

The use of macroalgae (*Gracilaria changii*) as bio-adsorbent for Copper (II) removal

Lavania-Baloo¹, Nordin Idayu¹, Ibrahim Umar Salihi¹, Jamari Zainoddin²,

¹Department of Civil and Environmental Engineering, Universiti Teknologi PETRONAS (UTP), 32610 Bandar Seri Iskandar Perak, Darul Ridzuan, Malaysia

²Fishery Research Institute, Pulau Sayak, Kedah, Malaysia

lavania.baloo@utp.edu.com

Abstract. Biosorption of heavy metals using marine macroalgae biomass can be an effective process and alternative to conventional methods. Activated carbon was developed from macroalgae (*Gracilaria changii*) and used as adsorbents for the removal of copper (II) from wastewater. *Gracilaria changii* based activated carbon (GCBAC) was prepared using muffle furnace at a constant temperature of 300 °C for 1 hour. Batch adsorption experiments were conducted to investigate the effects of important parameters such as pH, contact time, initial metal concentration and adsorbent dosage on the removal of Cu (II) from synthetic aqueous solution. Batch adsorption study shows that removal of Cu (II) using GCBAC relied upon pH, contact time, initial metal concentration and GCBAC dosage. The optimum conditions parameters were found to be pH 6.0, time of 60 minutes and GCBAC dosage of 0.3 g, respectively. Adsorption data was described better by Freundlich isotherm model with R^2 value of 0.7936. The maximum Cu (II) adsorption capacity of GCBAC was found to be 0.07 mg/g. The experimental adsorption data obtained fitted well into Pseudo-second-order kinetic model, with R^2 value near unity. Thus, GCBAC can be used as an effective adsorbent for the removal of Cu (II) from aqueous solution.

1. Introduction

Heavy metals are harmful to public health due to their toxicity, non-biodegradable nature and widespread presence in the natural environments. Several process industries such as metal plating, mining operations, tanneries, etc, use a lot of water in their production process, and as such generate large volume of wastewater at the end. The wastewater generated contains different contaminants that are harmful to the environment if discharged without proper treatment. One of the major contaminant of concern is the heavy metals. This is due to their toxicity, and their existence poses environmental-disposal problem [1, 2]. The numerous metals that are significantly toxic to human, plants and the ecological environments includes, copper, chromium, lead, mercury, manganese, cadmium, etc [3]. Copper becomes toxic at elevated level even though it is a required element; as such the level of copper in the natural environment and its availability for biological function is very essential. Since Cu (II) is widely used in production processes, potential or actual sources of Cu (II) pollution are many. Cu (II) can be present as contaminant in food, mainly in mushroom, liver, shellfish, chocolate and nuts [3]. Several conventional methods such as neutralization, chemical precipitation, ion exchange and electrochemical treatment were used to remove heavy metals in wastewater. Most of these methods are more suitable for high concentration of heavy metals. The techniques failed in certain cases, they are



not cost-effective, generate excess sludge that requires special disposal system and not environmentally friendly [4]. Further, these techniques are not suitable for the removal of heavy metals especially at lower concentrations in the range of 1-100 mg/L [5]. Adsorption technique is found to be the most effective and efficient method for the removal of heavy metals from aqueous solution [4]. Commercial activated carbon (AC) is the most widely used adsorbent in the adsorption process. However, it is found to be expensive and thus has restricted its widespread usage. In recent time, many researchers have reported the use of industrial by-products as adsorbent to replace the commercial AC. Industrial by-products used for the production of AC include; lignite, agronite shells, rice husk, natural zeolites, kaolinite, lignin, peat, clay, bagasse, etc [6, 7]. Macroalgae or generally known as seaweed, are natural sources that have the potential to be used as bio-adsorbent for heavy metals removal. It is economically feasible to culture seaweed in large scale [8, 9]. It has been used widely in developing industrial product such as chemicals, soil conditioner, food and pharmaceutical products [10, 11]. It has been reported that China alone commercially produces about 4.2×10^6 tons of *Laminaria* sp.. Macroalgae and considered as the largest producer [12]. Recently, global cultivation and production of macroalgae increases from 95% to 99.6% in year 2012. This is because most of the Asian countries have joined the league of macroalgae production and includes Indonesia (20.6%, 3.9 million tons), Philippines (9.5 %, 1.8 million tons) North Korea (4.7%, 901 700 tons), South Korea (2.3%, 444 300 tons), Japan (2.3%, 432 800 tons) and Malaysia (1.1%, 207 900 tons) [13]. Seaweed consists of three distinct groups; brown, red and green seaweed. This study was carried out to investigate the potential of red seaweed (*Gracilaria changii*) for the adsorption of Cu (II) from aqueous solution through batch adsorption experiment. Parameters such as pH, initial concentration of Cu (II) ions, contact time, and adsorbent dosage were tested in this study. Langmuir and Freundlich isotherm models were used to fit experimental data. Pseudo-first-order and pseudo-second-order kinetic models were used to evaluate the controlling mechanism of the biosorption process.

