Potential use of green algae as a biosorbent for hexavalent chromium removal from aqueous solutions

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Abstract

The hexavalent chromium Cr(VI) poses a threat as a hazardous metal and its removal from aquatic environments through biosorption has gained attention as a viable technology of bioremediation. We evaluated the potential use of three green algae (Cladophora glomerata, Enteromorpha intestinalis and Microspora amoena) dry biomass as a biosorbent to remove Cr(VI) from aqueous solutions. The adsorption capacity of the biomass was determined using batch experiments. The adsorption capacity appeared to depend on the pH. The optimum pH with the acid-treated biomass for Cr(VI) biosorption was found to be 2.0 at a constant temperature, 45 °C. Among the three genera studied, C. glomerata recorded a maximum of 66.6% removal from the batch process using 1.0 g dried algal cells/100 ml aqueous solution containing an initial concentration of 20 mg/L chromium at 45 °C and pH 2.0 for 60 min of contact time. Langmuir and Freundlich isotherm equations fitted to the equilibrium data, Freundlich was the better model. Our study showed that C. glomerata dry biomass is a suitable candidate to remove Cr(VI) from aqueous solutions.

1. Introduction

Heavy metal pollutants are health hazards and health risks since they influence the metabolism and normal functioning of living cells in humans. Due to their adverse effect on biological systems, heavy metals are considered as a serious environmental problem worldwide (Lesmana et al., 2009; Kousalya et al., 2010; Módenes et al., 2010). The increased industrial activities have increased the discharge of heavy metals causing damage to ecosystems due to their accumulation in the environment. In this context, toxic metal pollutants, such as Cr(VI) deserves attention (Lesmana et al., 2009). It leaks out along with industrial waste waters into the soil, percolates down in the soil and mixes into the groundwater causing a health hazard when consumed as drinking water (Zayed and Terry, 2003). The concentration of chromium in drinking water should not exceed 0.05 mg/L (WHO, 1993). During the past few decades, the Cr(VI) levels in aquatic and terrestrial ecosystems have increased tremendously; the sources include leather tanning and finishing, dyeing, fertilizers, photography, electroplating, textile, steel, manufacturing and packaging (Zayed and Terry, 2003; Rao and Rehman, 2010; Saha and Orvig, 2010; Zhang et al., 2010).

Inhalation of vapors containing Cr(VI) particles affects the respiratory system and cause lung cancer and chronic inflammation of the bronchioles and pulmonary fibrosis (Myers et al., 2008). Moreover the inhalation and transport of materials that contain Cr(VI) are known to cause nasal septum perforation, asthma, bronchitis, pneumonia, inflammation of the larynx and trachea cancer (Gong et al., 2010; Saha and Orvig, 2010).

Cheaper and more effective techniques to clean and remediate heavy metal contaminated waters have been developed continuously. The choice of the appropriate technique depends on several factors, such as the initial metal concentration, water sanitation, capital and operational cost, as well as the environmental effects. Traditional techniques, such as the chemical precipitation, ion exchange, reverse osmosis and electrical dialysis have been used...
irrespective of their merits and demerits (Fu and Wang, 2011). In fact, traditional methods have been found to be ineffective, especially when the metal concentrations have been in the range of 1–10 mg/L. Furthermore, these techniques generate great quantities of sludge and consume great amounts of chemicals. They are also very expensive and unrealistic to be used widely in low-income countries (Gupta and Rastogi, 2008; Murphy et al., 2009; Vinod et al., 2010; Wang and Chen, 2009).

In this context, new bioremediation technologies for the removal of heavy metals need more attention. Efforts to devise and adopt biological techniques as alternatives to the physical processes have been adopted (Tien, 2002). One technique, biosorption, has shown its potential as an efficient and low-cost technology to remove heavy metal ions from wastewaters. This flexible process is capable of producing high-quality cleaned effluents. Moreover, due to the reversible adsorption process, the biosorbents used can be renewed through desorption in some cases (Gupta et al., 2017; Burakov et al., 2018).

Biosorption has some major advantages compared to the traditional techniques. It has relatively low costs, it is efficient also in diluted solutions, it minimizes the formation of chemical and/or biological sludges, it needs no nutrient addition, the biosorbent may be regenerated and it gives the possibility to recover the metals (Carmona et al., 2005; Deng et al., 2007; Vinod et al., 2010; Fu and Wang, 2011; Al-Homaidan et al., 2014, 2015, 2016; Gupta et al., 2017).

One easily available and potential group of organisms to be used as metal biosorbents is algae. Algae contain functional groups, such as sedimentation, ion exchange and membrane processes have been adopted (Tien, 2002). One technique, biosorption, has shown its potential as an efficient and low-cost technology to remove heavy metal ions from wastewaters. This flexible process is capable of producing high-quality cleaned effluents. Moreover, due to the reversible adsorption process, the biosorbents used can be renewed through desorption in some cases (Gupta et al., 2017; Burakov et al., 2018).

