

Removal of Cd⁺⁺ from Contaminated Water Using Bio-surfactant Modified Ground Grass as a Bio-sorbent

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Abstract— Bio-sorbent activated carbon adsorption method has been applied in removing the Cd⁺⁺ ion from cadmium contaminated water. Dry ground grass has been chosen as a carbon source while bio-sorbent rhamnolipid has been used to activate of the carbon. Different bio-sorbent-grass doses were prepared and characterized by the Scanning Electron Microscopy, Atomic Absorption Spectroscopy and Fourier Transform Infrared Spectroscopy.

Results indicates that both porosity and surface roughness are very essential and required for the adsorption of Cd⁺⁺ ion. In addition, cadmium ion adsorption was significantly influenced by the change in the pH value of the media. The highest removal value of 85.77 % of the Cd⁺⁺ was recorded at pH 7 at 40mg of rhamnolipid. Increase in the concentration of rhamnolipid also increases the removal of the cadmium ion. Fourier Transform Infrared spectroscopy (FTIR) spectrum of the rhamnolipid modified grass before the adsorption indicates the presence of characteristic functional groups of O-H, C-H, N-H and P-O that are required to facilitate the adsorption of the cadmium ions. While the spectra of rhamnolipid modified grass after the adsorption shows a new peak and slightly shift of mostly peaks that reveals the adsorption of the cadmium ions. Results shows that modified grass could be potentially used in the heavy metal remediation and provides an efficient, economical and biodegradable bio-sorbent for the removal of the toxic and heavy metals from the environmental and industrial contaminated wastewater.

Keywords— *Rhamnolipid, biomass, adsorbent, cadmium, water treatment.*

1. INTRODUCTION

Heavy metals are the largest group of the trace elements that are industrially and biologically important. Heavy metals are considers to be toxic for the living organism if present in excess

amount, however, small quantities of Cu, Co, , Mo, Zn and Cr elements are required for the living organisms. . Industrial wastewaters and mining industries are the main source of heavy metals. Wastewaters resulted from battery manufacturing process, petroleum refining metal plating, pigment and paint manufacture, pesticides, photographic printing and industries, etc. are very rich in heavy metals [1]. The biggest problem associated with these heavy metals is their non-biodegradability, thus they can easily accumulate in living tissues and causes many different types of diseases and disorders [1].

Discharge of the heavy metals particularly cadmium, chromium and lead into the natural environment can cause numbers of environmental problems [2]. They have been proven to cause several diseases such as hypertension, anemia, renal dysfunction, cardiovascular, nervous system disease and potential carcinogenic element [3]. High accumulation of the heavy metals in agricultural land around mining regions, raises the heavy metal uptake by edible crops, this is of great dilemma to the inhabitants of the areas due to the potential health risk [4]. Cadmium is one of the most toxic metals that affects human, animals and plants [5]. Wastes from industrial process are the main anthropogenic through which cadmium enter into the environment [1].

Many methods have been implemented to remove heavy metals from wastewater such as reverse osmosis, membrane filtration, flotation, electrochemical treatment, precipitation and adsorption on the active carbon [6]. However, most of these methods are expensive and not suitable [7]. Activated carbon is the most used adsorbent technique; however, it is competitively expensive. Using lignocellulosic biomass waste materials, could offer a cheaper and economical substitution process [8].The term biomass refers to organic material that are from plants, trees, herbs, crops, algae origin. This includes grass,

agricultural wastes, wood, woody crops, herbaceous species, aquatic plants, industrial residues, waste paper, wood wastes, municipal solid waste, sawdust, bio-solids, food processing waste, algae and animal wastes [9].

Low-cost biological sorbents such as sugar cane husk, sawdust [10], moss [11] orange peel [12] and coconut shell [13, 14] have been introduced as a method for heavy metals removal from the wastewaters. Plant leaves have also been considered as an alternative cheap, economical and efficient sorbent solution for removing the heavy metal ions from wastewater, e.g. reed and sage for the removal of cadmium [15].

Lua et al., (2009) [16] used lawn grass as a novel bio-sorbent for the removal of the cadmium metal from aqueous solutions. Ground grass principally composed of protein, fibres (cellulose, hemi-cellulose and lignin), amyllum, pectin, and chlorophyll, etc., provide active sites that increase the removal ability of the toxic metal ions or from aqueous solution. In addition, cellulosic biomass contain various polar functional groups, such as alcohols, ketones, aldehydes, hydroxyl, carboxylic, ether and phenolic groups. At appropriate conditions, these functional groups are able to bond with the heavy metals and forming complexes in the aqueous solution by losing a pair of electrons [6]. Recently, the use of surfactants in wastewater treatment has been preferred in order to separate metal ions and other toxic substances [17]. Rhamnolipid belongs to the group of glycolipid bio-surfactants and has been intensively used in several remediation technologies due to many reasons such as; it is biologically produced by microorganisms which has great structural variety by which give a unique metal binding capacities and selectivity over other synthetic surfactants or chelates. Furthermore, ground grass is a solid waste during the process of gardening and costless. Combination of Bio-surfactant and ground grass offer a surface modified ground grass which has been chosen for the adsorption of the Cd (II) on the basis of above advantages.

II. EXPERIMENTAL SECTION

A. Materials

1. Bio-mass preparation (Collection, cleaning and grinding)

Grass was collected from garden located in Newcastle, North East of England, washed with deionized water in order to remove mud, sand and the other contaminants, then dried in the oven at about 60 °C for 12 hours. The dried grass was ground in a miller and sieved at particle size of 150 to 250 µm in diameter.