2. Material and methods

2.1 Preparations of algal biomass-based activated carbon

The macroalgae sample used was *Gracilaria changii* and was collected from Fishery Department Langkawi, Malaysia. The material was washed with excess tap water followed by distilled water to get rid of salt and particulate materials. It was then dried in an oven at 70 °C for 24 hours. The dried material was grind and sieved to size 300 µm. The material was then treated chemically using 0.2 M HCl before physical activation at a temperature of 300 °C for 1 hour. The physical activation was carried out using a muffle furnace (Protherm PLF 110/45). The produced *Gracilaria changii* based-activated carbon (GCBAC) was then cooled and stored in a tight before use.

2.2 Preparation of synthetic solution

A stock solution was prepared by dissolving calculated weigh of Cu (II) chloride salt in 1 L of distilled water to give a concentration of 1000 mg/L. To obtain further required concentrations, the stock solution was diluted appropriately. The chemical employed are of analytical grade, obtained from Merck (Germany).

2.3 Batch adsorption experiments

Batch adsorption experiments were conducted using 0.1 g of GCBAC in 100 mL of Cu (II) solution with predetermined concentrations using 250 mL conical flasks. The flasks were clamped in an orbital shaker (Protech Model 722) and shaken at 150 rpm at room temperature. At the end of predetermined time, the mixture was filtered using Whatman's glass microfiber filter paper. The filtered solution was analysed for residual Cu (II) concentration using Atomic Absorption Spectrometer, AAS (Model AA 6800 Shimadzu). Effect of pH on the adsorption of Cu (II) using GCBAC adsorbent was investigated by varying the initial pH of the solution in the range of pH 1.0 to pH 8.0. The working solutions were adjusted using either 1M HCl or 1M NaOH. 0.1 g of GCBAC was placed into the flasks containing

100 mL of Cu (II) solution and was agitated on a shaker at 150 rpm for 2 hours at room temperature (25 ± 1 °C). The concentration of Cu (II) in the solution was fixed to be 25 mg/L. A pH meter (Model EW 53013) was used to measure the pH of the solution. Batch adsorption experiment was also conducted to investigate the effect of initial metal concentrations and contact time. 100 mL of synthetic Cu (II) solution having initial concentrations of 5, 10, 15 and 20 mg/L and 0.1 g of CGBAC was placed in a series of 250 mL Erlenmeyer flasks and agitated at 150 rpm. Flasks were withdrawn from the shaker at the end of predetermined time interval of 10, 20, 30, 60, 90, 120 minutes, and the solution was analysed for the residual Cu (II) concentration. The effect of CGBAC dosage on the removal of Cu (II) from aqueous solution was investigated by varying the dosages from 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g. The pH of the solution was adjusted to the optimum value obtained. The optimum contact time was also adopted. Other parameters such as agitating speed and initial metal concentration were fixed at 150 rpm and 20 mg/L, respectively. Metal removal efficiency and adsorption capacity were evaluated using Eq. 1 and Eq. 2, respectively.

$$R = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (1)$$

where, R is the Cu (II) removal efficiency (%), C_i is the initial copper concentration and C_e is the residual copper (mg/L) concentrations at equilibrium.

$$Q_c = \frac{(C_i - C_e)V}{W} \quad (2)$$

where, Q_c is the adsorbent adsorption capacity (mg/g), C_i is the initial copper concentration and C_e is the residual concentration copper (mg/L) at equilibrium, V is volume of aqueous copper solution (L) and W mass of CGBAC (g).

