.94	16
<i>Chlorella vulgaris</i>	Cu ²⁺	1.14–1.47	16
<i>Arthrospira plantensis</i>	Cu ²⁺	17.3	17
<i>Spirulina plantensis</i>	Cr ⁶⁺	12.3–16.8	18
<i>Chlorella vulgaris</i>	Cr ⁶⁺	10.2–13.7	18
<i>Chlorella vulgaris</i>	Cr ⁶⁺	0.5–15	18
<i>Chlorella miniata</i>	Cr ³⁺	14.7–41.2	19
<i>Spirulina plantensis</i>	Zn ²⁺	2.1	20
<i>Chlorella vulgaris</i>	Zn ²⁺	2.2	20
<i>Chlorella vulgaris</i>	Hg ²⁺	42.1	Present work

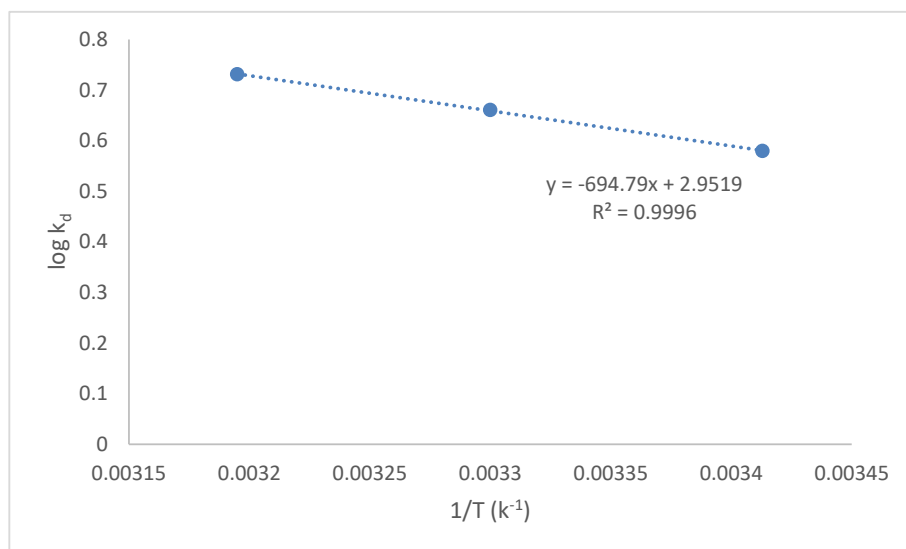


Figure 8. Thermodynamic plot (log K_d vs. 1/T) of adsorption of Hg(II) ions on to algal biomass: pH = 6, C_i = 100 mg/L, dose = 1 g/L, contact time = 120 min.

Table 5. Thermodynamic parameters for the adsorption of Hg(II) on algal bioadsorbant.

Temp(K)	1/T	C _e (g/l)	K _d	log k _d	ΔH (KJ/mol)	ΔS (J/KMol)	ΔG (KJ/mol)
293	0.003413	0.045	3.88	0.5797	+27.58	+56.48	-0.0268
303	0.003300	0.048	4.583	0.6608			-0.0214
313	0.003195	0.052	5.384	0.7311			-0.02644

spontaneous nature of the process. We can observe here as the temperature increases, the adsorptivity increases (consider the calculated values of C_e & K_d from Table 5). This may be probably credited to the endothermic nature i.e., positive value of ΔH (+27.58 KJ/mol) of the

sorption process moreover the endothermic pore diffusion has much influence in the sorption process on both adsorbate and adsorbent over diverse range of temperature. The high positive value of heat of enthalpy designates that the adsorption process is expected due to robust

