Asian Journal of Water, Environment and Pollution, Vol. 19, No. 2 (2022), pp. 63-69.
DOI 10.3233/AJW220025

Chlorophycean Micro Alga as a Potential Bioremediant: An Investigative Study Using Carbendazima Group C Carcinogenic Fungicide

Sulakshana Karkala[1,2], Michelle Rodrigues[3], Sachin Patavardhan[2], Leo D'Souza[2] and Shashi Kiran[2]*

[1]Department of Biotechnology, Mangalore University, Mangalore, India
[2]Laboratory of Applied Biology, St. Aloysius College, Mangalore, Karnataka, India
[3]Department of Biological Sciences, University of Toronto, Toronto, Canada
✉ skirannivas@gmail.com

Received February 6, 2021; revised and accepted September 17, 2021

Abstract: Agro-pollution caused by persistent pesticides is an increasing environmental concern. The misuse of pesticides resulting in reduced clearance has prompted an urgent need for developing removal methods. In this regard, biosorption using algae is an attractive option. Algal biomass has been an effective demonstrator of heavy metal bioremediation. Carbendazim is a systemic pesticide used in controlling plant diseases. It has been reported to show nematicide effects making it severely toxic to earthworms. It is a classified Group C Human Carcinogen because it causes chromosomal loss and non-disjunction in mammalian reproductive cells. This investigation estimates the biosorption efficiency of lyophilised chlorophycean *Chlorella thermophila* (Accession number: MN006612) biomass on carbendazim. Bio-adsorption has shown to increase with pH, showing maximum adsorption at pH 10.

Key words: Carbendazim, chlorophycean, biosorption, carcinogen, bioremediant.

Introduction

High global demand for food crops has led to increased agricultural productivity. The disproportionate agricultural output is facilitated by increased use of pesticides with a slow clearance rate resulting in their accumulation in the soil or water table as well as their exposure to the general population (Trunelle et al., 2014). The available treatment options like membrane filtration, hydrogen peroxide treatment and ozone treatment are not designed to trap and remediate complex organic molecules (Ardal, 2014; Naturvardsverket, 2008; Zaini et al., 2010). Agro-pollution caused by the slow dissolution of pesticides is an environmental concern. While the emphasis is being put on the reduced use of such pesticides, other methods such as bioremediation must be employed to facilitate resource cleanup. The misuse of pesticides resulting in low clearance and high toxicity has led to an urgent need for efficient removal methods.

Carbendazim (methyl-2-benzimidazole carbamate) is a common systemic pesticide, intended for controlling plant diseases (National Research Council Regulating Pesticides in Food, 1987). Carbendazim is also a decomposition product of benomyl and thiofanate pesticides (Gadd, 2009; Laurella et al., 2015; Massoud, 2008). It has shown nematicide effects making it severely toxic to insects (International Programme on Chemical

*Corresponding Author

Safety, 1993). It is a classified Group C Possible Human Carcinogen (US Environmental Protection Agency USEPA, 2018) since it causes chromosomal loss and non-disjunction in mammalian reproductive cells (Aire et al., 2005). Pesticide persistence is correlated to its capacity to be disintegrated via lysis (Ardal, 2014; PPDB 2014). Carbendazim (half-life:6-25 weeks) (Andrade et al*.,* 2016) has been shown to stay intact for up to a week at a near-neutral pH (Al-Ebaisat, 2011) rendering it a persistent water pollutant.

