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Original Paper

Bio-Sorption of Cadmium, Arsenic, and Lead by Dead Sargassum Algae and Mangrove Leaves: A Green Approach for metals Removal from Aqueous Solutions Using Experimental Designs

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Abstract

In this study the ability of Mangrove leaves to bio-sorb three metal ions, namely arsenic, cadmium and lead from aqueous solutions was investigated. Removal of the metal ions by the dead biomasses was affected by experimental parameters such as pH, contact time, biomass dosage and initial metals ion concentrations. In this investigation optimization of different parameters were performed simultaneously in presence of a mixture of the three metals in aqueous solutions. The initial condition to optimize adsorption conditions to remove arsenic, lead and cadmium was consisted of 20 mg. L^{-1} metals concentrations, 10 gr. L^{-1} biomass dose, and 60 minute contact time, 25 °C environmental temperature and pH 5. The results showed that under optimized condition, the removal efficiency of arsenic, lead and cadmium were 100, 97 and 99% by Sargassum and 92, 99 and 92% by Mangrove leaves from 10 mg L^{-1} aqueous solution of the metal ions. The results demonstrated that the bio sorbent can perfectly remove the three metal ions from aqueous solutions.

Key words: Heavy Metal, Bio Sorption, Dead Bio Sorbents, Sargassum Macroalgae, Mangrove Leaves.

1- Introduction

Heavy metals, such as cadmium (Cd), lead (Pb) and arsenic (As), are known to be non-biodegradable and significantly toxic, even at low concentrations (Agah et al., 2012). These metals, introduced into the environment from both natural and anthropogenic sources, can accumulate in different trophic levels and transfer to the human body through the food chain, causing serious diseases and disorders (Environmental Protection Agency, 1999; Ulmanu et al., 2003). Therefore, the selection of an appropriate treatment method is critical from both environmental and economic points of view (Nourbakhsh et al., 2002). Biosorption using dead biomass is a method in which pollutants, such as heavy metals, are adsorbed from aqueous solutions onto adsorbents.

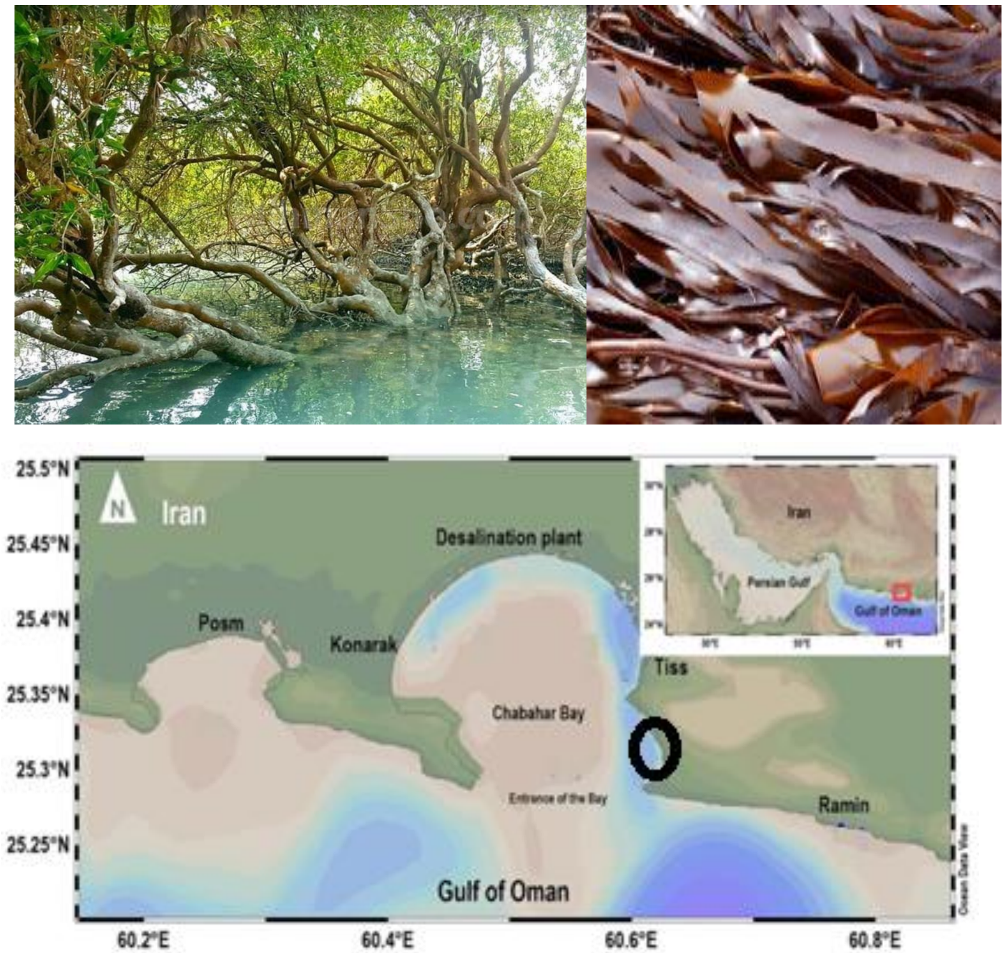
The mechanisms of bio sorption are generally based on physico-chemical interactions between metallic ions and the functional groups present on the cell surface, such as electrostatic interactions, ion exchange and metal ion chelating or complexation (Özer et al., 2005) Paknikar. Functional groups, such as carboxyl, hydroxyl, amine, sulphonate and phosphoryl groups, are present in cell wall components, such as polysaccharides, lipids and proteins (Dziwulska et al., 2004; Jayakumar & Govindaradjane, 2017).