3. Results and discussions

3.1 Effect of pH

This study was carried out to investigate the effect of initial pH of the solution on the removal of Cu (II) using CGBAC. The pH of the solution was varied from pH 1.0 to pH 8.0. Fig. 1 shows the plot of Cu (II) removal efficiency against initial pH of the solution. From the graph, it can be observed that Cu (II) removal efficiency is less at low initial pH and then increased continuously as the pH is increased until it reaches an optimum pH of 6.0 and then decline. At low initial pH (pH 2.0 - pH 4.0) there was competition between the Cu (II) ions and hydrogen ions in the solution for an active site on the GCBAC surface. However, as the pH of the solution was increased, the surface of GCBAC becomes less positively charged and the electrostatic attraction between the Cu (II) ions and the GCBAC surface is likely to increase, as such the Cu (II) ions adsorption increased. The decrease in the adsorption of Cu (II) at high initial pH level due to the formation of soluble hydroxyl complexes [7]. GCBAC works best at pH value of 6.0 with corresponding Cu (II) removal efficiency of 24.22 %. pH value of 6.0 is selected as the optimum pH and used in the study of the effect of initial metal concentration and contact time (section 3.2).

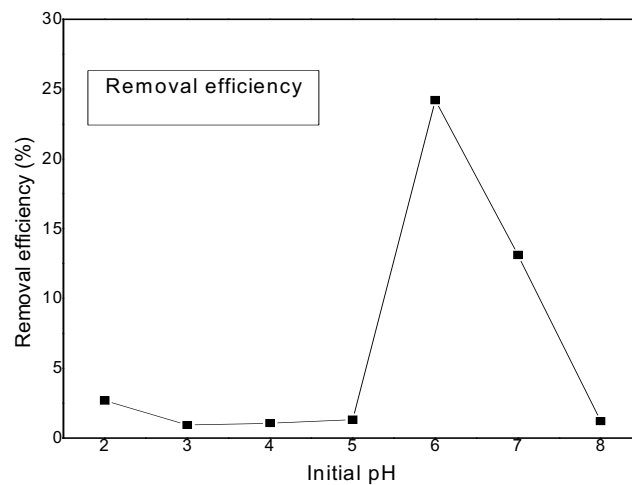


Figure 1. Effect of pH on Cu (II) adsorption (initial Cu (II) concentration 25 mg/L, contact time 2 hours, GCBAC dosage 0.1 g, agitation speed 150 rpm and temperature 25 ± 1 °C).

3.2 Effect of contact time and initial metal concentrations

This study was carried out to investigate the effect of initial metal concentrations and contact time on the removal of Cu (II) using GCBAC. Fig. 2 shows the effect of initial metal concentrations and contact time on adsorption of Cu (II) by GCBAC. It has been observed that there was rapid adsorption of Cu (II) increases during the first 30 minutes of contact time. However, as the contact time increases, the adsorption rate decreases gradually and then become steady until equilibrium removal was achieved. There were more available active sites on the surface of GCBAC at the initial time. However, as the contact time increases the available pores on adsorbents are fully occupied by metals ion and the removal decreases until equilibrium. At this stage, the adsorption is controlled by the rate of transport of the metal ions from the outer to the inner site of the adsorbent material [14]. Equilibrium removal was attained at contact time of 60 minutes. Further significant removal was not observed afterwards. Contact time of 60 minutes was considered to be optimum and used in the study of the effect of GCBAC dosage on Cu (II) removal (section 3.3). The available binding site, thus resulting high removal efficiency whereas, at higher concentration, adsorption is low due to the saturation of binding site of the adsorbent.

