Hexavalent chromium removal from water by microalgal-based materials: Adsorption, desorption and recovery studies

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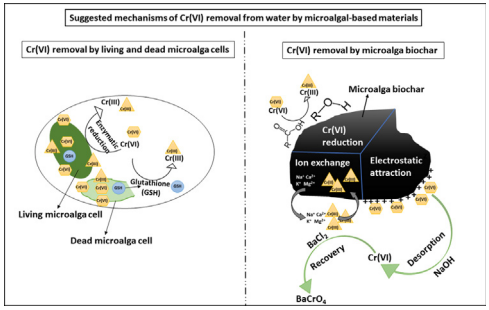
GRAPHICAL ABSTRACT



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ABSTRACT

The current study presents a comprehensive comparison towards the potential of different microalgal-based materials for the removal of hexavalent chromium (Cr(VI)) from water. Among the tested materials, microalgal biochar showed the highest removal efficiency (100%) of Cr(VI). The highest monolayer estimated adsorption capacities were 23.98, 25.19 and 24.27 mg/g at 5, 22 and 35 °C, respectively. Experimental data showed good compliance with pseudo-second-order kinetic model. The results of continuous column studies showed that the column removal efficiency increased from 52.33 to 57.58% by increasing the adsorbent dose from 0.125 to 0.200 g. Desorption efficiency of Cr(VI) by 0.1 M NaOH was increased from 51.16 to 59.41% by sonication bath as compared to roller shaker. More than 97% of desorbed Cr(VI) was recovered in less than 10 min by $BaCl_2$. This study shows that non-living microalga materials are more effective than living cells in the removal and recovery of Cr(VI) from water.

1. Introduction

Chromium (Cr) is one the most abundant heavy metals in the environment. Different industrial activities such as chromate mining, leather tanning, pigment synthesis, textile dying, metal electroplating, wood preservation, fertilizer and fungicide production are the main sources of Cr enrichment into the water systems (Pradhan et al., 2017). Hexavalent form of chromium (Cr(VI)) is more toxic than Cr(III). Elevated concentrations of Cr(VI) can cause many adverse effects to human health such as, liver problem, kidney damage, internal hemorrhage, chronic bronchitis, emphysema, nasal irritation, skin, lung, and stomach cancer, and DNA damaging by interface with DNA polymerase (Chhikara et al., 2010). World Health Organization (WHO) recommends a maximum allowable concentration of 50 ppb Cr in drinking water (Sessarego et al., 2019). Hence, there is a pressing need to remove Cr from contaminated water and wastewater prior to its discharge in order to protect the environment, aquatic life and human health.

Conventional methods to remove metals from water include chemical precipitation, reduction, chemical oxidation, lime coagulation, ion exchange, solvent extraction, evaporation recovery, adsorption, electrodeposition, reverse osmosis, and electrodialysis (Ahluwalia and Goyal, 2007). These methods are mostly ineffective or expensive, particularly when the concentrations of metal ions in solution range between 1 and 100 mg/L (Kumar et al., 2015). Besides conventional physico-chemical methods for metals removal from water, microorganism such as bacteria, fungi and microalgae have also been applied (Fernández et al., 2018). Among them, microalgal-based materials have been found better and can be considered as alternative to conventional methods for metals removal from water.

Depending on the wastewater treatment conditions, such as initial metal concentration, wastewater volume, treatment cost and time, different forms of living microalgae cells and non-living microalgal-based materials could be applied to remove metal ions from water. Living microalgae cells have some advantages such as eco-friendly, ease of handling, user-friendly, year round occurrence, recyclable/reusable, fast growth rate, large surface to volume ratio, no synthesis required, useful in both batch and continuous systems and applicability to water treatment with relatively low concentration of heavy metals (Kumar et al., 2015). While the advantages of non-living microalgae materials are outstanding uptake capacity, low cost, time and energy saving, renewability, ease of handling, reusability, applicable at very high or low pH and temperature, possibility of physical and/or chemical methods modifications, possibility of conversion to biochar and production of biofuel from algal mass after adsorption (Cheng et al., 2019).

Several species of microalgae such as *Scenedesmus obliquus*, *Chlorella pyrenoidosa*, *Chlamydomonas reinhardtii*, *Scenedesmus incrassatulus* and *Chlorella vulgaris* have been studied for the removal of different concentrations of Cr(VI) from the water with removal efficiencies ranged from < 40–100% (Shen et al., 2019). Yen et al. (2017) investigated the removal of Cr(VI) by using living and dead cells of microalgae. They found that Cr removal by living microalgae cells occurred not only through the adsorption, but also via biological mechanisms, such as enzymatic reduction of Cr(VI) to Cr(III). Pagnanelli et al. (2013) reported that biosorption–bioreduction process was involved in the removal of Cr(VI) by *Chlorella vulgaris*, during which majority of the biosorbed Cr(VI) was reduced to Cr(III) on the cell wall of microalgae (Pagnanelli et al., 2013). Thus, microalgae can reduce the toxic effects of Cr(VI) by converting it to non-toxic Cr(III).

Microalgae biomass and it's residue, after lipid extraction or other processing, can also be used as biochar (after pyrolysis) and used as adsorbent for Cr(VI) removal. Recently, Amin and Chetpattananondh (2019) converted the residue of *Chlorella* sp. to biochar for the removal of heavy metals from water. The adsorption capacity of synthesized biochar at 450 °C (BC-450) towards Cr(VI), Ni(II) and Zn(II) was 15.94, 24.76 and 17.62 mg/g, respectively.

The aim of the current study was to evaluate the removal of Cr(VI) with different microalgal-based materials such as living microalgae, *Scenedesmus quadricauda*, microalgal pellets (wet microalgal biomass), microalgal powder (dried microalgae biomass), chemically modified biomass (after HCl, NaOH, NaCl, and CH_3OH treatments), and microalgal biochars (MB) at different temperatures viz., 300, 500 and 700 °C (named as MB-300, MB-500, and MB-700). The best material was selected for further investigations such as isotherm and kinetic studies as well as fixed bed column study for the removal of Cr(VI) from water. The collected data from this study present a comprehensive comparison towards the potential of different microalgal-based materials for the removal of Cr(VI) from water. In addition, this work also reports desorption and recovery of Cr(VI) after adsorption process, which are necessary for sustainable application of microalgae in wastewater treatment.

