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Optimisation of Heavy Metals Uptake from Leachate Using Red Seaweed *Gracilaria changii*

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Abstract

Heavy metal is one of the pollutants in landfill leachate besides organic and inorganic pollutants. The presence of heavy metal is alarming due to its harmful nature; makes it incompatible to be discharged into water bodies before treatments. There are many treatment techniques to remove heavy metals from wastewater, where some of them even involve the coupling of one or more techniques to facilitate and improve the removal efficiency. However, the adsorption using seaweed is one of the known techniques to eliminate heavy metals from wastewater efficiently. Therefore, this study introduced a new adsorbent for heavy metal adsorption: red seaweed *Gracilari changii*. The effect of operational parameters such as leachate pH (2-7), seaweed dosage (2-10 g), rpm (10-100), and contact time (10-60 min) on the optimum adsorption of *Gracilaria changii* was studied. At optimum pH (pH=5), seaweed dosage (10g), rpm (rpm=50) and contact time (30min), *Gracilaria changii* showed maximum metal ion removal of 45%, 35%, and 30% for Fe^{2+}, Cr^{6+} and Ni^{2+} respectively. The adsorption was rapid and reached equilibrium after t=30min in general. This optimisation result can be used as a reference to study the effect of different dosages of the adsorbent towards the removal rate.

Keywords: Seaweed, Adsorption, Leachate, Heavy metals, Adsorbent

1 Introduction

Leachate is the dark form of liquid generated via percolation of rainwater through dumping of solid wastes into landfills. Rainwater undergoes biochemical processes with wastes and also with the water contents of the waste itself (1). Random studies showed that $0.2m^3$ of leachate are generated from every one metric ton of municipal solid waste (2). The qualities and quantities of leachate vary from one site to another depending on factors: moisture content, landfill age, climate, site hydrology, and the degree of waste stabilisation (3).

Leachates are a mixture of colour components, heavy metals, ammoniacal nitrogen, organic compounds, and inorganic compounds (4,5). Among these, heavy metals are the most toxic compounds and draw great attention due to their negative impact towards both living organisms and the environment as a whole (6). The presence of heavy metals in leachate are sourced from used batteries, electronic wastes, paint, construction materials, mines, fertilisers, and others (7,8) . The most commonly found heavy metals in leachate are Iron (Fe), Chromium (Cr), Arsenic (As), Nickel (Ni), Lead (Pb), Copper (Cu), Cadmium (Cd), and Mercury (Hg); are threats to living organisms even in small amounts (9–12).

In practice, different modes of treatment methods have been adopted for the treatment of leachate: biological, physical, chemical, and physico-chemical techniques. Nevertheless, the preference of a technique or coupling of techniques is solely based on the characteristics of leachate (13). Lately, the removal of heavy metals by adsorption method using various types of adsorbents received great interests, with seaweed being one of them. Seaweeds are macroalges and consists of 10,000 naturally existing species. These seaweeds can vary in size and typically grow up to 30 meters in length. Although seaweed has plant-like physical structure and components, they are not genuine vascular plants, but are referred as marine algae. Marine algae belongs to the Kingdom Protista group, which by default are neither plants nor animals.

There are three different groups of seaweeds and they are identified based on the colour of their thallus namely brown, green, and red algae. A number of studies show that different types of seaweeds have been used for the adsorption of heavy metals from wastewater. There are also vast studies on utilising red seaweeds as an adsorbent for removal of heavy metals. However, to date, there are no reported studies on *Gracilaria changii* specifically as an adsorbent for the purpose of wastewater treatment. Therefore, this study focused on determining the optimal conditions for the removal of Fe^{2+}, Cr^{6+} and Ni^{2+} from leachate using the biomass of *Gracilaria changii*.

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2 Materials and Methods

2.1 Leachate

The leachate sample collection was done at Worldwide Landfill Sdn. Bhd., Jeram, Selangor. The raw leachate sample was collected and immediately transferred to laboratory in a sealed high-density polyethylene (HDPE) container and stored at 4^0C to reduce chemical and biological reactions (14).

2.2 Metal Solution

The stock solutions of Fe (II), Cr(VI) and Ni (II) were prepared from Iron (II) sulphate heptahydrate ($FeSO_4.7H_2O$), Potassium dichromate ($K_2Cr_2O_7$) and Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) being dissolved in distilled water. During the course of the experiment, the preferred constant concentration of 20mg/L for each metal ion solution was achieved by diluting the stock solution further with distilled water (15). The pH of the solutions was altered to the required level using 0.1 M NaOH and 0.1 M H_2SO_4.