2. Materials and methods

2.1. Preparation of biosorbents

Three green algal taxa, namely C. glomerata, E. intestinalis and M. amoena were selected. They were collected from the watercourse of Wadi Hanifa, Riyadh city, Saudi Arabia. The algal samples were thoroughly washed with plain water followed by another wash with distilled water to remove all the adhering dirt and unwanted material and finally squeezed to remove excess water. The algal biomass was dried at room temperature for three days followed by drying in a hot air oven at 90 °C for two hours. The dried nonliving biomass particles were crushed and sieved to select particles of the desired size (<0.45 μm). The prepared samples were stored in closed plastic bags at room temperature until used (Al-Homaidan et al., 2014, 2015, 2016).

2.2. Chromium solution preparation

A stock solution of chromium (1000 mg/L) was prepared by dissolving 2.83 g of K2Cr2O7 (AnalaR Grade, BDH) in 1 L of distilled and deionized water. Serial dilutions in the range of 10–50 mg/L were prepared and used.

2.3. Factors affecting heavy metal biosorption

All biosorption experiments were conducted in 250 ml Erlenmeyer flasks with 100 ml of the metal solution. The basic experiment was with a metal concentration of 20 mg/L, pH 2.0 and one gram of algal biomass. The flasks containing the algal biomass and the chromium solution were shaken in an environmental shaker at 200 rpm, at 25 °C for 60 min. All experiments were conducted in triplicate and the results are presented as mean ± SD.

The effects of the incubation conditions: pH, the amount of used biomass, metal concentration, temperature and the contact time on the biosorption of chromium were studied by changing the basic experiment explained above. Additional experiments were performed at six different pH levels (pH 2, 3, 4, 5 and 6) by adjusting the metal solution pH using 0.1 M HCl or 0.1 M NaOH. Four different algal biomass concentrations (400, 700, 1000 and 1400 mg/100 ml), five different chromium concentrations (10, 20, 30, 40 and 50 mg/L) and three different temperatures were tested (25, 35 and 45 °C). The residual level of chromium in the flasks was measured after 30 and 60 and 90 min of incubation. All other process conditions were as in the basic experiment explained above.

2.4. Chromium analysis

After the incubation, the algal biomass in the flasks was removed by filtering the solution through 0.45 μm filter paper. The filtered solutions were measured for the chromium concentration with VARIAN Fast Sequential Atomic Absorption Spectrometer (Model AA240FS) using acetylene gas flame. The removal efficiency of chromium was calculated as removal percentage (R %) from aqueous solutions.

2.5. Isotherm adsorption

The biosorption equilibrium, i.e. the relationship of the metal concentration remaining in the solution and the concentration that adsorbed on the biomass at a constant temperature, were described with nonlinear Langmuir and Freundlich isotherm equations.

Langmuir equation: The Langmuir model suggests that the adsorption occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir isotherm is represented in the following equation:

\[ q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \]

where

- \( q_e \): the amount of metal ions adsorbed per unit volume of adsorbent (mg/g).
- \( C_e \): the metal ions remaining in solution at equilibrium (mg/L).
- \( q_{max} \) and \( K_L \) are Langmuir constants related to adsorption capacity and the energy of biosorption, respectively.
- \( K_L \): statically linked penchant for binding sites (Febrianto et al., 2009).

Freundlich Equation: The Freundlich isotherm model also suggests a monolayer sorption but with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The general form of this model is:

\[ q_e = K_f C_e^{1/n} \]

where

- \( K_f \) stands for adsorption capacity and \( n \) for adsorption intensity.
The logarithmic form of Eq. (1) is:
\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2) \]

\( K_f \): constant related to the efficiency of adsorption 1 / n: adsorption density (Febrianto et al., 2009; Wang et al., 2009).

3. Results and discussion

3.1. Effect of pH

Hydrogen ion concentration in liquids influence the transport of other ions in a given aqueous solution. Several studies have monitored the influence of pH on metal sorption. Our results (Fig. 1) indicated that pH influenced the rate of biosorption of Cr(VI). The maximum adsorption of Cr(VI) was observed at pH 2.0 for all three algal biosorbents and the biosorption efficiency declined along with the increase in pH from highly acidic (pH 2.0) to pH 6.0. At pH 2 and pH 5, the corresponding uptake yield values were found to be 55.0% and 10.1% for C. glomerata; 43.1 and 1.67% for E. intestinalis and 45.58 and 3.07% for M. amoena.

At low pH values, the biosorbent is assumed to be positively charged due to protonation. Dichromate ion acts as the anion and leads to an electrostatic attraction (Boddu et al., 2003). The occupation of the adsorption sites by anionic species, such as HCrO₄⁻, Cr₂O₇²⁻, CrO₄²⁻ and the competitiveness of the oxyanion of chromium and OH⁻ ions in the bulk may explain the decrease in the adsorption above pH 4 (Das et al., 2000; Dönmez and Aksu, 2002). These results indicate that the pH effect the solubility of metals and on the ionization state of the carboxylate, phosphate and amino groups in the cell walls of the biosorbent (Rao Popuri et al., 2007).