2. Materials and methods

2.1. Chemicals and preparation of solutions

Cr(VI) solution was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in deionized water. Phosphoric acid (50% in deionized water) and 1,5-diphenylcarbohydrazide (5% in acetone) solutions were used for the analysis of Cr(VI) concentration in solution. pH of solution was adjusted via 0.1 and 1 M of HCl and NaOH solutions. 0.1 M NaOH was used for desorption of Cr(VI). $BaCl_2{\cdot}2H_2O$ salt was used for the recovery of Cr(VI).

2.2. Microalga strain and cultivation condition

Scenedesmus quadricauda was purchased from Culture Collection of Algae and Protozoa (CCAP), Scotland, UK and used as model microalga in this study. Bold Basal Medium (BBM) solution was prepared according to the guidelines of CCAP. *S. quadricauda* was cultivated in 1 L glass jar (DURAN®). Microalga cells with initial concentration of 0.272 nm optical density (OD) were inoculated to the medium. The culture was illuminated under 16 h light and 8 h darkness photoperiod and 110 μmol/m^2.s light intensity was provided by the florescent lamp. Culture was aerated by compressing atmosphere air (0.03% CO_2) at 22 °C.

The correlation between the dry weight (DW) of microalga and OD was monitored using Eq. (1):

$$DW(g/L) = a \times OD_{680} - b \quad (1)$$

where, OD_{680} is the optical density of microalga at 680 nm and a and b are the constants.

2.3. Cr(VI) removal from water using living microalgal cells

Cr(VI) removal from water with living microalga was examined by the addition of Cr(VI) solution to microalga culture. The addition of Cr (VI) to the culture was carried out in the lag (day 1) and log (day 4) phases of the growth. In both cases, Cr(VI) was injected to the medium through one-time and gradually modes. In the first mode, 100 mL of Cr (VI) solution (10 mg/L) was added to 900 mL of microalga culture to provide 1 L of 1 mg/L solution. In the second mode, 100 mL of Cr(VI) solution with 10 mg/L concentration was added to 900 mL of microalga culture during 4 days (25 mL/day), to provide 1 L of 1 mg/L Cr(VI). Microalgal growth and Cr(VI) concentrations were measured after 4, 8 and 12 days of cultivation in five experimental units as follows:

Experimental unit 1: BBM medium without addition of Cr(VI) solution (control), *experimental unit 2*: one-time addition of 100 mL Cr(VI) solution with 10 mg/L concentration to 900 mL microalga cultivation medium at lag phase (day 1) of microalga growth (lag/one-time), *experimental unit 3*: gradually (25 mL/day) addition of 100 mL Cr(VI) solution with 10 mg/L concentration to 900 mL microalga cultivation

medium at lag phase (days 1–4) of microalga growth (lag/gradually), *experimental unit 4*: one-time addition of 100 mL Cr(VI) solution with 10 mg/L concentration to 900 mL microalga cultivation medium at log phase (day 4) of microalga growth (log/one-time), *experimental unit 5*: gradually (25 mL/day) addition of 100 mL Cr(VI) solution with 10 mg/L concentration to 900 mL microalga cultivation medium at log phase (days 4–8) of microalga growth (log/gradually). To measure Cr(VI) concentration, 5 mL of sample was taken. The liquid was centrifuged, and subsequently filtered with 0.45 µm membrane filter (BIOFILR Syringe Filter). Following centrifugation and filtration, the reagents (phosphoric acid 50% and 1,5-diphenylcarbohydrazide 5%) were added to the solution. Finally, the concentration of Cr(VI) was analyzed at 540 nm using the UV-spectrophotometer (UV-2401PC). The removal percentage of Cr(VI) was measured as follows:

$$R(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where, R (%) is the removal efficiency of Cr(VI), C_i(mg/L) and C_e (mg/L) are the initial and final (equilibrium) concentrations of Cr(VI), respectively.

2.4. Cr(VI) removal from water using dead microalga

Cr(VI) removal from the water was investigated using microalgal powder (dry), microalgal pellet (wet), chemically pretreated microalgal biomass and microalgal biochar (MB).

2.4.1. Batch studies of Cr(VI) biosorption

To find the adsorbent with the highest Cr(VI) removal efficiency, batch biosorption experiments were carried out at three different initial Cr(VI) concentrations (1, 5 and 10 mg/L) and four adsorbent amounts (0.25, 0.50, 1.00 and 2.00 g/L). Based on the preliminary results, the adsorbent, MB-500 showed highest Cr(VI) removal efficiency and thus, was selected for further experiments.

2.4.2. Column studies of Cr(VI) biosorption

Column study was conducted to investigate the adsorption of Cr(VI) using MB-500. Column tests were carried out using a column with 100 mm height and 6.6 mm inner diameter. The fix bed column tests were carried out with two flow rates (1.00 and 2.00 mL/min) and two adsorbent amounts (0.125 and 0.200 g). A peristaltic pump was used to pump Cr(VI) solution through the column from top to bottom. Cr(VI) solution was collected at certain time intervals and the residual concentration of Cr(VI) was determined as presented in Section 2.3.

Parameters of column were evaluated as follows:

$$q\text{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ads}\, dt \quad (3)$$

$$q_{bed} = \frac{q_{total}}{M} \quad (4)$$

$$m_{total} = \frac{C_0 \times Q \times t_{total}}{1000} \quad (5)$$

$$Y(\%) = \frac{q_{total}}{m_{total}} \times 100 \quad (6)$$

$$V_{eff} = Q\times \quad (7)$$

$$C_{eq} = \frac{m_{total} - q_{total}}{V\text{eff}} \times 1000 \quad (8)$$

The parameters of Eqs. (3)-(8) are defined as follows:

q_{total} (mg): the total adsorbed quantity, Q (mL/min): the flow rate, t_{total} (min): the total time of operation, C_{ads} (mg/L): the adsorbed Cr(VI) concentration on the adsorbent, q_{bed} (mg/g): the experimental maximum adsorption column capacity, M (g): the weight of adsorbent in the column, m_{total} (mg): the total amount of adsorbate delivered to the column system, C_0 (mg/L): the initial Cr(VI) concentration, Y (%): the total removal efficiency of column, V_{eff} (mL): the passed volume of effluent through the column and C_{eq} (mg/L): the concentration of Cr(VI) in effluent.

