Removal of Lead using Activated Carbon Derived from Red Algae (*Gracilaria Changii*)

Mubeen Isam^{1,*}, Lavania Baloo¹, Nasiman Sapari¹, Idayu Nordin¹, Saba Yavari¹, and Wesam Al-Madhoun¹

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

Abstract. Red algae-derived activated carbon was evaluated for its ability to remove lead (Pb) from synthetic aqueous solution. The activated carbon was prepared at a constant temperature of 300°C for 1 hour using a muffle furnace. Effect of pH contact time, initial ions concentration, and activated carbon dosage as important operating variables on the reaction process were also investigated. The batch experiment was conducted for adsorption experiment. The maximum lead uptake capacity was obtained at pH 6 and operation time of 30 min. the maximum uptake capacity of Pb (II) was found to be 0.1 mg/g. This work confirms the potential use of red algae *Gracilaria changii* for the removal of heavy metals from wastewater.

1 Introduction

Pollution of water with heavy metals is a serious problem that endangers human health. If not managed and treated properly, heavy metals can accumulate in the food chain and cause major health. Heavy metals industries such as petroleum refinery, mining, and electroplating produce wastewater loaded with heavy metals that are discharged to the receiving environment directly or indirectly. The most common heavy metals are iron (Fe), chromium (Cr), zinc (Zn), cadmium (Cd), cobalt (Co), copper (Cu), and lead (Pb). Pb is involved widely in industries such as lead batteries, explosive industries, paint and dyes, and electroplating[1]. A large quantity of lead ions is discharged into the environment[2]. According to EPA, allowable levels of Pb ions in drinking water is 0.015 mg/L [3]. Pb has serious effects on the human nervous system and can cause a headache, hypertension, fatigue, anemia, and even death [3], [4].

Different methods have been used for removal of heavy metals from wastewaters such as ion exchange, chemical precipitation, membrane filtration, coagulation, and flocculation. These methods are either ineffective or expensive when heavy metals are in low concentrations. Other pitfalls are the complexity of the operation and large area requirement[5]. Adsorption is considered as an effective and relatively economical in the removal of heavy metals in wastewater. It can offer flexibility in both operation and design. Since adsorption is reversible, regeneration of adsorbent is also possible by desorption process [6]–[9] Adsorption using activated carbon can offer high efficiency due to the high

* Corresponding author: Mubeen.isam@gmail.com

surface area, characteristics of surface chemistry, and a high degree of porosity. High costs of commercial activated carbon led to a growing research that aims to find cheaper alternatives. Adsorbents that are required little processing, by-products of another industry or abundant in nature can be considered low-cost materials [10]. Researchers have been focusing on producing low-cost adsorbents from carbonaceous materials such as hazelnut husk [11], rice husk [12], grape seeds [13], and palm solid waste [14]. and macroalgae [15]–[18]. Macroalgae showed a potential in removing heavy metals due to their small uniform particle size and number of different metal binding sites on the cell walls[19]. Red macroalgae can be found abundantly in coastal areas in Oceania, Africa and Asia[20]. Red algae *Gracilaria changii* is considered to be the most abundant macroalgae in Malaysia[21]–[23]. The utilization of such resource would also provide a favourable choice for controlling environmental degradation and eutrophication of oceans caused by algae[24]. This study aims to examine the performance of *G.changii* for the adsorption of Pb (II) from aqueous solution through batch adsorption experiment. Different operating parameters were investigated such as pH, contact time, initial ions concentration, and activated carbon dosage.

2 Materials and Methods

2.1 Chemicals and solutions

The stock solution of Pb (II) (1000 mg/L) was prepared using lead chloride (PbCl_2) and then was diluted appropriately with distilled water to obtain desired concentrations. 0.1 M of hydrochloric acid (HCl) and 0.1 M of sodium hydroxide (NaOH) were used for pH adjustment. All used chemicals were of analytical grade, provided by Merck (KGaA, Darmstadt, Germany).

2.2 Preparation of activated carbon

Red macroalgae (*Gracilaria changii*) was collected from Fishery Department of Langkawi, Malaysia. The biomass was washed with tap water followed by distilled water to remove salt and other impurities. After that, the biomass was dried at 70°C for 24 hours in an oven. The dried biomass was grinded and sieved to a particle size of 300 μm and then was pre-treated with 0.2 M HCl. Thermal activation was carried out at a temperature of 300°C for 1 hour using a muffle furnace (Protherm PLF 110/45). The produced activated carbon was cooled and stored in glass bottles before use.

2.3 Chemicals and solutions

2.3.1 Scanning electron microscopy (SEM)

Scanning electron micrograph was analysed and clearly revealed by scanning electron microscopy (SEM, Supra 55 VP, Carl Zeiss-Germany) at a magnification (3000X).

2.3.2 Adsorbent surface area

The surface area of the adsorbent was determined through Brunauer-Emmett-Teller (BET) analysis (BET, TriStar II 3020, micromeritics-UK).

2.3.3 Functional groups determination (FT-IR)

Fourier transform infrared spectroscopy (FTIR, Spectrum one, Perkim Elmer-US) was used to determine the activated carbon functional groups involved in the adsorption process.

2.4 Batch Adsorption Experiments

Effects of operating variables including pH (2-8), contact time (10-120 min), initial ions concentrations (5-20 mg/L), and adsorbent dosage (1-6 g/L) were evaluated on the activated carbon efficiency in removal of lead ions from aqueous solution.