Previous studies have investigated the use of inexpensive adsorbents, such as sawdust, for the removal of lead from aquatic environments (Abdel-Ghani et al., 2007), In India, cadmium and zinc were removed from aqueous environments using two types of rice and pea husks (Patel et al., 2013). Pine tree sawdust was also examined in Mexico for the removal of cadmium and lead (Hidalgo-Vázquez et al., 2011). The application of cheap and natural adsorbents, including carbon materials and agricultural residues, has been studied in many previous studies and suggested as alternatives to conventional technologies, such as sedimentation, ion exchange, and membrane extraction, for the removal of heavy metals.

Chabahar Bay is a semi-enclosed marine environment and as the largest bay located in the southeastern coast of the Gulf of Oman (Map 1). This bay has sensitive ecosystems such as sea grasses, Mangrove forests, coral reefs and micro and macroalgae.

During recent years over than 347 species of marine algae have been recognized and reported from this area including 167 Rhodophyta, 79 Chlorophyta, 80 Phaeophyta, 15 Cyanophyta and 6 Diatoms. Sargassume is one of the dominant macro algae in this area (map 1). Hara Forests, also known as Mangrove forests in Chabahar rise up to 5 to 10 meters, depending on their biological conditions. The mangrove tree leaves are oval shaped and always green, the upper surface of the leaves is green and its lower surface is gray (map 1).

In this research, dried brown algae (*Sargassum sp. (Phaeophyceae*)), one of the native algae of southern Iran, and dead leaf of mangrove tree (Avicennia marina) were used as non-living natural adsorbents.



Map 1- A typical sargassum macroalga and mangrove forests in the sampling area, Chabahar Bay.

The main objective of this study was to investigate the adsorption of cadmium, arsenic and lead ions from aqueous solutions using dry biomass of Sargassum algae and mangrove leaves as natural adsorbent, and to evaluate the effects of different parameters on the adsorption process. Unlike other studies that optimized different parameters for individual metals, in this investigation optimization of different parameters were performed simultaneously in presence of a mixture of the three metals in aqueous solutions.

1- Experimental

In this study, the samples of Sargasssum algae and mangrove leaves were collected by hand and spatula from bed of Chabahar port during autumn 2014 (Map 1). They were placed in plastic bags and icebox and then transferred to the laboratory for further treatments. The masses were washed with saline water (salinity of 35 psu) to remove mud and subsequently with tap and distilled water. The samples were surface-dried in laboratory condition (24℃) and then weighed before being freeze-dried (Operon bench Top Model OPR-FDB- 5503) for 24 hours.