2.5. Desorption of Cr(VI)

The saturated MB-500 was collected after conducting adsorption experiment under optimal condition. Desorption experiments were performed in two steps. In the first step, the effect of 0.1 M NaOH and deionized water was investigated on Cr(VI) desorption using a shaker. To conduct desorption experiment, a known amount of saturated MB-500 (10 g/L) was added to 5 mL of desorbent solution and was shaken for 5, 30 and 60 min.

The second step of desorption experiment was carried out to evaluate the effect of sonication on desorption efficiency. For this purpose, Cr(VI) desorption efficiency was studied under the same experimental conditions as step one, except that a sonication bath was used instead of shaker. In both steps, the solution was filtered and the amount of desorbed Cr(VI) was measured as already explained in Section 2.3. Desorption capacity (mg/g) and efficiency (%) were calculated according to Eqs. (9) and (10) (Daneshvar et al., 2017):

$$q_{e,de} = \frac{V_{de} \times C_{fde}}{M_{de}} \quad (9)$$

$$D\% = \frac{q_{e,de}}{q_{e,s}} \times 100 \quad (10)$$

where, $q_{e,de}$ (mg/g) is the desorption capacity of MB-500 at equilibrium time, V_{de} (L) is the volume of desorbent solution, C_{fde} (mg/g) is the concentration of Cr(VI) in desorbent solution at equilibrium, M_{de} (g) is the saturated mass of MB-500 used in desorption experiment, D (%) is the percentage of desorption and $q_{e,s}$(mg/g) is the adsorption capacity of MB-500.

2.6. Recovery of Cr(VI)

Recovery experiment was conducted according to the method reported by (Zelmanov and Semiat, 2011). Cr(VI) was recovered by the addition of $BaCl_2{\cdot}2H_2O$ to Cr(VI) solution after desorption process. Different amounts of $BaCl_2{\cdot}2H_2O$ were added to 5 or 10 mL of a solution containing Cr(VI) to make 0.5 to 5 mM of $BaCl_2{\cdot}2H_2O$ The pH of solution was adjusted to 10 and vortexed for 1 min. Then, the tubes were kept on a shaker for 10 min. Subsequently, the solution was filtered using cellulose acetate membrane filters with pore size of 0.45 µm (Sartorius™). The percentage of Cr(VI) in filtrate was determined according to Eq. (1) as described in Section 2.3.

2.7. Analysis and statistics

The experiments were conducted in duplicate and Microsoft® Excel® for Office 365 MSO (16.0.10730.20348) was used to calculate the mean ± standard deviation (SD) values. The MATLAB software (Version R2012a) and Solver were used for the isotherms and kinetic modeling.

3. Results and discussions

3.1. Cr(VI) removal by living S. Quadricauda

The microalga *S. quadricauda* was used for the removal of Cr(VI) at low concentration (1 mg/L). In this study, the addition of Cr(VI) to microalga cultivation medium was performed one-time and gradually. In first case, 100 mL Cr(VI) with 10 mg/L concentration was added to 900 mL microalga cultivation medium on first day of cultivation. In latter case, the same volume (100 mL) of same concentration (10 mg/L)

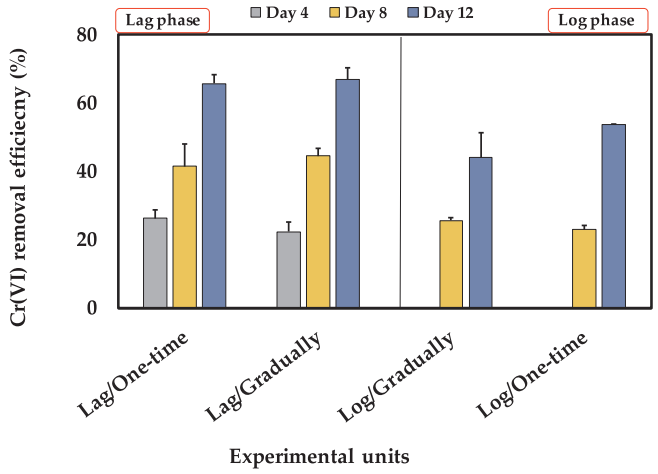

Fig. 1. Effect of one-time and gradually addition of Cr(VI) in lag and log phases on Cr(VI) removal by microalga.

of Cr(VI) solution was added to 900 mL medium for 4 days (started from 1st day of experiment) at a rate of 25 mL/day. One-time addition of 100 mL Cr(VI) was performed on first day (lag phase) and 4th day of cultivation (log phase). Gradual addition at a rate of 25 mL/day was conducted during day 1 to day 4 (lag phase) and day 4 to day 8 (log phase). As depicted in Fig. 1, removal efficiency of Cr(VI) increased within 12 days in all experimental units. The maximum removal efficiency was obtained as 67.03% for the gradual addition of Cr(VI) solution in the lag phase. However, this value (67.03%) was not significantly higher than when Cr(VI) was added one-time in lag phase (65.69%). As can be seen from Fig. 1, microalga showed higher Cr(VI) removal efficiency when Cr(VI) solution was added in the lag phase, as compared to the log phase. A possible explanation of it could be the longer exposure time in the lag phase (12 days) as compared to log phase (8 days).