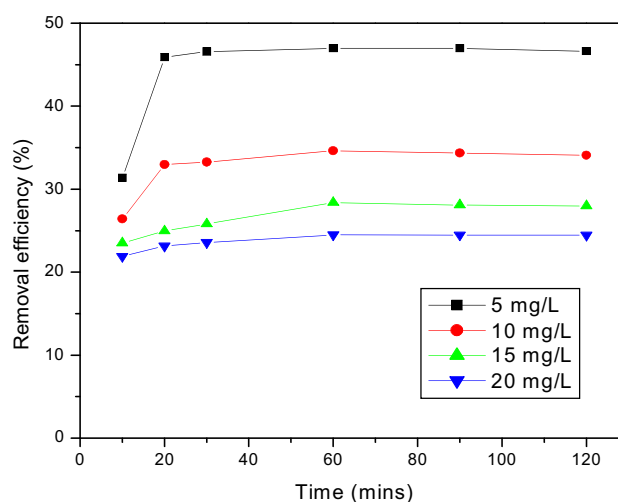


Figure 2. Effect of contact time on Cu (II) adsorption (contact time 2 hours, GCBAC dosage 0.3 g, pH 6.0, agitation speed 150 rpm and temperature 25 ± 1 °C).

It was also observed that Cu (II) removal efficiency decreases with the increase in initial Cu (II) concentration (Fig. 3). This is because, at low initial metal concentration, there were few Cu (II) ions in the solution compared to the available number of active sites on the GCBAC surface; as such the Cu (II) ions can easily be adsorbed. On the other hand, at high initial metal concentrations, there were more Cu (II) ions than the available active sites on the CGBAC surface. Thus, the initial Cu (II) concentration was at 5 mg/L with removal efficiency of 47.0%.

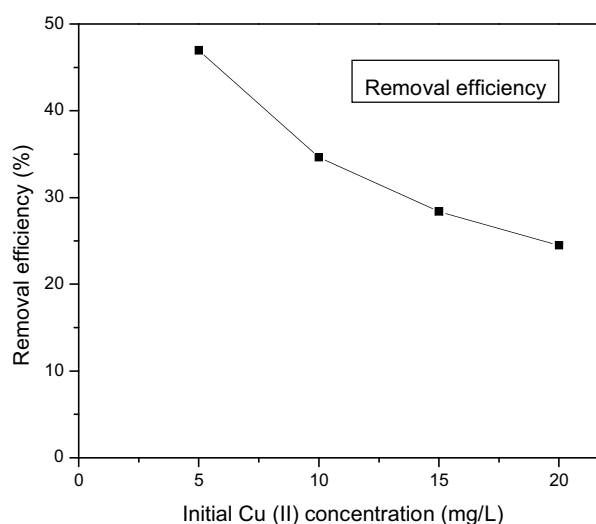


Figure 3. Effect of initial metal concentration on Cu (II) adsorption (contact time 2 hours, GCBAC dosage of 0.3 g, pH 6.0, agitation speed 150 rpm and temperature 25 ± 1 °C).

3.3 Effect of adsorbent dosages

This study was carried out to investigate the effect of adsorbent dosage on the removal of Cu (II) by CGBAC adsorbent. Fig. 4 shows Cu (II) removal efficiency unit weight of GCBAC. From Fig. 4, it is observed that the removal efficiency of Cu (II) increase with the increasing of adsorbent dosage. This is due to more active sites of CGBAC becomes available with every increment of dosage, thus making the Cu (II) ions penetrate easily into the sorption sites. No significant removal was observed when the GCBAC dosage was increased to 0.3 g. At this point, it is expected that the concentration of Cu (II) ions in the solution and the concentration of the adsorbed ions on the CGBAC surface are in equilibrium with each other.

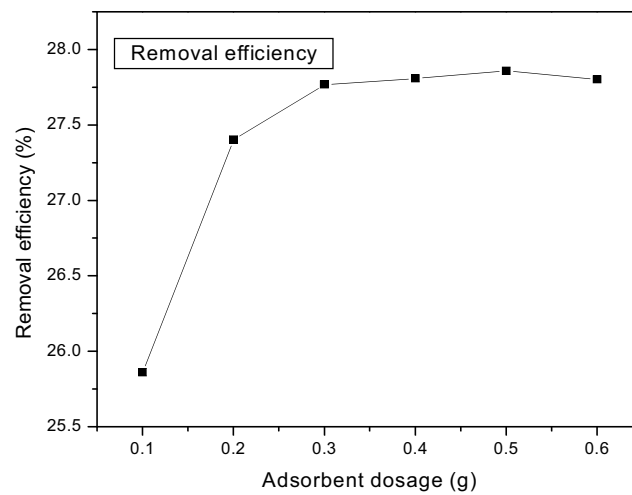


Figure 4. Effect of adsorbent dosage on Cu (II) adsorption (contact time 1 hour, pH 6.0, initial concentration 20 mg/L, agitation speed 150 rpm and temperature 25±1 °C).