As the adsorption capacity of natural adsorbents increases with expansion of their active level, hence the dried samples were grounded using a mill (Wagtch international) to reach the appropriate grain size. The powdered materials were used as adsorbents experiments were conducted at room temperature (Mousa et al., 2013; Raftari et al., 2011). A solution consisted of 10 ppm lead; cadmium and arsenic were prepared from the standardized samples to determine the optimal pH.

The experiments were carried out in 100 ml Erlenmeyer flasks containing 100 ml mixture of the three metal ions. Six Erlenmeyer flasks in two sets, which were consisted of 100 mL of 10 ppm individual metals, were adjusted to pH values of 4, 5 and 6, respectively. Hydrochloric acid (HCl) 2% and sodium after sieving to obtain 0.25 mm particles (250 microns mesh). All heavy metals standard solutions (1000 µg. mL^{-1}) using in this research were made by CHEM-LAB Company specialized in chemical production in Belgium.

The sorption of metal ions in aqueous solution is affected by different parameters, including pH of solution, biomass dosage, temperature, contacts time and ions concentrations. According to (Murphy et al., 2007), pH is an important parameter affecting bio sorption of heavy metals. It is revealed from literature that optimum pH is in the range of 4-6 for maximum metals bio sorption (Areco et al., 2012; Sarı & Tuzen, 2008).

In this study, initial adsorption factors were consisted of pH 5, contact time of 60 min, 3g L^{-1} biomass (mangrove leave and sargassum algae) and heavy metals (10 PPM). All hydroxide (NaOH) 0.1% normal were used for pH adjustment. 3g L^{-1} biomass was introduced to 100 mL, mixed by magnetic stirrer (200 rpm) for one hour as contact time. All processes were performed under 22 ±2 °C. To accelerate the separation of the masses from the solution, the solutions were centrifuged at 1600 rpm for 2 minutes and finally filtered under vacuum filtration system (cellulose acetate filter 0.45 micrometers). This process was performed separately for Sargassum and mangrove leaves. The eluents were analyzed by Inductively Coupled Plasma Optical

Emission Spectroscopy (ICP-OES) using the Spectro Arcos Ametek model in a laboratory that had ISO 17025 to determine residual amounts of cadmium, arsenic and lead ions. In this step the optimized pH was selected. The process was then continued to select an optimized contact time. In accordance with the basic condition and selected pH, one gr of masses were contacted with 10 ppm solutions in 10 Erlenmeyer flasks in two sets, during 10, 30, 60, 90 and 120 minutes of contact times to select an optimized contact time. Finally, the adsorptive capacity of both adsorbents was In this study, the capacity of each bio sorbent to remove the metal ions (Brahmbhatt et al., 2012) was measured by contacting one gram of biomass with 100 mL of 100 ppm individual metal ions under optimized conditions.

3- Results and Discussion

measured at concentrations of 10, 20 and 50 ppm and selected pH and contact time (Brahmbhatt et al., 2012). The masses separation process and analysis of eluents were the same as above. In all analyses, the adsorption rate was determined by subtracting the remaining concentration in the eluent from the initial concentration. All subsequent sorption experiments were carried out under magnetic stirrer (200 rpm) and at room temperature (25±1 °C) (Mousa et al., 2013; Raftari et al., 2011).

3-1 Effect of pH

The effects of pH were tested at pH values of 4, 5, 6 and 7. Figure 1 showed that optimum pH for maximum arsenic adsorption was 4 for Sargassum algae, while it was 5 for the other two elements.

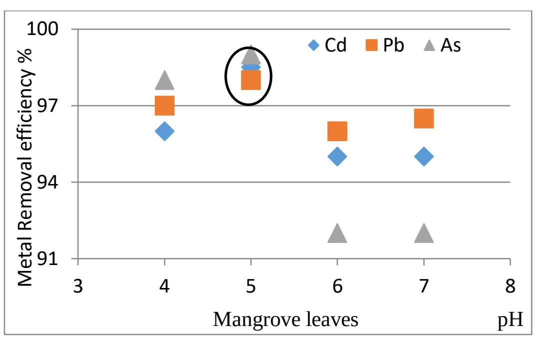


Figure 1- Effect of pH on metals removal.