Natural biosorbents are gaining an upper hand in bioremediation technology. They are competent, innocuous and inexpensive (Bulgariu, 2017). They require minimal prepping, release no harmful chemicals, are recyclable, renewable and offer excellent retention support (Bilal 2017; Bule, 2018; Bulgariu 2017; Centella, 2017; Davis, 2003; Donmes, 1999; Romera, 2007). Biosorption using algae is an attractive option due to its low cost, high efficiency, minimisation of secondary wastes and environmentally friendly approach (Utomo et al., 2016). Biosorption using dead biomass is advantageous since it is not governed by physiological conditions or limited by toxicity (Aksu, 1998). Algal biomass can effectively remediate heavy metals (Mehta and Gaur, 2005; Monteiro et al., 2012; Rath, 2012; Utomo et al*.,* 2016), heavy radionuclides (Bule, 2018; Pohl, 2006), accumulate arsenic, gold, silver (Cerniglia, 1993; Mata, 2009) and pesticides (Sibi, 2014; Tam et al., 2002; Tsang et al., 1999). *Chlorella* has been extensively cultivated in a variety of nutritive modes. This belongs to the class chlorophycean and has been investigated for its biosorption and bioaccumulation properties, in remediating heavy metals and organic compounds (Aksu and Donmes, 2006; Tam et al., 2002; Tsang et al., 1999). The organism used in our study is a novel species, *Chlorella thermophila* (Accession Number: MN006612), isolated from a saline water reservoir in Mangalore, India. Preliminary investigation of this organism has confirmed its resilient growth in varying pH, temperature and salinity. The focus of this investigation was to estimate the biosorption efficiency of lyophilised, *Chlorella thermophila* (Accession Number: MN006612), biomass on carbendazim using high performance liquid chromatography (HPLC). Adsorbent dosage, the effect of pH, concentration and temperature on adsorption were studied. The experimental data were fitted into adsorption isotherms. We confirm that this is the first applicative report of *Chlorella thermophila* as an effective bioremediate, from India.

Materials and Methods

Preparation of Powder Adsorbent-Adsorbate

Axenic cultures of *Chlorella thermophila* (GenBank accession Number: MN006612) were obtained from the Laboratory of Applied Biology, St Aloysius College, Mangalore, India. The strain was isolated from a freshwater pond in Surathkal lighthouse, Mangalore (13.0060 °N, 74.7897 °E). They were cultured in Blue Green 11 Medium (Andersen et al. 2005) at 27±1 ^{o}C, 16:8 light: dark cycle. Algal cells were harvested after 45-days by centrifuging at 10,000 RPM for 10 minutes. The cell pellet was washed twice with deionized water, air-dried and subsequently lyophilised (Operon FDB-5003).

A stock solution of carbendazim (5000 ppm) was prepared by dissolving 50 g carbendazim in 50ml mobile phase (HPLC grade water (Mili-Q type-1): Merck HPLC Grade Methanol; Ratio:8.5:1.5). Further experimentation was performed at the required dilution.

Optimisation of Adsorbent Dosage- Carbendazim Adsorption

About 20-100 mg of lyophilised algal powder was added to carbendazim solutions of 10-50 ppm (1 ml volume each) and shaken at 200 RPM (24 hours, 30 ^{o}C). Post adsorption, the sample was subjected to centrifugation at 12000 RPM for 15 mins at 0ºC. The supernatant was analysed using Waters HPLC system equipped with Waters 515 pump, 2489 UV-Vis detector and Rheodyne injector module. The separation was done through Sunfire C-18 column (5 µm, 4.6 × 250 mm) with 1ml/min flow rate using HPLC grade water (Mili-Q type-1): HPLC grade methanol in 8.5:1.5 ratio as mobile phase. The detector was set to 280 nm and 320 nm. Data acquisition was done by Empower 2 software (Waters Corp.) and analysed for the percentage removal of carbendazim. The concentration of carbendazim abstracted was calculated as follows:

% removal of carbendaziem = $[(Ci - C_e)/C_i \times 100$ (Shanti and Selvarajan, 2012) (1)

$$q = [(C_i - C_e)/(V/\mathrm{m})]$$

(Kucuker et al., 2017; Kumar et al., 2018) (2)

where

q: carbendazim adsorbed (in mg/g)

C_{i}: Initial concentration of carbendazim in solution (mg/L)

C_{e}: final concentration of carbendazim in solution (mg/L)

V: carbendazim (Volume in litre)
m: Weight of algal adsorbent (in grams)

Effect of pH on Adsorption

The study on the effect of pH on biosorption was done by adding 100 mg of lyophilised MN006612 algal powder to 1 ml 50 ppm carbendazim solution set to pH of 2-10. pH was adjusted using 1N HCl or 1N NaOH. Samples were maintained as mentioned in section—Optimisation of Adsorbent Dosage–Carbendazim Adsorption, centrifuged and the supernatant was analysed.