Adsorption studies were conducted using batch equilibrium technique during which a 100 mL of a solution containing known initial ions concentration was mixed with a known amount of adsorbent (0.1g). It was then shaken at 150 rpm at room temperature ($25 \pm 1^\circ\text{C}$) using an orbital shaker (Protech Model 722). At the end of predetermined time, the mixture was filtered through Whatman's glass microfiber filter paper. The filtered solution was then analysed for the residual Pb (II) concentration using atomic absorption spectrometer (AAS, Model AA 6800 Shimadzu). Metal efficiency and adsorption capacity were calculated using Eq. 1 and Eq. 2, respectively.

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

Where, R is the Pb (II) removal efficiency (%), C_i is the initial lead ions concentration and C_e is the residual concentration (mg/L) at equilibrium.

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

Where Q_c is the activated carbon adsorption capacity (mg/g), V is volume of aqueous lead solution (L) and W is the mass of the adsorbent (g).

3 Results and Discussions

3.1 Adsorbent characteristics

Fig. 1 shows morphology and surface texture of the red algae-derived activated carbon. Based on the figure, there were pores on the surface of the produced activated carbon. These pores were available for the metals ions to bind during the adsorption process. However, after undergoing adsorption of Pb (II), insignificant pores were observed on the surface of the activated carbon (refer Fig.1). After exposure of the adsorbent to heavy metals solution, the metals ions occupy the available free binding sites on the surface of activated carbon and can replace with some of the cations initially present on the adsorbent surface through ion-exchange mechanism [25]. GCAC was subjected to elemental analysis before and after adsorption process are shown in table 1. The results from BET analysis showed the value of

BET surface area for the produced activated carbon under detection level of the analyser was 0.8950 m²/g.

Table 1. Elemental analysis before and after adsorption

Element Symbol	Element Name	Weight Concentration (Before)	Weight Concentration (after)
C	Carbon	92.1	53.8
O	Oxygen	7.3	20.8
Cu	Copper	0.0	0.0
Pb	Lead	0.0	57.1

Fig 1 SEM images of the produced activated carbon before (a) and after (b) Pb (II) adsorption (3000X)

Results of FTIR analysis for the produced activated carbon is presented in Fig. 2. Spectra at 3406.59, 2917.58, 1610.44, 1113.89, 792.92, and 614.60 cm⁻¹ represented O-H stretching, carboxylic/phenolic stretching bands, primary amine N-H bending, C-C stretching vibration, aromatic C-H out-of-plane bending, and alkyne C-H bending, respectively [26]. The decreased intensities of the peaks after adsorption of Pb (II) on the activated carbon showed that these functional groups got involved during the adsorption process [27].

3.2 Effect of pH

Fig. 3 shows the activated carbon efficiencies in the removal of Pb (II) within various pH values (2-8). It can be observed that the highest removal efficiency was obtained at pH 6 (45.53%). The uptake capacity of Pb (II) was 9.60 mg/g at this pH. Adsorption of Pb ions enhanced as pH increased to the optimum value and then showed a decline [28]. These results suggested that the adsorption of Pb ions on the activated carbon was mainly because of ionic attraction. The adsorbent consisted of weakly acidic and basic functional groups, thus as pH value increased the activated carbon surface became more negatively charged. At optimum pH (= 6), ligands exposed with negative charges were available in the highest concentrations, but the amount of competing for hydrogen ions was in the lowest level which resulted in greater binding of the cation heavy metals to the weak acidic groups. Further increases in pH value decreased adsorption of the metal ions may be due to precipitation and lower polarity of Pb (II) at higher pH values [28].

Fig 3 FTIR spectra before and after adsorption

3.3

Effect of contact time and ion concentration

Fig 2 Effect of pH on Pb (II) adsorption

Fig. 4 shows the effect of contact time on adsorption of Pb (II) by the produced activated carbon. It was found that the equilibrium time for the ions adsorption was 30 minutes which is similar to study done by Jalai et.al using non-living biomass[29]. At optimum contact time, the available pores on adsorbents are fully occupied by adsorbate molecules/ions causing the removal to not significantly change and adsorption process already reached equilibrium [30], Fig. 6 shows the effect of initial concentration of metals ions on removal efficiency at optimum contact time. Percentage of the metal ions removal decreased with increasing initial ions concentration. This can be attributed to saturation of the adsorbent binding site and insufficient surface area to accommodate more metal ions available in the solution. At lower concentrations, all metal ions could react with the available binding site resulting in high removal efficiencies.

Fig 4 Removal Efficiency (%) of Pb (II) at different initial metals ion concentration and contact time

Fig 5
Removal Efficiency (%) of Pb (II) at different initial metals ion concentration and optimum contact time

3.4 Effect of adsorbent dosage

Fig. 6 presents the removal efficiency per unit weight of the produced adsorbent. It was observed that the removal efficiency of Pb (II) increased with the increase in adsorbent dosage from 1 to 3 g/L. There were insignificant changes when the dosage exceeded 3 g/L with removal efficiency of 63.11 %.

Fig 6 Removal Efficiency (%) of Pb (II) at different adsorbent dosages

4 Conclusion

Red algae activated carbon was prepared and characterized for the removal of lead from synthetic solution. The presence of porosity was indicated by SEM and BET analysis. The chemical function groups were illustrated by FTIR. The study showed that parameter such as pH, contact time, initial lead concentration, and adsorbent dosage have a significant effect on the uptake capacity. The maximum lead uptake capacity was obtained at pH 6 and operation time of 30 min. The investigation showed the potential of macroalgae-derived activated carbon as an efficient low-cost adsorbent for removal of lead ions.

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5 References

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