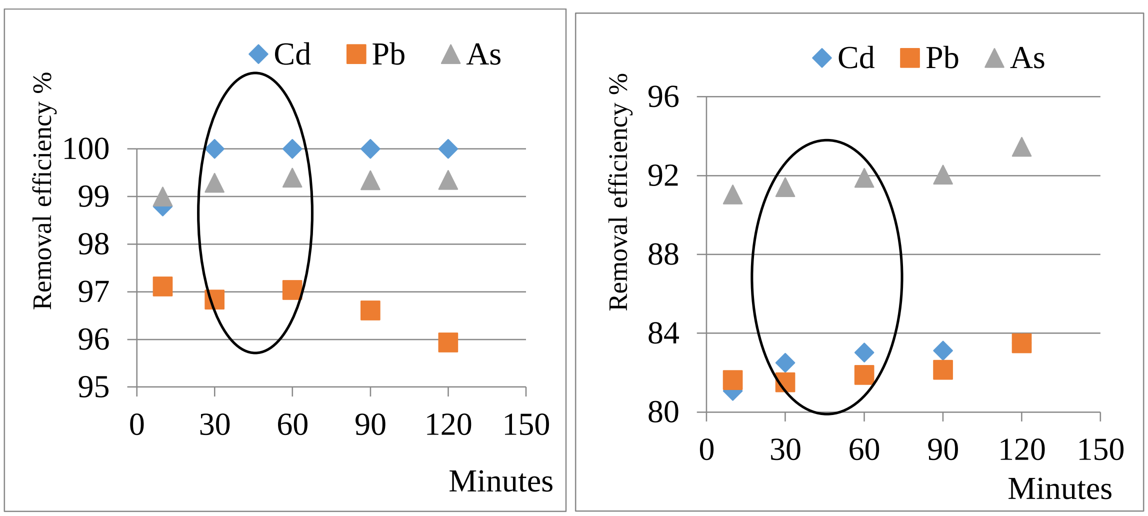
The adsorption of elements by green algal biomass was hindered at lower pH values due to increased concentration of positively charged hydrogen ions in the solution. This was because these hydrogen ions competed with metal ions for binding on the active sites (the functional groups) on the surface of the algal cell wall (Dönmez et al., 1999).

The results indicated that pH 5 was a suitable choice, as it resulted in higher removal of lead and cadmium, and also caused less corrosion, making it more appropriate for industrial applications. Therefore, pH 5 was selected as default option.

3-2 Effect of contact time

In this study, the biomass were used at a concentration of 3 gr. L^{-1} for removal of three ions (10 ppm per metal ion) during different contact times consisted of 10, 30, 60, 90 and 120 minute at pH 5. The solutions were filtered after each contact times and analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy. Statistical analysis indicated that there were no significant differences in the recovery of adsorption of the three ions at different contact times. The removal efficiency at 30 and 60 minutes was almost the same.

The results showed that the amount of each heavy metal adsorption was almost the same at 30 and 60 minutes, with relatively higher removal efficiency of arsenic and lead for Sargassum (>99% and 97%, respectively) at 60 minutes (see Figure 2).