Cr(VI) removal from water/wastewater with microalgae has been investigated by other researchers. Das et al. (2017) showed that cultivated *C. vulgaris* in diluted tannery wastewater decreased the concentration of Cr(VI) from 3.22 mg/L to zero within 12 days of incubation (Das et al., 2017). Chen et al. (2016) reported that the extracted chloroplast from *C. vulgaris* exhibited nearly 70% removal efficiency of Cr(VI) with 17 mg/L concentration (Chen et al., 2016). Uptake of heavy metals by living microalgae is a biphasic process. Cr(VI) ions first interact with the positively charged groups (Han et al., 2007) such as amine groups, present on the microalgal cell wall, and then Cr(VI) ions can enter the microalgal cells via ionic carriers existing on the cell membrane (Shanker et al., 2005). Reduction of Cr(VI) to Cr(III) also has a main role in the removal of Cr(VI) from water. Chromium reductase is a known enzyme in reduction of Cr(VI) to Cr(III) (Kováčik et al., 2015). In addition, Yen et al. (2017) explained that the released glutathione (GSH) from the damaged cells of *Chlorella vulgaris* to medium might reduce Cr(VI) to Cr(III) (Yen et al., 2017). Furthermore, Aharchaou et al. (2017) indicated that the majority of Cr(VI) was accumulated by organelles, heat-stable proteins (HSP), and granules in microalgal cell (Aharchaou et al., 2017). However, the role of organelles inside the microalgal cells for Cr(VI) bioreduction has not been completely discovered yet (Chen et al., 2016).

According to the obtained results, the inhibitory effect of chromium on the growth of *S. quadricauda* was observed in all experimental units as compared to the control. As illustrated in Fig. 2(a), microalga showed different patterns of growth when Cr(VI) solution was added to the medium at lag phase gradually (25 mL/day) and one-time. In the control group, microalga grew exponentially until day 12 after four days lag phase. One-time addition of Cr(VI) to the medium in lag phase strongly decreased the growth of microalga for four days (day 0 to day

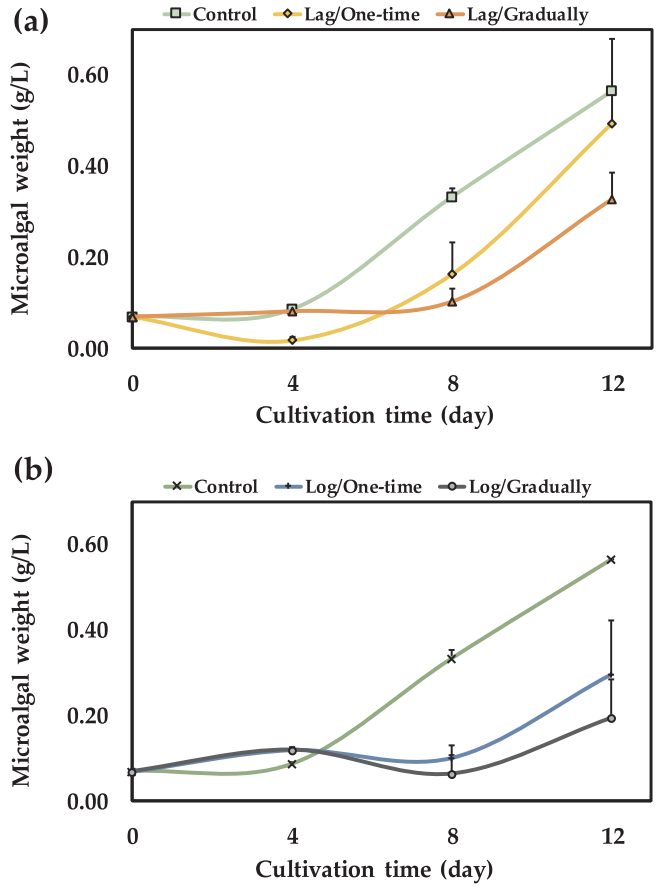

Fig. 2. Effect of one-time and gradually addition of Cr(VI) on microalgal growth: addition of Cr(VI) in lag (a) and log (b) phases.

4); but after that, microalga entered to log phase and grew exponentially for eight days (day 4 to day 12). Gradual addition (25 mL/day) of Cr(VI) to the medium in lag phase inhibited the growth of microalga for 8 days (day 0 to day 8); then, microalga grew exponentially for 4 days (day 8 to day 12). Maximum dry weight of microalga for one-time and gradual exposure modes in the lag phase were 0.49 and 0.33 g/L, respectively. Gradual addition of Cr(VI) solution to the medium of *S. quadricauda* appears to inhibit the growth of microalga for a longer time. *S. quadricauda* showed better adaptation to one-time addition of Cr(VI) solution to the microalga medium. Fig. 2(b) shows the effect of gradual and one-time addition Cr(VI) to the medium at the log phase. Until day 4, *S. quadricauda* showed a similar growth pattern in control and experimental units. Then following addition of Cr(VI) to the experimental units on day 4, growth of microalga decreased until day 8, as compared to the control. In both gradual and one-time exposing modes in log phase, microalga adapted to Cr(VI) solution and grew exponentially from day 8 to day 12. Maximum dry weights of *S. quadricauda* for gradual (25 mL/day) and one-time addition of Cr(VI) in log phase were 0.19 and 0.30 g/L, respectively. Apparently, higher removal efficiency of Cr(VI) and lower inhibition rate of *S. quadricauda* growth was attained as chromium solution was added in lag phase as compared to log phase. Microalgal cells have more time to regulate their physiology in response to Cr(VI) at longer exposure time (for 12 days) as compared to shorter exposure time (8 days). In addition, 4 days more exposer time increases the chance of interactions between microalgal cells and Cr(VI).

Volland et al. (2012) stated that Cr(VI) damages the microalgal cells severely due to the activity of reactive oxygen species (ROS) and disruption of iron homeostasis (Volland et al., 2012). In their study, transmission electron microscopy (TEM) showed structural changes

such as condensed cytoplasm, growing of vacuolization, and dark precipitations in the microalgal cell wall of *Micrasterias denticulata* after exposing to Cr(VI), which resulted in stopping of cell development after mitosis. Moreover, net photosynthesis of *M. denticulata* decreased to 1/10 of control level because of the damaging of photosynthetic pigments. The destructive effects of Cr(VI) on cell viability, chlorophyll content, and mitochondrial proteins as well as ROS production and lipid peroxidation were also reported in *Scenedesmus quadricauda* (Kováčik et al., 2015).