Study of Temperature on Carbendazim Adsorption Process

Temperature studies were carried out by examining percentage adsorption at temperatures ranging from 0°C to 50°C. About 100 mg of lyophilised algal powder was added to 1 ml 50 ppm of carbendazim solution, vortexed well and kept for 24 hours at the respective temperatures. Post adsorption, the sample was analysed as above.

The standard free energy (ΔG^o) was calculated as per Albadarin et al. (2012):

$$\Delta G° = -RT \ln K_c \quad (3)$$

K_c: Thermodynamic equilibrium constant

$$K_c = q_e/C_eK_c = q_e/C_e \quad (4)$$

q_e: equilibrium concentration of carbendazim adsorbed (mg/L)

C_e: Equilibrium concentration of carbendazim in solution (mg/L)

Equilibrium Study of Carbendazim Adsorption on Lyophilised Microalga Bioadsorbent Powder

About 20-100 mg of lyophilised MN006612 was suspended in 1ml solutions of 10-50 ppm carbendazim. Each tube was shaken at 200 RPM for 24 hours at 30 °C and adsorption was measured. The results were fitted into the Langmuir-Freundlich isotherm models.

The linear form of the Langmuir equation (Dada et al., 2012; Kucuker et al., 2017) is:

$$(1/qe) = [(1/bqmC_e) + (1/qm)] \quad (5)$$

C_e: Equilibrium concentration of carbendazim (mg/L)

q_m: Maximum amount of carbendazim adsorbed per unit weight of adsorbent (slope of $1/q_e$ Vs $1/C_e$ plot)

b: Adsorbate-adsorbent complex dissociation coefficient (intercept of 1/qe Vs 1/Ce plot)

Separation factor (R_L) was calculated by the following equation (Kumar et al., 2018):

$$R_L = 1/(1 + bC_i)\ R_L = 1/(1 + bCi) \quad (6)$$

b: complex dissociation coefficient

C_i: Initial concentration of carbendazim in solution (mg/L)

The Freundlich isotherm equation is as follows:

$$\log qe = \log Kf + 1/n \log Ce \text{ (Wang et al., 2010)} \quad (7)$$

K_f: Freundlich constant indicative of relative adsorption capacity of adsorbate

n: Freundlich coefficient representing deviation from linearity of adsorption

Both of the above are calculated by plotting log q_e Vs log C_e

Statistics and Data Analysis

Triplicate studies were performed. Data analysis was done using Graph Pad Prism 6 and Microsoft Excel. Graphical data has been represented as mean ± SD.

Results

Optimisation of Adsorbent Dosage- Carbendazim Adsorption

Figure 1 shows the effect of different adsorbent doses on increasing adsorbate doses for 24 hours. A relationship between concentrations of adsorbate-adsorbent doses and effective removal of adsorbate is established. As the adsorbent dose increases, the effective removal of adsorbate also increases, linearly. The same can be seen

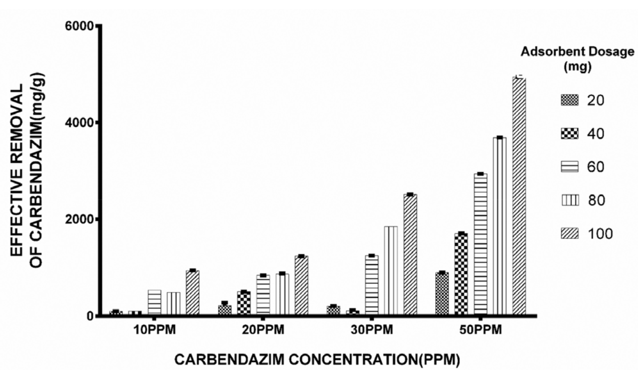

Figure 1: Effect of adsorbent dosage- carbendazim adsorption (adsorbate concentration: 10-50 ppm; time:24 Hours; T:28 °C) (*N*=3).

with the increase in adsorbate concentration. At a lower concentration of carbendazim, the effective removal by adsorbent is almost uniform. A marked difference of removal can be seen at higher concentrations of both adsorbate and adsorbent. The highest effective removal of carbendazim was seen at 100 mg of adsorbent and 50 ppm of carbendazim.

Effect of pH on Adsorption

Figure 2 shows the influence of pH variation versus the percentage of adsorption. The percentage of carbendazim adsorbed decreased with an increase in the pH. The percentage of adsorption by the microalgal biosorbent was highest at pH 2. It steadily decreased and was lowest at pH 8.