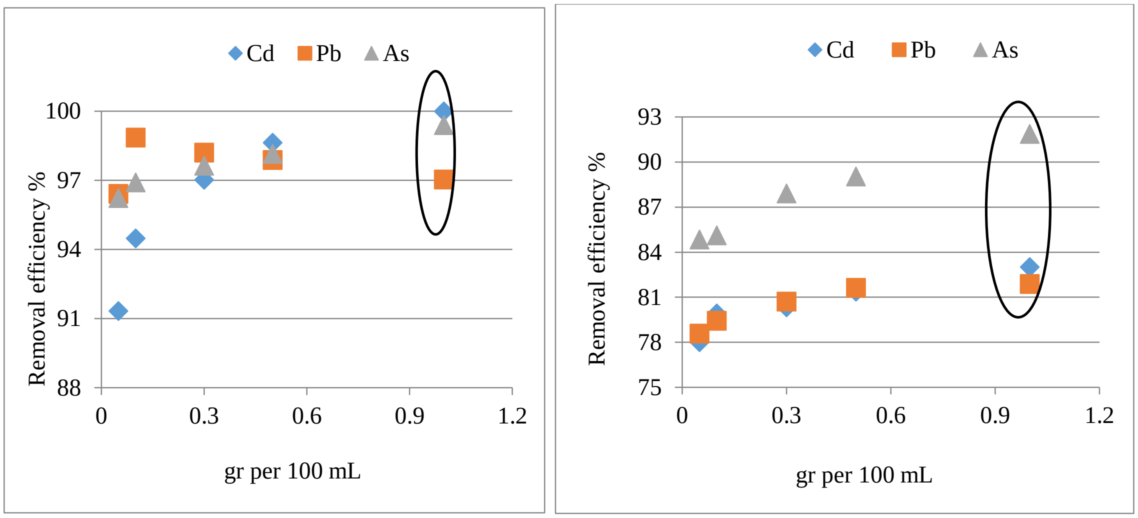
Sargassum

Mangrove leaves

Figure 2- Effect of contact time on metals removal.

3-3 Effect of sorbents dosages

The influence of different doses of bio sorbents (Sargassum and Mangrove leaves) on removal efficiency of metal ions from aqueous solution was examined using constant optimized pH and contacts time constant (5 and 60 minutes, respectively). The bio sorbents doses for simultaneously adsorption of the three ions were 0.5, 1, 3, 5 and 10 gr L^{-1} (Figure 3). The optimal amount of each adsorbent (Sargassum algae and mangrove leaves) was found to be 10 gr. L^{-1} with adsorption efficiencies of 99, 97, 100 and 92, 82, 83, respectively.



Sargassum Mangrove leaves

Figure 3- Effect of sorbents doses on metals removal.

The results indicated that the removal efficiency of heavy metals increased with increasing weight of adsorbents, which is consistent with the findings of (Abdel-Ghani et al., 2007).his increase in removal efficiency could be due to the compounds secreted from the cells.

3-4 Effect of concentration of pollutants

Several researchers (Areco et al., 2012; Ghoneim et al., 2014; Sarı & Tuzen, 2008) have reported on the effect of metal ion concentrations on the bio sorption of metals. According to these investigations, lower removal efficiency at higher concentrations was due to the saturation of binding sites (Naja & Volesky, 2006).To assess the effect of metal concentration on adsorption, different metal concentrations of 10, 20, and 50 mg/L were examined at the optimized parameters of pH 5 with 10 g/L of Sargassum and mangrove leaf bio sorbents during a 60-minute contact time (see Figure 4).

The results showed that the bio sorbents provided more than 90% removal efficiency of the three metals at concentrations of 10 ppm. At 50 ppm, the maximum and minimum adsorptions were observed for Pb and Cd by the two bio sorbents. Consistent with the findings of (Ghoneim et al., 2014; Puranik & Paknikar, 1999), our results indicated that the adsorption of cadmium ions on biomasses decreases with increasing ion concentration and their completion of adsorption.