3.2. Batch adsorption studies of Cr(VI) removal

3.2.1. Removal of Cr(VI) by cell pellets and dried mass of S. Quadricauda

The effects of different initial concentrations of Cr(VI) (1, 5 and 10 mg/L) and biomass dosages (0.25. 0.50, 1.00 and 2.00 g/L) of microalgal pellet and powder on Cr(VI) removal efficiency were investigated. The initial solution pH was adjusted to 2 while temperature and contact time were kept constant at 22 °C and 240 min, respectively. The removal efficiency of Cr(VI) either by microalgal pellet or microalgal powder increased as the adsorbent dosage increased. However, the removal efficiency of Cr(VI) decreased as initial Cr(VI) concentration increased (Fig. 3(a and b)). The maximum removal efficiency of Cr (VI) with 1 mg/L initial concentration using 2 g/L of microalgal pellet and microalgal powder was noted as 47.72% and 96.62%, respectively.

Functional groups on the surface of microalgal pellets play a key role for metal ions removal, in the same way as dried microalgae. Also, as a resistance mechanism against the high concentration of heavy metals, microalgal cells excrete the toxic elements by the expansion of energy-driven efflux pumps. The excreted Cr(VI) might be masked with the released metabolites of microalgal pellets outside of the cell (Monteiro et al., 2012). Hence, the majority of Cr(VI) removal possibly occurred on the microalgal pellet cell walls by functional groups and outside of the cells, by the released metabolites.

Microalga *S. quadricauda* always forms colonies of two, four or eight cells, arranged linearly; microalgal cells are elongated ellipsoidal and terminal cells have long spiny bulges (Bellinger and Sigee, 2015). After drying of microalgal mass, these cells are separated and break to smaller particles. Thereby, cell surface was greatly increased in dried microalga as compared to microalgal pellets, which mostly contain the cellular colonies of *S. quadricauda*. In addition, the cell walls and membranes of microalgae have biochemical compounds such as proteins, polysaccharides, and lipids. These compounds consist of functional groups namely carboxyl, phosphate, sulfhydryl, hydroxyl, diphosphorus trioxide, amino, amide, primary amine groups, aromatic compounds, halide group and aliphatic alkyl groups, which could react with metal ions (Kumar et al., 2015). By increasing the cell surface area (by breaking the cell walls), existing functional groups become available for the metal ions adsorption, thus, leading to the higher removal efficiency of Cr(VI) by microalgal powder as compared to microalgal pellets.

3.2.2. Cr(VI) removal by chemically modified biomass of S. Quadricauda

The effect of chemical modifications of *S. quadricauda* biomass using HCl, NaCl, NaOH, and CH_3OH treatments on Cr(VI) removal from aqueous solution was studied. Initial solution pH was adjusted to 2 and adsorption experiments were performed at initial Cr(VI) concentration of 5 mg/L and 22 °C for 240 min. The removal efficiency was significantly increased as microalgal weight increased in all untreated and treated biomass, except the NaCl treated biomass. Maximum removal efficiency of 73.63% was achieved by raw biomass of *S. quadricauda*. It shows that different chemical modifications, used in this study, did not improve the removal efficiency of Cr(VI).

3.2.3. Cr(VI) removal by S. Quadricauda biochars

The removal efficiency of Cr(VI) by three types of microalgal biochars, synthesized at 300 (MB-300), 500 (MB-500) and 700 °C (MB-700), was investigated. Adsorption experiments were performed with 1, 5 and 10 mg/L of initial Cr(VI) concentrations and 0.25, 0.50, 1 and 2 g/L biochar dosages for 240 min of contact time. Initial solution pH was adjusted to 2.0 and temperature was kept constant at 22 °C. As it is presented in Fig. 3(c, d and e), each biochar showed different behavior in response of increasing adsorbent dosage and initial Cr(VI) concentration towards Cr(VI) removal efficiency. The removal efficiency of Cr(VI) increased by increasing the dosages of MB-300 and MB-700 up to 1 g/L. While the removal efficiency of Cr(VI) significantly decreased when the initial concentration of Cr(VI) increased from 1 to 5 and 10 mg/L. In case of MB-500, it showed a remarkable removal efficiency at 1, 5 and 10 mg/L initial Cr(VI) concentrations. The maximum removal efficiency of 1 mg/L initial Cr(VI) concentration by 2 g/L of MB-300 and MB-700 was found to be more than 97% (Fig. 3(c and e)). The