Effect of Temperature on Adsorption:

Biosorption was found to be inversely proportional to temperature. Biosorption increased with a decrease in temperature as seen in Figure 3. It is optimal between

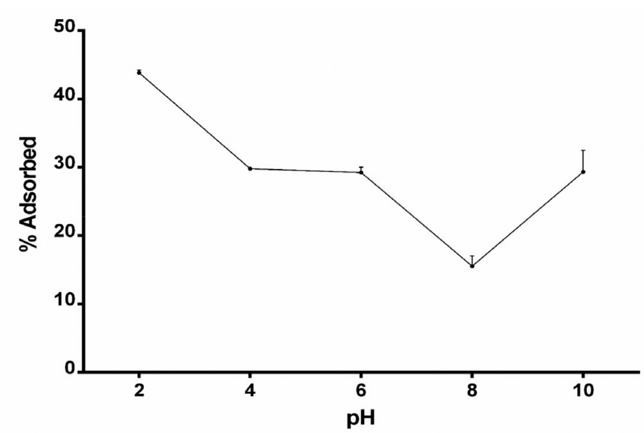

Figure 2: Effect of pH on adsorption (24 hours; 28 °C) maximum adsorption seen at pH 2 for 50 ppm of adsorbate on 100 mg of adsorbent (*N*=3).

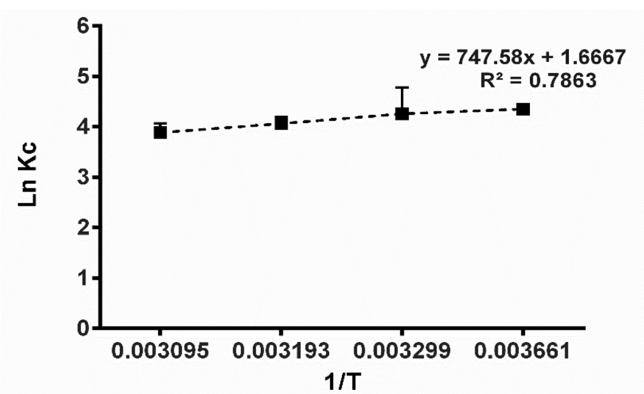

Figure 3: Adsorption of carbendazim on microalgal biomass is inversely proportional to the temperature. Lower the R^2 value, adsorption is considered spontaneous (*N*=3).

0 °C and 30 °C. Values of standard free energy (ΔG^o) were negative.

Adsorption Isotherms

Adsorption parameters were fitted into the Langmuir and Freundlich isotherms. Adsorption constant ‘b’ was found to be 2.15, 2.07 and 4.19 L/g for the adsorbent doses of 60 mg, 80 mg and 100 mg, respectively. RL values ranged from 0.02 to 0.04. The Freundlich parameter ‘*n*’ was between 1.5-2.85.

Discussion

Optimisation of Adsorbent Dosage—Carbendazim Adsorption

Biosorption is a passive integrated process involving metabolically independent reactions, surface adsorption and complexation, ion exchange and precipitation (Ardal, 2014). Microalgae can affix to organic, hydrophobic compounds (Casserly et al., 1983). A multitude of factors affects this. One of them is the adsorbent-adsorbate dosage ratio. Yapar et al. (2005) stated that increased concentrations of adsorbent increase the overall adsorption achieved, regardless of the initial concentration of the adsorbate. Our results show a marked increase in adsorption linearly across the different treatments. Maximum adsorption of carbendazim was seen with the highest adsorbent-adsorbate dosage ratio. Secondly, contact time affects the degree of biosorption. Increasing the contact time increases adsorption upto optimal time. Post this, the adsorption curve hits a plateau of constancy as confirmed by Ibrahim (2011, 2016). Different biosorbents tend to have different optimal absorption peaks, with microalgae having a range of 60-300 minutes (Ahamad, 2018; Ibrahim, 2011).