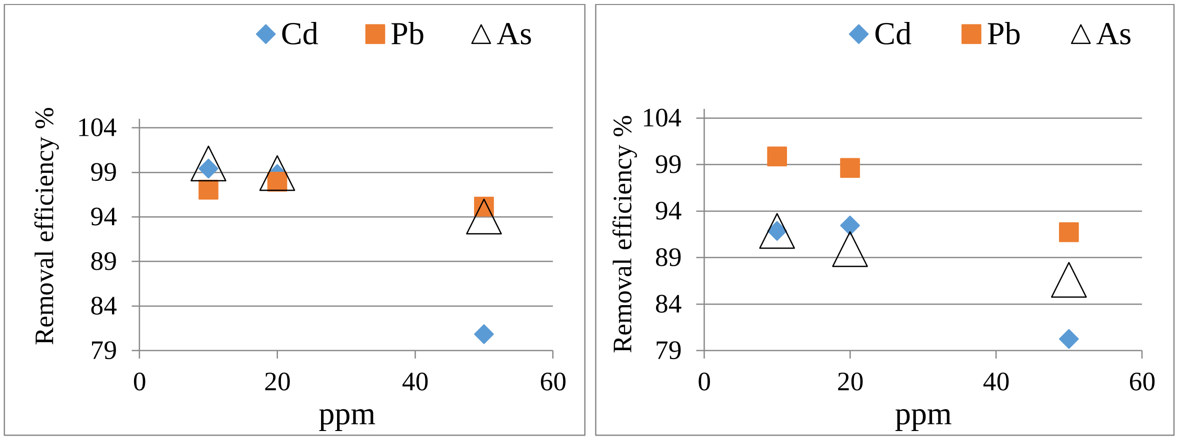


Figure 4- Effect of Initial Concentration on metals removal.

In this study, the efficiency of metals removal decreased with increasing initial concentrations of metals, which can be attributed to the lower ion exchange bands.

3-5 Effect of Temperature

In this study the effect of different temperatures (15, 25 and 35°C) on metal ion uptake capacity of the biomasses were investigated. Anova analysis indicated that there was no significant correlation between metal removal efficiency by the two bio sorbents at 15 and 35 °C (P>0.05). This result is consisted with the findings of (Lodeiro et al., 2006; Tüzün et al., 2005), which reported that metals uptak Mousa e was almost independent of temperature variation. The difference between metal removal efficiency between 15 and 35 °C was only 2%, which can be considered legible.

The precision of analysis was evaluated by comparing the metal removal efficiency under similar conditions. The precision of cadmium, lead and arsenic analysis was 99±2, 96±1 and 96±5 %, respectively.

Our results showed that under optimized condition, the minimum efficiency of simultaneously removal of the three metal ions from their 100 ppm aqueous solutions by 10 gr. L^{-1} adsorbents was 90%.

3- Conclusion

At the optimized condition of pH 5, metals concentrations of 10 mg. L^{-1}, biomass dose of 10 gr. L^{-1}, 25 °C and a contact time of 60 minute, the removal efficiency of arsenic, lead and cadmium were 100, 97 and 99% by Sargassum and 92, 99 and 92% by Mangrove leaves from 10 mg L^{-1} aqueous solution of the metal ions. Both adsorbents can be used to remove metal ions from aqueous solutions under optimized conditions, but

Sargassum macroalgae had a relatively higher adsorption capacity. This algae is a relatively economical biomass and is easily available in abundance.

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Refrences

Abdel-Ghani, N., Hefny, M., & El-Chaghaby, G. A. (2007). Removal of lead from aqueous solution using low cost abundantly available adsorbents. *International Journal of Environmental Science & Technology*, *4*(1), 67-73. https://doi.org/10.1007/BF03325963

Agah, H., Fatemi, S., & BAEYENS, W. (2012). A survey on the accumulation of trace metals in local fishermen hair from the Northern Persian Gulf.

Areco, M. M., Hanela, S., Duran, J., & dos Santos Afonso, M. (2012). Biosorption of Cu (II), Zn (II), Cd (II) and Pb (II) by dead biomasses of green alga Ulva lactuca and the development of a sustainable matrix for adsorption implementation. *Journal of hazardous materials*, *213*, 123-132. https://doi.org/10.1016/j.jhazmat.2012.01.073

Brahmbhatt, R. N., Patel, V., & Jasrai, R. (2012). Removal of cadmium, chromium and lead from filamentous alga of Pithophora sp. of industrial wastewater. *International journal of Environmental sciences*, *3*(1), 408-411. https://doi.org/10.6088/ijes.2012030131039

Dönmez, G. Ç., Aksu, Z., Öztürk, A., & Kutsal, T. (1999). A comparative study on heavy metal biosorption characteristics of some algae. *Process biochemistry*, *34*(9), 885-892. https://doi.org/10.1016/S0032-9592(99)00005-9

Dziwulska, U., Bajguz, A., & Godlewska-Żyłkiewicz, B. (2004). The use of Algae Chlorella vulgaris immobilized on cellex-T support for separation/preconcentration of trace amounts of platinum and palladium before gfaas determination. *Analytical Letters*, *37*(10), 2189-2203. https://doi.org/10.1081/AL-200026696

Environmental Protection Agency, U. (1999). Integrated Risk Information System (IRIS) on cadmium: national centre for environmental assessment. In: Office of Research and Development Washington DC.