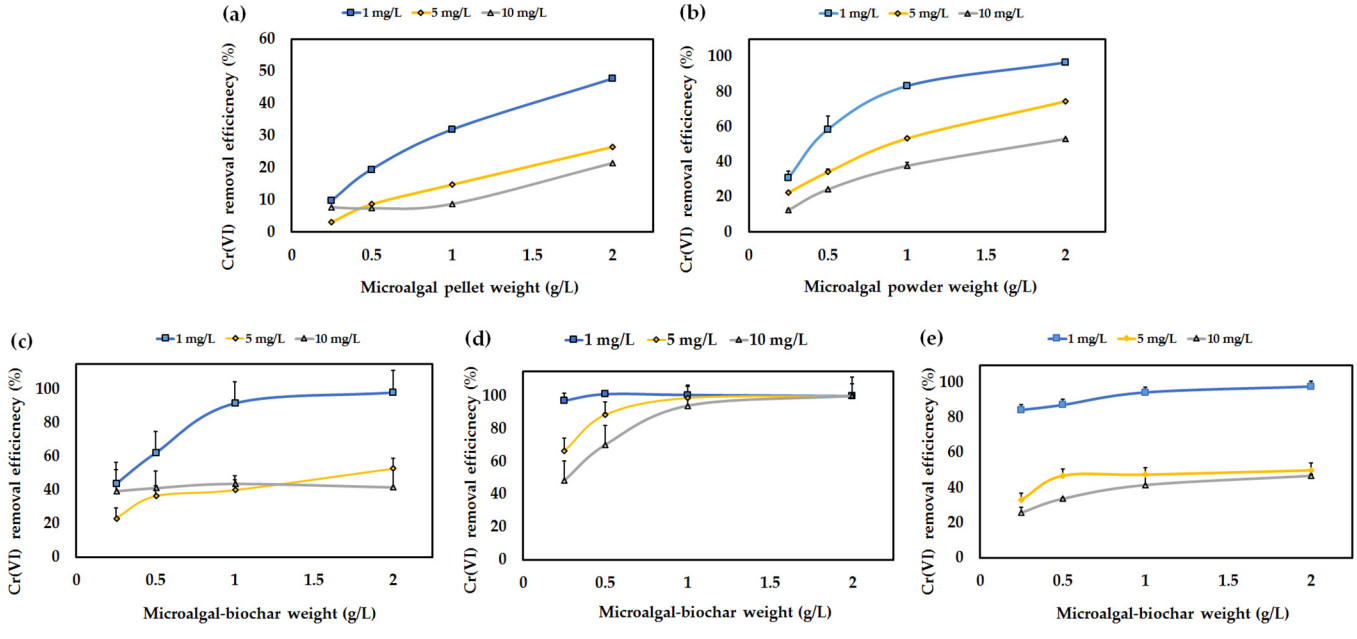

Fig. 3. Cr(VI) removal efficiency by microalgal pellet (a), microalgal powder (b), MB-300 °C (c), MB-500 °C (d), and MB-700 °C (e): [pH: 2, contact time: 240 min, temperature: 22 °C].

removal efficiency of all the studied initial Cr(VI) concentrations by 2 g/L of MB-500 was 100% (Fig. 3(d)). In addition, the removal efficiency of 5 mg/L Cr(VI) by 0.25, 0.50, 1.0 and 2.0 g/L of MB-500 was significantly increased more than 3.3, 2.8, 1.9 and 1.4 times, respectively, as compared to the same amount of raw biomass of microalga. These findings show that synthesis of suitable microalgal biochar can increase the removal efficiency of Cr(VI) from water as compared to raw microalgal biomass, especially at lower adsorbent dosages.

During pyrolysis, cellulose, hemicellulose and lignin of microalgal biomass undergo cross-linking, depolymerization, and fragmentation reactions, producing mainly biochar, bio-oil, and gaseous products. The composition of these products depends on the pyrolysis temperature, reaction time, and heating rate (Cha et al., 2016). Thus, the adsorption capacities of biochars mainly relies on the biochar production conditions. Several researchers have examined the effect of pyrolysis temperature on the adsorption capacity. Zhang et al. (2015) stated that the amount of produced biochar and acidic functional groups (such as carboxyl and hydroxyl groups) were decreased by increasing the pyrolysis temperature, conversely the basic functional groups (i.e. amine groups), ash, pH, carbon stability, and gaseous yield were increased (Zhang et al., 2015). Zhu et al. (2014) produced activated char at various pyrolyzing temperatures, 300 to 700 °C, in the presence of nitrogen gas (Zhu et al., 2014). They reported that the pH, pore volume, the content of ash, specific surface area, and aromaticity were enhanced as pyrolyzing temperature was increased, whereas the polarity index was decreased.

In this study, the maximum removal efficiency of Cr(VI) was acquired using MB-500. Increasing pyrolysis temperature increases the %C in the biochar and decreases the %O and surface hydrophilicity (Sohi et al., 2010). Also, at higher temperature the ratio of O/C and H/C and polarity index [(O + N)/C] is decreased (Cha et al., 2016) on the biochar surface. Cr(VI) removal efficiency decreased by increasing the pyrolysis temperature above 500 °C. It might be related to an excessive loss of acidic functional groups and polarity index at high temperature.

3.3. Column adsorption studies of Cr(VI)

The amount of adsorbent (column bed) and flow rate are two important factors, which affect the shape and parameters of breakthrough curve. Here, the effects of these parameters were tested with three experiments. In experiment one, initial concentration of Cr(VI) (C_0), adsorbent amount (M) and flow rate (Q) were, 5 mg/L, 0.125 g and 1 mg/L, respectively. In experiments 2 and 3, the column bed and flow rate increased to 0.200 g and 2.00 mL/min, respectively at 5 mg/L Cr(VI) concentration. Fig. 4 illustrates the effect of aforementioned parameters on breakthrough curve. The computed parameters of column studies are presented in Table 1. As can be seen from Table 1, by increasing the column bed from 0.125 g to 0.200 g, all the column parameters including t_b, t_{total}, q_{bed}, m_{total}, $Y(\%)$ and V_{eff} except C_{eq} increased. These results revealed that increasing the amount of MB-500 effectively improved the performance of column capacity and increased the total Cr (VI) removal efficiency in the column. The breakthrough point appears after 60 min (C_t/C_0 = 0.018) and 150 (C_t/C_0 = 0.023) in cases of 0.125 and 0.200 mg column bed, respectively. The exhaustion time also increased from 550 to 810 min as column bed increased from 0.125 to 0.200 mg. In the beginning of the experiment, all the adsorption sites are available on the fresh adsorbent and none of Cr(VI) ions can escape from the column. Gradually, the upper part of adsorbent or column bed (in top-down mode) will be saturated as it is in direct contact with Cr (VI) solution. Thus, the adsorption zone will be transferred to the lower part, which is unsaturated. As the adsorption zone moves from upwards to downwards, higher Cr(VI) concentration is observed to the collecting effluent. The concentration of Cr(VI) in the effluent solution keeps increasing until the entire adsorption zone is saturated (exhaustion time). The time, where the effluent concentration reaches greater than 90% of influent is usually called the exhaustion time. The reason for increasing

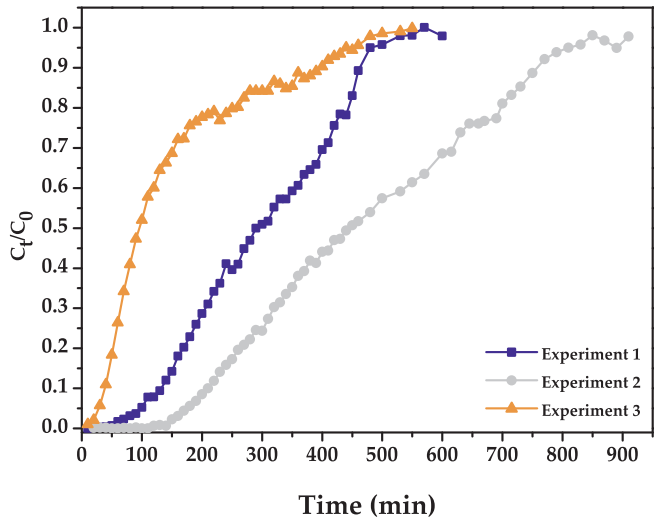

Fig. 4. Effect of adsorbent amount and flow rate on the breakthrough curves of Cr(VI) removal from water by MB-500 [Experiment 1: adsorbent amount: 0.125 mg, flow rate: 1 mL/min, initial Cr(VI) concentration: 5 mg/L, Experiment 2: adsorbent amount: 0.200 mg, flow rate: 1 mL/min, initial Cr(VI) concentration: 5 mg/L, Experiment 3: adsorbent amount: 0.125 mg, flow rate: 2 mL/min, initial Cr(VI) concentration: 5 mg/L].

the breakthrough time, exhaustion time, column adsorption capacity and column removal efficiency can be explained due to the availability of more adsorption zone in higher column bed (Kundu et al., 2004).