Effect of pH on Adsorption

Algal biosorption is pH-dependent with acidic conditions encouraging biosorption (Aksu and Donmes, 2006; Mehta and Gaur, 2005). Surface functionality varies with the charging of the surface functional groups. These fluctuate with protonation or deprotonation (Yang et al., 2004). At higher pH, surface operational groups like amines and carboxyl groups undergo deprotonation, augmenting electrostatic attraction (Ahamad, 2018; Bilal, 2018; Kumar, 2006; Jiang, 2017). A mild variation in pH causes an increase in the biosorption process; however high pH can negatively affect the process and result in precipitation (Wang, 2006). In the natural environment, pH can influence the sorption of pesticides to the soil (Ardal, 2014). Our studies showed that variation in pH affected the adsorption of carbendazim onto the lyophilised biomass. Maximum adsorption was seen at pH 2 for 50 ppm of adsorbate on 100 mg of adsorbent. Gondar et al. (2013) proved a correlation between decreasing pH and increased sorption of hydrophilic pesticides. It is noted that the adsorption of carbendazim on lyophilised *Chlorella thermophila* (Accession number: MN006612) decreased with an increase in pH (Figure 2). This can be attributed to alkali hydrolysis of carbamates creating an inactive form of the pesticide (Schilder, 2008). Alternatively, higher pH can lead to hydroxide anion complexation (Bilal, 2018; Jiang, 2017). It is also recorded that the solubility of carbendazim decreases with increased pH (International Programme on Chemical Safety 1993).

Effect of Temperature on Adsorption

Biosorption is heavily impacted by temperature changes (Romera, 2007). Thermovariance causes disparity in thermodynamic parameters, triggering an overall deviation in biosorption (Zeraatkar, 2016). The effect of temperature on the biosorption process is nature dependent; exothermic processes slow down biosorption when under the influence of higher temperature. Heightened temperature results in photo-oxidative damage to the benzene ring of carbendazim, causing abiotic degradation (International Programme on Chemical Safety, 1993). The temperature increase may also result in denaturation of the biosorbent (Ahamad, 2018). Our studies have also shown that biosorption is optimal between 0 ^oC to 30 ^oC. Higher temperatures show a slight decline in biosorption.

Adsorption Isotherms

Langmuir Isotherm models describe monolayer adsorption (Jiang et al., 2017). Lower values of b indicate a smaller radius of the adsorbent. As the R^2 value approaches 1, adsorption is considered spontaneous. The data obtained for ΔG^o (Table 1) confirm the spontaneous adsorption of the adsorbate on the adsorbent. Carbendazim adsorption on adsorbent fits into the Langmuir isotherm model (Supplementary information file SI 1). For promising adsorption, separation factor R_L must be between 0-1 (Kumar et al., 2018). The R_L values obtained are between 0.02 to 0.04, thus proving that adsorption on lyophilised *Chlorella thermophila* is favourable. The Freundlich isotherm models describe multilayer heterogeneous adsorption (Jiang et al., 2017). The experimental data were best fitted to the Freundlich isotherm. The Freundlich parameter '*n*' is a suggestive value of multi-layered adsorption favourability (Supplementary information file SI 2). Value of '*n*' ranged from 1.5 to 2.84, indicating that carbendazim-*Chlorella* adsorption is a physio-process. From the isotherm data, it can be noted that carbendazim-*Chlorella* adsorption occurs as complex mono-multilayer adsorption.

Table 1: Values of ΔG^o at various temperatures confirming that carbendazim-adsorbent adsorption is spontaneous

Temperature (K)	*ΔG^o(KJ)*
273.15	-9.886
303.15	-9.679
313.15	-9.232
323.15	-8.829

Conclusion

Pesticide residues accumulate in agro-run off and the water table (Rath, 2011; Tikou et al., 1996) Globally, microalgal bioremediative methods are being explored as a feasible and eco-friendly alternative to traditional methods (Zaini et al., 2010). Lyophilised biomass of chlorophyceaen is a potentially cheaper alternative bioremediate for carbamate pesticides. An optimised adsorbent dose of 100 mg, in the pH range of 2-6, at temperatures between 0-50 ^oC has shown to effectively cause a percentage removal of carbendazim up to 94%. Adsorption onto the adsorbent is fitted well into the Langmuir and Freundlich isotherms, thus confirming both monolayer and multilayer adsorption of the adsorbate, proving it to be a favourable alternative to other inorganic substitutes. This is per the studies that have confirmed the sustainable and low cost bioremediation technology using *Chlorella* and other microalgal species for the removal of pesticides.