3.4 Effect of adsorbent dosages

Langmuir and Freundlich isotherm models were used to interpret the relationship between the GCBAC adsorbent and the Cu (II) ions adsorbed on the adsorbent surface. The models will indicate the metal uptake capacity and the information regarding the differences in metal uptake by various species [18]. According to Wang and Chen [5], Langmuir and Freundlich are represented as in Eq.3 and Eq. 4 below:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L} \right) \left(\frac{1}{b} \right) + C_e \left(\frac{1}{b} \right) \quad (3)$$

where C_e is equilibrium solute concentration in solution (mg/l), q_e is the amount of metal adsorbed, K_L is the equilibrium Langmuir constant and b is the bonding energy of adsorption required for monolayer formation. Plot of C_e/q_e against C_e will give a straight line with $1/b$ as slope and $1/K_L$ as intercept.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where $\log q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_F is the biosorption equilibrium constant representing the sorption capacity and n is a constant indicative of biosorption intensity. The plot of $\log q_e$ against $\log C_e$ will yield a straight line with $1/n$ as the slope

and $\log K_F$ as the intercept. Table 1 shows the coefficient values obtained for Langmuir and Freundlich isotherm models obtained from this study and comparison with other plant-based adsorbents.

Table 1 Freundlich and Langmuir isotherm parameters constant.

Adsorbent	Langmuir				Freundlich	
	Q_{max} (mg/g)	b	R^2	R_L	K_F	R^2
GCBAC	0.07	0.05	0.5691	0.51	3.38×10^{27}	0.8742

From Table 1, it can be seen that Freundlich isotherm model indicates high coefficient of determination R^2 of 0.8742 compared with Langmuir model with low R^2 of 0.5691. This shows that adsorption of Cu (II) using GCBAC follows Freundlich isotherm model. Freundlich isotherm indicates the surface heterogeneity of the adsorbent, thus the surface of *Gracilaria changii* is made up of small heterogeneous adsorption patches which are similar to each other with respect to adsorption phenomenon [9, 12]. This indicates that the adsorption occurred at the heterogeneous and multilayer surface of the GCBAC adsorbent, with maximum mesopores surface area of 0.8950 m²/g. The Langmuir equilibrium parameter R_L for GCBAC was found to be 0.51. This is within the range for favorable adsorption ($0 < R_L < 1$) [14].

3.5 Adsorption kinetics studies

Kinetic study is the function of solute uptake rate has been evaluated for this study. The experimental results obtained were used to evaluate the kinetics of Cu (II) ions adsorption. Pseudo-first-order and pseudo-second-order kinetics models were used to study the rate of kinetics on GCBAC adsorbent. Eq. (5) and Eq. (6) were used to calculate the rate constants for pseudo-first and second-order kinetic models.

$$\text{Pseudo-first-order: } \log(q_e - q) = \log(q_e) - \left(\frac{k_1}{2.303} \right) t \quad (5)$$

where q_e is the adsorbed metal at equilibrium in (mg/g), q_t is the metal adsorbed at a given time (t) and k_1 is the pseudo-first-order rate constant (1/min). k_1 and q_e are determined from the slope and intercept of the plot of $\log(q_e - q_t)$ against time (t).

$$\text{Pseudo-second-order: } \frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (6)$$

where, q_t and q_e are the amounts of metal ions adsorbed at time t (h) in (mg/g) and at equilibrium, respectively. k_2 is the pseudo-second-order adsorption rate constant. Plot of t/q_t against t will give a straight line with k_2 and q_e are determined from the slope and intercept of the plot. Figures 5 and 6, show the plots of pseudo-first and second-order kinetics. The values of k_1 , k_2 , $q_{e,exp}$ and $q_{e,cal}$ were obtained from the slopes and intercepts of the plots and are presented in Table 2.