2.3 Preparation of Adsorbent

The red seaweed was collected from a cultivation pond in Kedah. The harvested seaweed was transferred to the laboratory in a container filled with seawater. The red seaweed was cleaned and dried. The seaweed was firstly washed with sea water, followed with tap water and lastly with distilled water to eliminate epiphytes, debris, sand and salts (16,17). The cleaned seaweed was subsequently oven-dried at 40^0C (18) for 24 hr in order to preserve the phytochemical content of seaweed. The red seaweed was not chopped into smaller sizes prior to oven-drying to prevent significant loss of bioactive compounds (19). The dried seaweed was crushed using a laboratory blender and sieved using a sieve shaker to obtain sample sizes ranging from 150 to 300 µm (20–22).

2.4 Optimization Study

Batch adsorption experiments were conducted at room temperature using a jar test apparatus comprised of six rotor paddles connected to a speed controller to adjust the rotational speed of the rotor paddles. Glass beakers of 1 litre volume was filled with 100ml leachate and desired amounts of seaweed was added. The solution was stirred for different contact time. After the reaction, the solution was allowed to settle and collected for heavy metals analysis (23). The supernatant was filtered using a glass microfibre filter to detach the solid and liquid phases. The precipitant was analysed for residual heavy metals concentration in the leachate (24) using atomic absorption spectrometry (25). The similar method was used throughout the experiment to investigate the effect of different parameters: pH level, seaweed dosage, rpm, and contact time on the adsorption rate.

3 Results and Discussions

3.1 Effect of pH

One of the major parameters in deciding the maximum adsorption ability of an adsorbent is the pH of a leachate. It influences the solubility of metals, the surface charge of the adsorbent and the ionisation of the functional groups on the cell walls. Hence, the effect of the pH value of the leachate varied over a range of 2-7 on the removal of metal ions was conducted and the results are as shown in Figure 1 (26). The sample was collected at t=10min, with seaweed dosage of 2g and showed an initial metal ion concentration of 20mg/L. It was visible that the removal percentage of all metal ions by *Gracilaria changii* increased with the increment of pH from 2-5 and was subsequently reduced as the pH increased further. This could be explained based on the functional groups of seaweed and the speciation of metal ions at varying pH levels. The cell wall of seaweed is made of polysaccharides, carboxyl, and sulphonate groups. These functional groups are negatively charged and at lower pH,, these groups are protonated with H^+. Therefore, seaweed is unable to hold the positively charged metal ions. At increased pH level of upto 5, the concentration of H^+ were relatively lower and therefore, the metal ions were able to bind with the negatively charged surface of the seaweed (15). The removal percentage started to reduce at pH>5 and the metal precipitation (formation of metal hydroxide complexes) could be the reason behind this occurence (27). Therefore, the optimum pH for heavy metals adsorption using *Gracilari Changii* in this study was 5. A maximum of 10%, 5% and 5% of metal ions were removed for Fe^{2+}, Cr^{6+}, and Ni^{2+}, respectively.

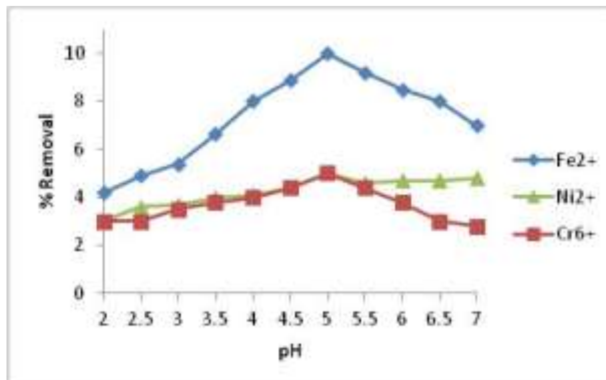

Figure 1: Effect of pH on removal percentage of metal ions

3.2 Effect of seaweed dosage

Seaweed dosage is one of the fundamental parameters in determining the optimum uptake of heavy metals. Therefore, the effect of seaweed dosage was studied by varying composition. Figure 2 shows that metal ion removal is proportional to the increasing seaweed dosage. As the mass increased from 2g to 10g, the removal percentage increased as well (28–30). As per the studied dosage range, 10g of seaweed is the optimum composition for maximum metal ion uptake for all three metals (31). Higher dosage offers higher surface area or greater active sites for binding of a constant metal ion concentration. Therefore, more metal ions bind on the surface of the seaweed and increased the removal rate (32). A maximum of 60%, 25% and 20% of metal ions were removed for Fe^{2+}, Cr^{6+}, and Ni^{2+}, respectively.

3.3 Effect of agitational speed

Figure 3 illustrates the effect of agitation speed of the rotor towards the heavy metals uptake by *Gracilari Changii*. The effect was studied within the range of 10-100 rpm. The results showed that the maximum removal of heavy metal ions occurred at 50 rpm. At lower agitation speed, the seaweed aggregated and did not spread within the liquid. Therefore, the active binding sites of the bottom layer were covered and not available for metal binding, while only the upper layer of the adsorbent was able to adsorb the metal ions. Thus, sufficient agitation speed is necessary to ensure that every active sites were readily accessible and exposed for heavy metal bindings (33). However, the removal percentage decreased above 50rpm. This can be explained by the increase in desorption capacity of the adsorbent at higher agitation speed (34). A maximum of 60%, 25% and 20% of metal ions were removed for Fe^{2+}, Cr^{6+}, and Ni^{2+}, respectively.