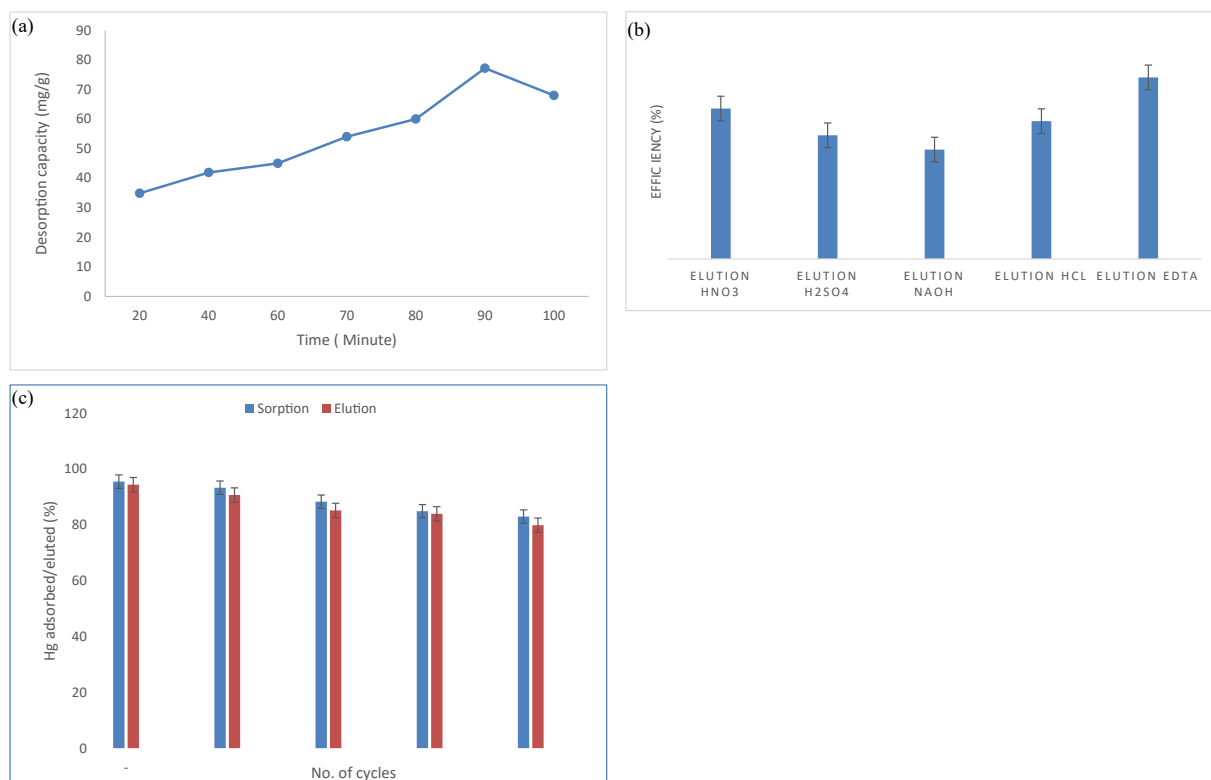


Figure 9. (a) Effect of time on desorption capacity of algal biomass: dose = 0.1 g/L, EDTA concentration = 0.1 mol/L (b) Percentage efficiency of five eluents 0.1N of each (HCl, NaOH, HNO₃, H₂SO₄, and EDTA) (c) Five Sorption/Desorption cycles: C_i = 100 mg/L, dose = 0.1 g/L, 0.1 N EDTA.

interactions between the Hg (II) ions and various functional groups on surface of algal bioadsorbant (Mohan et al., 2002). The randomness described by ΔS attributed to affinity of heavy metal ions (Hg^{+2}) towards algal bioadsorbant was calculated +56.48 J/mol K deliver suitability to increased randomness at solid - liquid boundary.

3.2.7. Recyclability & desorption studies

It is expected to reuse and regenerate the algal biomass as it is an important parameter for assessing the viability of adsorption process. In Figure 9 (b) five eluents (0.1 N of each HCl, NaOH, HNO_3 , H_2SO_4 , EDTA) in one adsorption/desorption cycle were established. Most of the stripping solutions showed good eluting capacity (HCl: 72.2%, HNO_3 : 78.8%, H_2SO_4 : 64.8%) due to at higher concentration of protons, established a robust competition for the active surface sites on the algal bioadsorbant. On the other hand, NaOH did not display good eluting capability. However, EDTA set to attain 95.1% recovery because in basic medium EDTA is deprotonated and with pronounced chelating properties, EDTA characterized exceptional stripping solution for heavy metals bounded to the porous matrix.

The study also revealed that 90 min of equilibration time was sufficient for the quantitative stripping (Figure 9(a)). Subsequently, the adsorption/desorption cycles were repeated for five cycles using 1 g of the adsorbent. The results obtained are furnished in Figure 9 (c). The sorption ability decreased from 95.5% to 79.87% upto five cycle by 8.36% which could be assume negligible and thus, the adsorbent can be reused.

4. Conclusions

Mercury metal ion biosorption on *Chlorella vulgaris* is strongly affected by parameters such as contact time, initial metal ion concentration, pH and temperature. The maximum biosorption was found 42.1 at pH 6. Both Langmuir and Freundlich equilibrium isotherm model is proved to be good fit for the experimental data of Hg^{2+} biosorption on *Chlorella vulgaris* biomass (Kumar et al., 2018). The kinetics of the biosorption of Hg^{2+} on the biomass could be described by a second-order kinetic model (Gupt et al., 2018). Free energy change (ΔG) with negative sign reflects the feasibility and spontaneous nature of the process. The positive enthalpy values indicate endothermic nature and negative entropy value point towards increase in randomness at solid liquid interface. The biomass of *Chlorella vulgaris* is mostly amorphous in nature. The marine microalgae is promising biosorbent for removal of metal ions from waste water streams.

Declarations

Author contribution statement

Mahendra Kumar: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Alak Kumar Singh: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Mohammad Sikandar: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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