Fig. 4 illustrates the effect of increasing flow rate on the shape of the breakthrough curve when the adsorbent amount and initial Cr(VI) concentration kept constant as 0.125 mg and 5 mg/L, respectively. The breakthrough and exhaustion time decreased from 60 to 10 and 550 to 450 min as the flow rate increased from 1 to 2 mL/min, respectively. However, by increasing the flow rate from 1 to 2 mL/min, q_{bed} increased negligibly from 12.56 to 12.88 mg/g; but column removal efficiency was decreased remarkably, from 52.33 to 31.57%. Contact time has a vital role in the adsorption process. An explanation for the steeper breakthrough curve and decreasing Y% value at higher concentration could be due to inadequate contact time between MB-500 and Cr(VI) ions. This observation is in agreement with a previous study of Cr(VI) sorption from water using modified montmorillonite clay nanocomposite (Setshedi et al., 2014).

3.4. Desorption experiments

During the adsorption process, pollutants transfer from liquid to solid phase. Desorption is necessary to manage the solid waste to avoid the production of secondary waste and recovery of valuable materials. As acidic pH (pH 2.0) was favorable for adsorption of Cr(VI), desorption of Cr(VI) from saturated MB-500 was performed using 0.1 M NaOH as a basic desorbent via shaking and sonication (Fig. 5). Desorption efficiency by 0.1 M NaOH was observed as 33.10, 47.24 and 51.16% after 5, 30 and 60 min of shaking. Desorption of Cr(VI) at basic pH can take place because of exchanging of CrO_4^{2-} (the dominant form of Cr(VI) in alkaline solution) with OH^-. In agreement with our results, Nakagawa et al. (2014) observed 75% desorption of Cr(VI) by NaOH solution at pH 12 (Nakagawa et al., 2014). They stated that attacking on adsorption sites by OH^- ions led to desorption of Cr(VI). In another study, the highest desorption efficiency of Cr(VI) was observed as 98.45% by 0.8 M NaOH solution (Akram et al., 2017). The authors explained that in high pH solution, electrostatic repulsion, due to negatively charged sites, increases desorption of Cr(VI) from the adsorbent.

Sonication was also studied in the desorption process. It increased desorption efficiency of Cr(VI) from MB-500 by 0.1 M NaOH. To make the desorption process more environmental friendly, Cr(VI) desorption

Table 1
Breakthrough parameters at fixed initial Cr(VI) concentration (C_0) and different adsorbent amount (M) and flow rate (Q).

	C_0 mg/L	M g	Q mL/min	t_b min	t_{total} min	q_{total} mg	q_{bed} mg/g	m_{total} mg	Y %	V_{eff} mL	C_{eq} mg/L
Experiment 1	5	0.125	1.00	60	600	1.57	12.56	3.00	52.33	600	2.38
Experiment 2	5	0.200	1.00	150	910	2.62	13.10	4.55	57.58	910	2.12
Experiment 3	5	0.125	2.00	10	510	1.61	12.88	5.10	31.57	1020	3.42

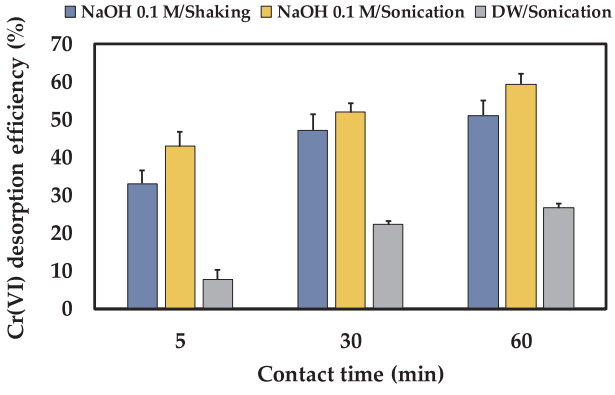

Fig. 5. The percentage of Cr(VI) desorption [Saturated MB-500 amount: 10 g/L, temperature: 22 °C, pH: without adjustment].

efficiency was also investigated using deionized water. However, desorption efficiency by deionized water on shaker was low (3.67%). Similar to our results, Cheng et al. (2011) found very low efficiency of Cr(VI) desorption by deionized water (less than 3%) and high desorption efficiency (more than 84%) by NaOH solution (Cheng et al., 2011). They concluded that Cr(VI) adsorption by chemical adsorption and ion exchange mechanisms is more steady to be desorbed during washing by deionized water

As Fig. 5 depicts, application of sonication bath improved the desorption of Cr(VI) by deionized water and 0.1 M NaOH. The percentage of Cr(VI) desorption by 0.1 M NaOH increased from 51.16 to 59.41% after 1 h of shaking and sonication, respectively. When deionized water was used as desorbent, desorption efficiency was 3.67% by shaking and 12.62% by sonication after 1 h. Increasing the desorption efficiency of Cr(VI) by ultrasound has been reported by (Jing et al., 2011). Authors explained that ultrasonic cavitation could break the affinity between adsorbate and adsorbent (Jing et al., 2011).