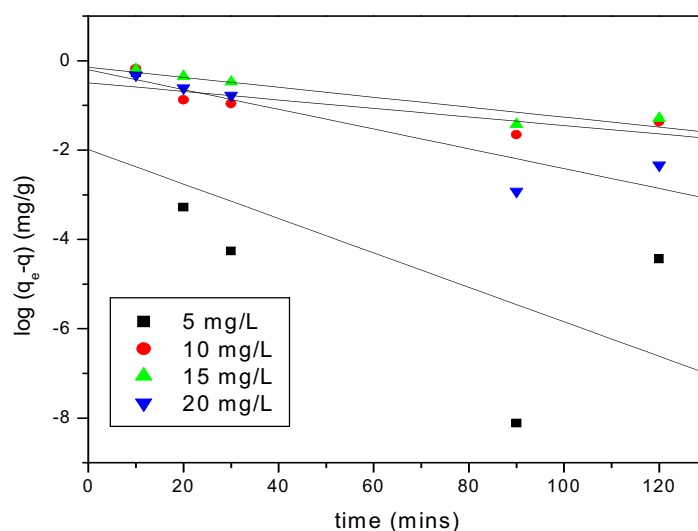


Figure 5. Pseudo-first-order kinetic plot

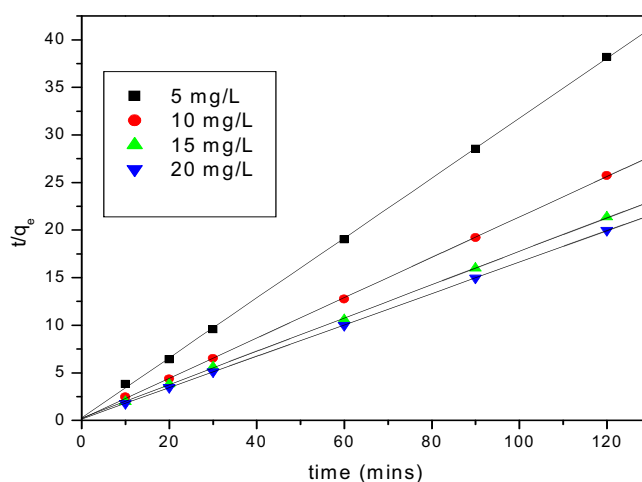


Figure 6. Pseudo-second-order kinetic plot

Table 2 Parameters values of pseudo-first-order and second-order models.

Adsorbent	Initial metals ions concentration (mg/L)		q _{e, exp} (mg/g)	Pseudo first-order model			Pseudo second-order model		
				q _{e, cal} (mg/L)	k ₁ (h ⁻¹)	R ²	q _{e, cal} (mg/g)	k ₂ (g/mg h)	R ²
GCBAC	Cu(II)	5	3.1521	24.7742	0.0836	0.2709	3.1776	0.3147	0.9997
		10	4.7036	2.2065	0.0207	0.3598	4.7169	0.212	0.9998
		15	5.6658	1.0723	0.0246	0.6198	5.7078	0.1752	0.9998
		20	6.0094	1.0271	0.0491	0.6066	6.0643	0.1649	1.0000

As can be seen from Table 2, pseudo-second-order kinetic model presented high values of coefficient of determination (R^2). All the values were close to unity. There was a significant deviation

between the experimental $q_{e, exp}$ values and the pseudo-first-order calculated $q_{e, cal}$ values for GCBAC adsorbent. This indicates a poor fit of the pseudo-first-order model to the experimental data. On the other hand, the calculated $q_{e, cal}$ values obtained from pseudo-second-order model agreed effectively with the experimental $q_{e, exp}$ values. Therefore, it can be concluded that the adsorption of copper ions onto GCBAC is a pseudo-second-order reaction model. This suggests that the rate limiting step is a chemisorption or chemical adsorption that involves valence forces by means of electrons exchange between the adsorbent (GCBAC) and the adsorbate (copper ions). A similar phenomenon was also reported on the adsorption of copper onto cashew nut shell [15], papaya wood [16] and modified oak sawdust [17].