3.2. Effect of biomass dosage

The Cr(VI) removal increased along with the increase in the dosage of the biosorbent up to a level of 1.0 g/100 ml in the solution (Fig. 2). The removal of Cr(VI) for C. glomerata, M. amoena and E. intestinalis were found to be 55.01, 54.58 and 43.1% of Cr (VI), respectively. Each species had their highest removal at the concentration of 1000 mg/100 ml.

The removal of the metal ions increased along with the increase in biosorbent concentration up to 1.0 g/100 ml and thereafter, decreased with further increase in the concentration. The increase is probably attributed to the availability of more biosorbent and consequent larger availability of the surface area for the sorption of metal ions (Aoyama, 2003). At the highest biomass concentration, however, the formation of large blocks of adsorbent particles may have resulted in lesser surface area available for the sorption of chromium ions (Baral et al., 2006).

3.3. Effect of temperature

Temperature is an independent factor which influence greatly several metabolic processes and transport phenomenon in biological systems. In aqueous systems, the temperature influences to the transport of ions across media. Our results showed that the incubation temperature had a positive effect (Fig. 3) on the sorption process and thus the rate of removal of chromium ions increased along with the increase in the temperature from 25 °C to 45 °C. This indicates that the process of adsorption is endothermic. The percentage removal of metal ions reached 66.60, 48.07, and 53.53, respectively by C. glomerata, E. intestinalis and M. amoena at 45 °C. This observation was in agreement with that observed by other scientists (e.g. Khazami and Capart, 2005; Rajasimman and Murugaiyan, 2010), who suggested that the increase in the temperature leads to an increase in the spreading rate of adsorbed molecules on the outer layer and within the absorbent pores. It has also been suggested that a high temperature may result in low viscosity of the solution leading to an increase in the pores of the adsorbents and a consequent enhancement in the surface area.
for adsorption. Ultimately, the enhanced surface area available contribute to the spread and penetration of chromium ions inside the pores of the algae, leading to increased chromium biosorption (Rajasimman and Murugaiyan, 2010).

3.4. Effect of contact time

The equilibrium time required for the biosorption of Cr(VI) on C. glomerata, M. amoena and E. intestinalis with a biosorbent concentration of 1000 mg/100 ml at different time intervals were determined. The adsorption capacity of the biosorbent sharply increased along with increase in the contact time and attained equilibrium in 60 min for all the three algal biosorbents studied (Fig. 4). The adsorption remained constant after 60 min, which indicated saturation. Therefore, the adsorption time was set to 60 min as constant for all the experiments. The adsorption was higher at the beginning probably due to the large surface area of the biosorbent available. Once the adsorbent capacity was exhausted at the equilibrium, the uptake was controlled by the transport of the metal ions from the exterior to the interior sites of the biosorbent particles (Verma et al., 2006).

3.5. Effect of the initial metal concentration

The rate of adsorption of Cr(VI) ions increased for the initial concentration of metal ions in the range of 10 mg/l to 20 mg/l in all algae (Fig. 5). The adsorption efficiency depends on two factors. Lower concentrations of chromium ions that provide a positive force and enhances the adsorption process, and the greater number of chromium ions that results in competition for binding sites available in the biomass (Bankar et al., 2009). Increase in the chromium concentrations above 20 mg/L resulted in a gradual decline in the removal percentage. This may be due to the saturation of the binding sites (Kiran et al., 2007; Al-Homaidan et al., 2014, 2015, 2016).

3.6. Isotherm adsorption

The results obtained for the adsorption of Cr(VI) by the algal biomass according to the different equations for Langmuir and Freundlich was reconciled. Langmuir constants were determined through the chart for Ce against Ce/qe, as shown in Fig. 6. Freundlich constants can be obtained through the graph Log Ce versus Log qe as shown in Fig. 7.

Further, Table 1 summarizes the correlation coefficients and constants for the Langmuir and Freundlich equations. The correlation coefficients, $R^2$, ascertained that the data were more compatible with the Freundlich than Langmuir model.
The correlation coefficients and constants for the Langmuir and Freundlich equations.

| Algal taxa     | Langmuir       | Freundlich     |
|----------------|----------------|----------------|
|                | $Q_{max}$ (mg/g) | $R^2$ | $K_L$ (mg/g) | N | $R^2$ |
| C. glomerata   | 3.77            | 0.035          | 0.904 | 0.19 | 1.44 | 0.949 |
| E. intestinalis| 2.97            | 0.024          | 0.658 | 0.10 | 1.34 | 0.868 |
| M. amoena      | 5.64            | 0.012          | 0.218 | 0.08 | 1.12 | 0.894 |

A comparative evaluation of the biosorption efficiency calculated is presented in Fig. 8 for the three algae. It was observed that C. glomerata was the most efficient in the removal of Cr(VI) from aqueous solution, followed by M. amoena and E. intestinalis. The removal efficiency might have differed because the algal species probably have different types and amounts of functional groups available for biosorption in their cell walls.

4. Conclusions

The results indicate that the green algae, particularly C. glomerata, have immense potential to be used in applications for effective and economical removal of Cr(VI) from aqueous solutions. Algae seem to be efficient at low metal concentrations under optimal conditions. However, further investigations are warranted to scale up the studies towards field applications.

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