Acknowledgement

This project was carried out as part of a minor research grant Sanction number 2106-MRP/15-16/KAMA002/UGC-SWRO granted to Dr Shashi Kiran from the University Grants Commission, Delhi. We acknowledge the support meted out by the Bartena Foundation and Mangalore Jesuit Educational Society, Mangalore.

Supplementary Information

Langmuir (SI 1) and Freundlich (SI 2) isotherms are available as supplementary information files.

Conflict of Interest

The authors declare no conflict of interests.

References

Ahmad, A., Bhat, A.H. and A. Buang (2018). Biosorption of transition metals by freely suspended and Ca-alginate immobilised with *Chlorella vulgaris*: Kinetic and equilibrium modeling. *Journal of Cleaner Production*. **171:** 1361-1375.

Aire, T.A. (2005). Short-term effects of carbendazim on the gross and microscopic features of the testes of Japanese quails (*Coturnix japonica*). *Anatomy and Embryology,* **210(1):** 43-49.

Aksu, Z. (1998). Biosorption of heavy metals by microalgae in batch and continuous systems. *In: Wastewater treatment with algae*. Springer, Berlin, Heidelberg. pp. 37-53.

Aksu, Z. and G. Dönmez (2006). Binary biosorption of cadmium (II) and nickel (II) onto dried *Chlorella vulgaris*: Co-ion effect on mono-component isotherm parameters. *Process Biochemistry*, **41(4):** 860-868.

Albadarin, A.B., Mangwandi, C., Ala'a, H., Walker, G.M., Allen, S.J. and M.N. Ahmad (2012). Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent. *Chemical Engineering Journal,* **179:** 193-202.

Al-Ebaisat, H. (2011). Determination of some benzimidazole fungicides in tomato puree by high performance liquid chromatography with SampliQ polymer SCX solid phase extraction. *Arabian Journal of Chemistry,* **4(1):** 115-117.

Andersen, R.A. (2005). *Algal culturing techniques*. Elsevier.

Andrade, T.S., Henriques, J.F., Almeida, A.R., Machado, A.L., Koba, O., Giang, P.T. and I. Domingues (2016). Carbendazim exposure induces developmental, biochemical and behavioural disturbance in zebrafish embryos. *Aquatic Toxicology*, **170:** 390-399.

Ardal, E. (2014). Phycoremediation of pesticides using microalgae. Swedish University of Agricultural Sciences.

Bilal, M., Rasheed, T., Ahmed, I., Iqbal, H.M.N. and E.G. Sada (2017). High-value compounds from microalgae with industrial exploitability—A review. *Front Biosci.*, **9:** 319-342.

Bilal, M., Rasheed, T., Sosa-Hernández, J.E., Raza, A., Nabeel, F. and H. Iqbal (2018). Biosorption: An interplay between marine algae and potentially toxic elements—A review. *Marine Drugs*, **16(2):** 65.

Bule, M.H., Ahmed, I., Maqbool, F., Bilal, M. and H.M.N. Iqbal (2018). Microalgae as a source of high-value bioactive compounds. *Front. Biosci (Sch. Ed.).*, **10:** 197-216.

Bulgariu, L and D. Bulgariu (2017). Sustainable utilization of marine algae biomass for environmental bioremediation. *In: Prospects and Challenges in Algal Biotechnology*. Springer, Singapore. pp. 179-217.

Casserly, D.M., Davis, E.M., Downs, T.D. and R.K. Guthrie (1983). Sorption of organics by Selenastrum capricornutum. *Water Research*, **17(11):** 1591-1594.

Centella, M.H., Arévalo-Gallegos, A., Parra-Saldivar, R. and H.M. Iqbal (2017). Marine-derived bioactive compounds for value-added applications in bio-and non-bio sectors. *Journal of Cleaner Production*, **168:** 1559-1565.

Cerniglia, C.E. (1993). Biodegradation of polycyclic aromatic hydrocarbons. *Current Opinion in Biotechnology*, **4(3):** 331-338.

Dada, A.O., Olalekan, A.P., Olatunya, A.M. and O. Dada (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. *IOSR Journal of Applied Chemistry*, **3(1):** 38-44.