In all cases, desorption efficiency increased sharply as reaction time enhanced from 5 to 30 min and then slowly increased up to 60 min. It shows that the reaction of 0.1 M NaOH with saturated MB-500 is fast to desorb Cr(VI). Maximum desorption efficiency was less than 60% after 1 h, which indicated that a portion of adsorbed Cr(VI) cannot be desorbed. It might be due to the strong binding of Cr(VI) with MB-500 or reduction of Cr(VI) to Cr(III) (Bhaumik et al., 2012).

3.5. Recovery experiments

Most often, desorbent solutions for Cr(VI) are basic in nature; although, in some cases, acidic solutions are also used. After desorption process, Cr(VI) is transferred from the solid phase (saturated adsorbent) to solution (desorbent), either by basic or acidic solutions. Disposal of this solution to the environment is another problem as Cr(VI) is highly toxic. Precipitation of Cr(VI) using barium chloride can solve this problem. By dissolving this salt (barium chloride) in high concentration of Cr(VI) solution, barium ions (Ba^{2+}) react with chromate ions (CrO_4^{2-}). Consequently, barium chromate with a bright yellow color is precipitated according to the following equation (Gupta and Babu, 2009):

$$Ba^{2+} + CrO_4^{2-} \rightarrow BaCrO_4 \quad (11)$$

In this study, 91.81% of Cr(VI) was precipitated with 0.5 mM of $BaCl_2$ and this value increased to more than 97% by using 1, 2 and 5 mM of this salt (data not shown). By this reaction, chromate ions in the aqueous phase can be collected in the solid phase. The management of a tiny volume of barium chromate is easier than higher volumes of Cr (VI) solution. The other advantages include the applications of barium chromate in industries as it has greater market value as compared to barium chloride (Mikhaylov et al., 2018).

3.6. Practical implications of this study and recommendations for future work

Due to the strict environmental policies, many technologies have been tested to reduce the concentration of hazardous pollutants to the permitted levels in water. In this study, microalgal-based products have been examined for the removal of Cr(VI) from water. There are convincing answers to the question '*why microalgal-based products are potential candidate for wastewater treatment?*'. Microalgae need four main elements namely light, CO_2, water and nutrients to grow (Zhuang et al., 2018). Cultivation of microalgae can be performed reasonably by providing water and nutrients from the wastewater, CO_2 from the flue gases and sunlight. The other advantage of microalgae is their growth ability in fresh-, brackish-, marine- and even in wastewater. Microalgae do not compete with food and feed as they could grow in different types of wastewaters and unsuitable lands for agriculture (Cai et al., 2013). In addition, indoor and outdoor cultivation of microalgae throughout the year is possible. According to the findings of this study, non-living microalgal-based materials especially microalga biochar are better for the removal of Cr(VI) from water as compared to the living microalgae cells. Lab scale experiments in this study showed that Cr(VI) removal by living cells is slow and not efficient. Usually, industrial wastewaters have a high concentration of Cr(VI) and a low concentration of nutrients (phosphorous and nitrogen compounds). At the industrial scale, higher concentrations of Cr(VI) inhibit the growth of microalgae cells. Dilution of the original wastewater containing Cr(VI) is not recommended as it will contaminate more freshwater. According to the results of this study, the implementation of Cr(VI) removal from water by microalga biochar is a practical solution as it is fast and efficient (100% removal efficiency from the Cr(VI) solutions of 1, 5 and 10 mg/L after 4 h). Microalga biochar can be practically used for real wastewater treatment, as harsh conditions such as acidic pH (pH 2) or higher concentration of Cr(VI) (up to 100 mg/L in this study), did not limit its application. Microalga biochar can be used in a fixed bed column to remove Cr(VI) from wastewater in a continuous mode. Compared to living microalga cells, collecting the microalga biochar from fixed bed column after the adsorption process is easier, faster and more affordable at large scale set up. The desorption of Cr(VI) from saturated microalga biochar can be performed using appropriate eluents. Followed by desorption, the recovery of Cr(VI) from a concentrate solution is performable to precipitate Cr(VI). Desorbed and recovered Cr(VI) can be recycled in industries. Microalga biochar after desorption of Cr(VI) by an appropriate desorbing agent such as NaOH, can be reused for Cr(VI) adsorption or dispose safer.

The results of this study showed that besides all the advantages, the commercial application of microalga for Cr(VI) removal is faced with several challenges that need to be addressed before scaling up this

technology. Cr(VI) removal from wastewater by living microalga cells is limited at higher concentration of Cr(VI), pH and temperature. Harvesting of microalgae after Cr(VI) removal and the recovery of tiny amount of absorbed Cr(VI) will be highly energy consuming and not sustainable. The maximum adsorption capacity of microalga biochar in this study (25.19 mg/g) is lower than the maximum adsorption capacity that has been reported by other adsorbents in the literature. For example, the maximum adsorption capacity of polyethylenimine (PEI)-alkali-biochar was 435.7 mg/g, which was significantly higher than 23.09 mg/g, the adsorption capacity of pristine biochar (Ma et al., 2014). Therefore, physical or chemical modification of microalga biochar is necessary to improve the adsorption capacity. These methods include steam activation, acid/alkali modification and impregnation with nanoparticles, which can increase surface area, porosity and elemental compositions of modified biochar and consequently enhance adsorption capacity (Ahmed et al., 2016). In this study, microalga was cultivated in BBM solution and the harvested biomass was directly converted to biochar. It is recommended for future works to cultivate microalgae in real wastewaters, enriched with nutrients, to make the process economically feasible. In addition, pyrolysis of microalgae residue, after lipid extraction, is suggested instead of direct conversion of microalgae biomass to biochar. Finally, future research should be focused on the investigation of the potential of microalgae biochar towards Cr(VI) and other heavy metals removal from real wastewater.

4. Conclusions

Use of living microalga cells for Cr(VI) removal from wastewater was found to be neither fast nor an efficient method (67.03% removal of 1 mg/L Cr(VI) after 12 days). On the other hand, microalga biochar with fast and high removal efficiency (100% removal of 1–10 mg/L Cr (VI) after 4 h) in a wide temperature range (5–35 °C) and pH 2 was found suitable. After adsorption, Cr(VI) can be desorbed and recovered from saturated biochar by suitable eluents. Enhancement of adsorption capacity of biochar by suitable modifications and applying it in the treatment of real wastewater is recommended for future works.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2019.122064.

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