4. Conclusions

The result obtained from this study indicated the potential use of *Gracilaria changii* based activated carbon (GCBAC) for the adsorption of Cu (II) ions from synthetically prepared wastewater. The experimental data well correlated with Freundlich isotherm and pseudo second-order kinetic model. pH, initial concentration of Cu(II) ions, contact time, and adsorbent dosage have significant effect on the Cu(II) adsorption by GCBAC. Thus, this study has proven that the use of macroalgae based activated carbon is effective for copper removal. Also, it is abundantly available and therefore would be cheaper and economically feasible activated carbon compared to the commercially available ones.

5. References

- [1] Fu F and Wang Q 2011 Removal of heavy metal ions from wastewaters: A review *J. Environ. Mngt.* **92** 407-18.
- [2] Ahluwalia S S and Goyal D 2007 Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technol.* **98** 2243-57.
- [3] Yu B, Zhang Y, Shukla A, Shukla S S and Dorris K L 2001 The removal of heavy metals from aqueous solutions by sawdust adsorption-removal of lead and comparison of its adsorption with copper *J. Hazard. Mater.* **84** 83-94.
- [4] Demirbas A 2008 Heavy metal adsorption onto agro-based waste materials: A review. *J. Hazard. Mater.* **157** 220-29.
- [5] Wang J and Chen C 2009 Biosorbents for heavy metals removal and their future. *Biotechnol. Adv.* **27** 195-26.
- [6] Mohan D, Pittman C U and Steele P H 2006 Pyrolysis of wood/biomass for bio-oil: a critical review. *Energ. Fuel* **20** 848-89.
- [7] Salih I U, Kutty S R M Isa, M H and Aminu N 2016 Zinc removal from aqueous solution using novel adsorbent MISCBA *J. Water Sanit Hyg Dev* **6** 377-88.
- [8] Chopin T, Buschmann A H, Halling C, Troell M, Kautsky N, Neori A, Kraemer G P, Zertuche-González J A, Yarish C and Neefus C 2001 Integrating Seaweeds into Marine Aquaculture System: A Key Toward Sustainability *J. Phycol.* **37** 6 975-86.
- [9] Neori A, Chopin T, Troell M, Buschmann A H, Kraemer G P, Halling C, Shpigel M, and Yarish C 2014 Integrated aquaculture: rationale, evolution and state of the art emphasizing seaweed biofiltration in modern mariculture *Aquaculture* **23** 361-91.
- [10] Troell M, Halling C, Nilsson A, Buschmann A H, Kautsky N, and Kautsky L 1997 Integrated marine cultivation of *Gracilaria chilensis* (Gracilariales, Rhodophyta) and salmon cages for reduced environmental impact and increased economic output. *Aquaculture* **156** 45-61.
- [11] Harrison E 1999 Treatment of metal-contaminated wastes: why select a biological process? *Trends Biotechnol.* **17** 462-65.
- [12] Lüning K and Pang S 2003 Mass cultivation of seaweeds: current aspects and approaches *J. Appl. Phycol.* **15** 115-19.

- [13] Baloo L 2015 *Semi-closed circulation integrated multi.trophic aquaculture treatment system using aquatic organisms as biofilters to improve shrimp effluent quality* (Malaysia: Universiti Teknologi Malaysia) pp 90-92.
- [14] Rafatullah M, Sulaiman O, Hashim R and Ahmad A 2009 Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. *J. of Hazard Mater* **170** 969-77.
- [15] SenthilKumar P, Ramalingam S, Sathyaselvabala V, Kirupha S D, and Kirupha S 2011 Removal of copper (II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination* **266** 63-71.
- [16] Saeed A, Akhter M W, and Iqbal M 2005 Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Sep. Purif. Technol.* **45** 25-31.
- [17] Argun M E, Dursun S, Ozdemir C and Karatas M 2007 Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *J. Hazard. Mater.* **141** 77-85.

Acknowledgements

Special gratitude to Dr. Zainoddin Jamari, the Director of Fishery Research Institute (FRI) Pulau Sayak, Kedah, for the technical support. The authors also thankful to Mr. Zaaba and all laboratory technologists from Environmental Laboratory, Civil and Environmental Engineering Department, Universiti Teknologi PETRONAS for the assistance and cooperation given throughout the project. Finally, we are indebtful to Universiti Teknologi PETRONAS for providing the financial assistant (STIRF grant).