Davis, T.A., Volesky, B. and A. Mucci (2003). A review of the biochemistry of heavy metal bio sorption by brown algae. *Water Research*, **37(18):** 4311-4330.

Dönmez, G.Ç., Aksu, Z., Öztürk, A. and T. Kutsal (1999). A comparative study on heavy metal bio sorption characteristics of some algae. *Process Biochemistry*, **34(9):** 885-892.

Gadd, G.M. (2009). Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, **84(1):** 13-28.

Gondar, D., López, R., Antelo, J., Fiol, S. and F. Arce (2013). Effect of organic matter and pH on the adsorption of metalaxyl and penconazole by soils. *Journal of Hazardous Materials*, **260:** 627-633.

Ibrahim, W.M. (2011). Biosorption of heavy metal ions from aqueous solution by red macroalgae. *Journal of Hazardous Materials*, **192(3):** 1827-1835.

Ibrahim, W.M., Hassan, A.F. and Y.A. Azab (2016). Biosorption of toxic heavy metals from aqueous solution by Ulva lactuca activated carbon. *Egyptian Journal of Basic and Applied Sciences*, **3(3):** 241-249.

International Programme on Chemical Safety (1993). Environmental Health Criteria 149 Carbendazim. IPCS INCHEM DATABASE. [Accessed 14 March 2019]. http://www.inchem.org/documents/ehc/ehc/ehc149.html.

Jiang, L., Zhou, W., Liu, D., Liu, T. and Z. Wang (2017). Biosorption isotherm study of Cd^{2+}, Pb^{2+} and Zn^{2+} bio sorption onto marine bacterium *Pseudoalteromonas* sp. SCSE709-6 in multiple systems. *Journal of Molecular Liquids*, **247:** 230-237.

Kucuker, M.A., Wieczorek, N., Kuchta, K. and N.K. Copty (2017). Biosorption of neodymium on *Chlorella vulgaris* in aqueous solution obtained from hard disk drive magnets. *PloS One*, **12(4):** e0175255

Kumar, K., Patavardhan, S., Lobo, S. and R. Gonsalves (2018). Equilibrium study of dried orange peel for its efficiency in removal of cupric ions from water. *International Journal of Phytoremediation*, **20(6):** 593-598.

Kumar, Y.P., King, P. and V.S.R.K. Prasad (2006). Removal of copper from aqueous solution using Ulva fasciata sp.-a marine green alga. *Journal of Hazardous Materials*, **137(1):** 367-373.

Laurella, S.L., Pis Diez, C.M., Lick, I.D., Allegretti, P.E. and M.F. Erben (2015). Evaluation of silica as an adsorbent for carbendazim from aqueous solutions. *International Journal of Engineering and Technical Research*, **3(2):** 96-101.

Massoud, A.H., Derbalah, A.S. and E.S.B. Belal (2008). Microbial detoxification of metalaxyl in aquatic system. *Journal of Environmental Sciences*, **20(3):** 262-267.

Mata, Y.N., Torres, E., Blazquez, M.L., Ballester, A., González, F.M.J.A. and J.A. Munoz (2009). Gold (III) bio sorption and bioreduction with the brown alga Fucus vesiculosus. *Journal of Hazardous Materials*, **166(2-3):** 612-618.

Mehta, S.K. and J.P. Gaur (2005). Use of algae for removing heavy metal ions from wastewater: Progress and prospects. *Critical Reviews in Biotechnology*, **25(3):** 113-152.

Monteiro, C.M., Castro, P.M. and F.X. Malcata (2012). Metal uptake by microalgae: Underlying mechanisms and practical applications. *Biotechnology Progress*, **28(2):** 299-311.

National Research Council (1987). *Regulating pesticides in food: The Delaney paradox*. National Academies Press.

Naturvårdsverket (2008). Avloppsreningsverkensförmågaatt ta hand om läkemedelsresterochandrafarligaämnen. Report 5794. [Accessed on 5 April 2020].http://www.naturvardsverket.se/Documents/publikationer/620-5794-7.pdf.