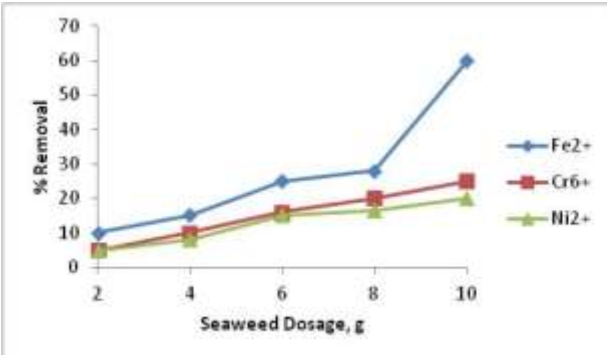

Figure 2: Effect of seaweed dosage on removal percentage of metal ions

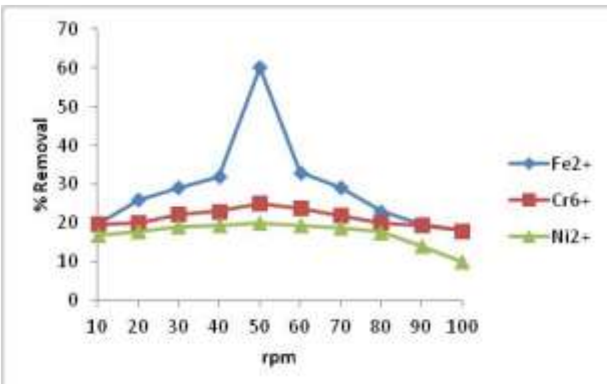

Figure 3: Effect of rotor's rotation on removal percentage of metal ions

3.4 Efffect of contact time

Figure 4 shows the efficiency of the seaweed adsorbent in adsorbing metal ions from the leachate with different contact time. In general, the adsorption increases with increased contact time for the first 10 to 30 min, and then the rate becomes constant at t=40-60 min. The decrease in adsorption indicates that the seaweed surface has reached a saturation level where all the active sites are not available for further bindings of metal ions (20). The different metal ions did not significantly affect the performance of the adsorbent, as the the removal of all of the metal ions increased with increased time. The maximum removal of Fe^{2+}, Cr^{6+} and Ni^{2+} was achieved at t=30min. No significant effect in removal was observed with further increase in contact time (35,36). A maximum of 62.5%, 29.3% and 30% of metal ions were removed for Fe^{2+}, Cr^{6+}, and Ni^{2+}, respectively.

4 Conclusions

This paper studied the optimum conditions for *Gracilaria changii* as a potential adsorbent in removing metal ions (Fe^{2+}, Cr^{6+} and Ni^{2+}) from landfill leachate. The optimisation of four different factors (pH, seaweed dosage, rpm and contact time) on adsorption rate was conducted at constant metal ion concentration of 20mg/L. The adsorption process was dependent on the pH of the solution and pH 5 is the optimum pH value for metal ion removal by *Gracilaria changii*. The adsorption process was rapid for the first 30 minutes and equilibrium was achieved at t=30min for all three metal ions studied.

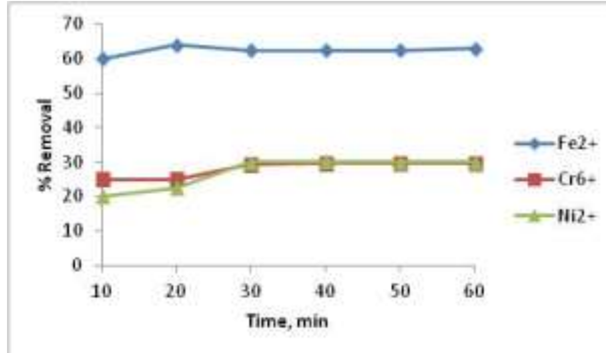

Figure 4: Effect of contact time on removal percentage of metal ions

Due to seaweed aggregation at lower agitation while desorption occured at higher speed, the optimum rotational speed was identified at 50 rpm for maximum removal of metal ions. Lastly, seaweed dosage of 10g was opted for maximum metal ion uptake as more active sites were available for binding. Taking into consideration of the results obtained from this optimisation study for ion concentration of 20mg/L, it can be concluded that these parameters can be used to investigate the effect of varying metal ions concentrations on the adsorption performance of *Gracilaria changii*. These optimum conditions show that *Gracilaria changii* can adsorb heavy metals and the performance can be improved in further investigations.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that the submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analysis and manuscript writing.

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