Ghoneim, M. M., El-Desoky, H. S., El-Moselhy, K. M., Amer, A., Abou El-Naga, E. H., Mohamedein, L. I., & Al-Prol, A. E. (2014). Removal of cadmium from aqueous solution using marine green algae, Ulva lactuca. *Egyptian Journal of Aquatic Research*, *40*(3), 235-242. https://doi.org/10.1016/j.ejar.2014.08.005

Jayakumar, V., & Govindaradjane, S. (2017). Biosorption of cadmium by green algae–a review. *Journal of Advanced Chemical Sciences*, 480-484.

Lodeiro, P., Barriada, J. L., Herrero, R., & De Vicente, M. S. (2006). The marine macroalga Cystoseira baccata as biosorbent for cadmium (II) and lead (II) removal: kinetic and equilibrium studies. *Environmental pollution*, *142*(2), 264-273. https://doi.org/10.1016/j.envpol.2005.10.001

Mousa, W., Soliman, S., El-Bialy, A., & Shier, H. A. (2013). Removal of some heavy metals from aqueous solution using rice straw.

Murphy, V., Hughes, H., & McLoughlin, P. (2007). Cu (II) binding by dried biomass of red, green and brown macroalgae. *Water research*, *41*(4), 731-740. https://doi.org/10.1016/j.watres.2006.11.032

Naja, G., & Volesky, B. (2006). Multi-metal biosorption in a fixed-bed flow-through column. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *281*(1-3), 194-201. https://doi.org/10.1016/j.colsurfa.2006.02.040

Nourbakhsh, M. N., Kiliçarslan, S., Ilhan, S., & Ozdag, H. (2002). Biosorption of Cr6+, Pb2+ and Cu2+ ions in industrial waste water on Bacillus sp. *Chemical Engineering Journal*, *85*(2-3), 351-355.

Özer, A., Özer, D., & İbrahim Ekİz, H. (2005). The equilibrium and kinetic modelling of the biosorption of copper (II) ions on Cladophora crispata. *Adsorption*, *10*(4), 317-326. https://doi.org/10.1007/s10450-005-4817-y

Patel, K. P., Tank, S., Patel, K. M., & Patel, P. (2013). Removal of cadmium and zinc ions from aqueous solution by using two type of husks. *APCBEE Procedia*, *5*, 141-144. https://doi.org/10.1016/j.apcbee.2013.05.025

Puranik, P., & Paknikar, K. (1999). Biosorption of lead, cadmium, and zinc by Citrobacter strain MCM B-181: Characterization Studies. *Biotechnology progress*, *15*(2), 228-237. https://doi.org/10.1021/bp990002r

Raftari, H., Moazami, H., Ganjidoust, H., & Ayati, B. (2011). Effects of natural absorbents on copper and lead removal.

Sarı, A., & Tuzen, M. (2008). Biosorption of Pb (II) and Cd (II) from aqueous solution using green alga (Ulva lactuca) biomass. *Journal of hazardous materials*, *152*(1), 302-308. https://doi.org/10.1016/j.jhazmat.2007.06.097

Tüzün, I., Bayramoğlu, G., Yalçın, E., Başaran, G., Çelik, G., & Arıca, M. Y. (2005). Equilibrium and kinetic studies on biosorption of Hg (II), Cd (II) and Pb (II) ions onto microalgae Chlamydomonas reinhardtii. *Journal of Environmental Management*, *77*(2), 85-92. https://doi.org/10.1016/j.jenvman.2005.01.028

Ulmanu, M., Marañón, E., Fernández, Y., Castrillón, L., Anger, I., & Dumitriu, D. (2003). Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material adsorbents. *Water, air, and soil pollution*, *142*(1), 357-373. https://doi.org/0.1023/A:1022084721990