Pohl, P. and W. Schimmack (2006). Adsorption of radionuclides (134 Cs, 85 Sr, 226 Ra, 241 Am) by extracted biomasses of cyanobacteria (*Nostoc Carneum, N. Insulare, Oscillatoria Geminata* and *Spirulina Laxis-Sima)* and *phaeophyceae (Laminaria Digitata* and *L. Japonica:* Waste products from alginate production) at different pH. *Journal of Applied Phycology*, **18(2):** 135-143.

PPDB (Pesticide Properties Data Base). United Kingdom. [Accessed on 07 July 2020] https://sitem.herts.ac.uk/aeru/ppdb/ .

Rath, B. (2012). Microalgal bioremediation: Current practices and perspectives. *Journal of Biochemical Technology*, **3(3):** 299-304.

Romera, E., González, F., Ballester, A., Blázquez, M.L. and J.A. Munoz (2007). Comparative study of bio sorption of heavy metals using different types of algae. *Bioresource Technology*, **98(17):** 3344-3353.

Schilder, A. (2008). Effect of water pH on the stability of pesticides. Michigan State University MSU Extension. [Accessed 10 March 2019]. https://www.canr.msu.edu/news/effect_of_water_ph_on_the_stability_of_pesticides.

Shanthi, T. and V.M. Selvarajan (2012). Removal of Cr (VI) and Cu (II) ions from aqueous solution by carbon prepared from henna leaves. *Journal of Chemistry* **2013:** 1-6.

Sibi, G. (2014). Biosorption of arsenic by living and dried biomass of fresh water microalgae-potentials and equilibrium studies. *Journal of Bioremediation & Biodegredation.* **5(6):** 1.

Tam, N.F., Chong, A.M.Y. and Y.S. Wong (2002). Removal of tributyltin (TBT) by live and dead microalgal cells. *Marine Pollution Bulletin*, **45(1-12):** 362-371.

Tikoo, V., Shales, S.W. and A.H. Scragg (1996). Effect of pentachlorophenol on the growth of microalgae. *Environmental Technology*, **17(10):** 1139-1144.

Trunnelle, K.J., Bennett, D.H., Ahn, K.C., Schenker, M.B., Tancredi, D.J., Gee, S.J. and B.D. Hammock (2014). Concentrations of the urinary pyrethroid metabolite 3-phenoxybenzoic acid in farm worker families in the MICASA study. *Environmental Research*, **131:** 153-159.

Tsang, C.K., Lau, P.S., Tam, N.F.Y. and Y.S. Wong (1999). Biodegradation capacity of tributyltin by two Chlorella species. *Environmental Pollution*, **105(3):** 289-297.

US EPA (2018). Chemicals Evaluated for Carcinogenic Potential Office of Pesticide Programs: U.S. Environmental Protection Agency Annual Cancer Report 2018. [Accessed on 07 July 2020]. http://npic.orst.edu/chemicals_evaluated.pdf .

Utomo, H.D., Tan, K.X.D., Choong, Z.Y.D., Yu, J.J., Ong, J.J. and Z.B. Lim (2016). Biosorption of heavy metal by algae biomass in surface water. *Journal of Environmental Protection*, **7(11):** 1547.

Wang, S., Yang, S., Jin, X., Liu, L. and F. Wu (2010). Use of low cost crop biological wastes for the removal of Nitrobenzene from water. *Desalination*, **264(1-2):** 32-36.

Yang, Y., Chun, Y., Sheng, G. and M. Huang (2004). pH-dependence of pesticide adsorption by wheat-residue-derived black carbon. *Langmuir,* **20(16):** 6736-6741.

Yapar, S., Özbudak, V., Dias, A. and A. Lopes (2005). Effect of adsorbent concentration to the adsorption of phenol on hexadecyl trimethyl ammonium-bentonite. *Journal of Hazardous Materials*, **121(1-3):** 135-139.

Zaini, M.A.A., Amano, Y. and M. Machida (2010). Adsorption of heavy metals onto activated carbons derived from polyacrylonitrile fiber. *Journal of hazardous Materials.* **180(1-3):** 552-560.

Zeraatkar, A.K., Ahmadzadeh, H., Talebi, A.F., Moheimani, N.R. and M.P. McHenry (2016). Potential use of algae for heavy metal bioremediation: A critical review. *Journal of Environmental Management*, **181:** 817-831.