B. Methods

1. Preparation of the rhamnolipid solution

Rhamnolipid type I (R1) and type II (R2) produced by *Pseudomonas aeruginosa* (Rahman et al., 2002) were used in this study. Three different concentrations of 0.075, 0.15, and 0.225% of rhamnolipid aqueous solutions were prepared. Each solution was divided into three parts. The pH of the solutions were adjusted at 4, 7 and 10 respectively using 0.1M HCl and 0.1M NaOH.

2. Preparation of bio-surfactant modified ground grass (BSMGG)

2g of ground grass was mixed with 40ml of each of rhamnolipid solution at different pH in 500ml conical flask, while 2g ground grass was mixed in 40ml deionized water in order to prepare unmodified ground grass (control sample). These flasks were agitated at 200rpm for 5h using an electrical shaker. The suspensions were left undisturbed to separate the liquid and the ground grass. The mixtures were filtered by using Whatman filter paper of grade 1 (0.2µm). The filtrates were discarded while the residues of the bio-surfactant modified ground grasses (BSMGG) were washed 5 times with 200ml distilled water to remove superficially held bio-surfactant. The BSMGG were dried in a hot air oven at 60 °C for 8 hours. The dried (BSMGG) bio-surfactant modified ground grasses were stored in the separate airtight universal tubes.

3. Preparation of Metal Solution

Cd⁺⁺ solution of 10 ppm concentration was prepared using 1000 ppm analytical grade cadmium solution (Cadmium nitrate Cd(NO₃)₂ in HNO₃). The pH was adjusted to 4 by adding 0.1M HCl.

4. Batch mode adsorption studies

BSMGG were weighed in 20, 30 and 40mg. 20ml of 10 ppm Cd⁺⁺ solution was added into a labelled 100ml conical flasks containing the weighed BSMGG separately. An orbital shaker was used to mix the samples for 2 hours at 200rpm at 32°C. The supernatant solutions were separated by centrifugation at 3000 rpm for 30 min at the end of the adsorption period. The supernatant was filtered and the amount of adsorbed Cd⁺⁺ was measured using PU 94 500 Philips Atomic Absorption Spectrophotometer (AAS). The amount Cd⁺⁺ is calculated from the concentrations of the cadmium ion in the solution before and after adsorption [18].

The removal percentage was calculated by subtracting final concentration from the initial metal concentration. The result is divided by the initial concentration value. The final value is the percentage amount of absorption of cadmium in the solution.

Mathematically as,

$$\% \text{ Removal of cadmium} = (C_i - C_f / C_i) \times 100$$

Where, C_i = Initial concentration of cadmium
C_f = final concentration of chromium after treatment

The residues were kept overnight at 60 °C to dry then stored in the air tight universal tubes for surface analysis using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM Hitachi model 3400s).

The unmodified and modified biomass adsorbents were analyzed using FTIR (Perkin Elmer, Spectrum 100 FT-IR Spectrometer) under ambient temperature. The spectra were collected from 4000 to 650 cm^{-1} and scanned for five times.

III. RESULTS AND DISCUSSION

1. Scanning electron microscopy analysis.

Figure 1 shows the SEM micrograph of the surface of the ground grass. It shows that the surface of the tested grass is rough and highly porous. SEM images figures 1-B and 1-C show the ground grass treated with HCl at pH 4 and NaOH at pH 10 respectively enhances the porosity and surface roughness compared to the unmodified grass. That indicates the pore volume and surface area increased which could lead to more uptake of the Cd^{++} .

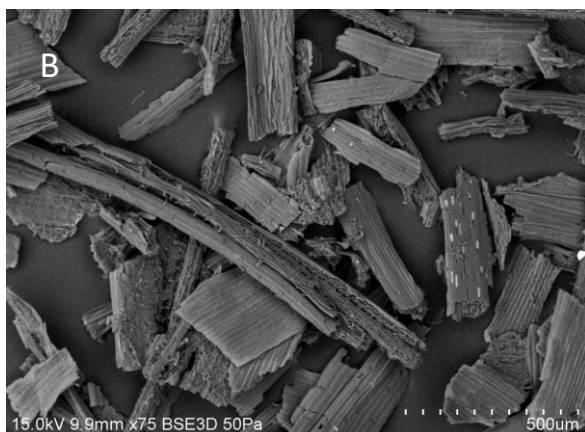


Fig. 1. SEM images of Ground Grass (A) without treatment (B) treated with HCl at pH 4 (C) treated with NaOH at pH 10.

2. Effect of pH on Cd^{++} adsorption

In order to optimize the pH of the adsorption of the cadmium ion; a series set of experiments were conducted. The efficiency of the adsorbent in the removing of the heavy metals depends upon the surface tension of the solution and surface activity of the sorbent. The effects of the pH on the removal of the Cd^{++} are clearly shown in the figures 2. The removal of the Cd^{++} at pH 4.0 is very low due to the protonated (H^+) nature of the solution. High concentration of H^+ already fills the adsorption sites and reduces the removal of metal ion. The highest Cd^{++} removal noted at the pH 7 because at this pH, the surface activity of the rhamnolipid is very high which increase the adsorption whereas, at pH above than 7, the removal of the metal ion was decrease due to the dissociation of the hydroxyl group of the rhamnolipid into carboxylate which reduced the surface activity. The solution of the rhamnolipid was appearantly very clear at pH 7.0 and was turbid below pH 7, However,, at pH 4, the precipitation was seen in solution. Zhang and Miller in 1992 [19] also reported that the precipitation was not visualized until the pH was decrease below 5.0 and the turbidity was seen at above pH 7.

At pH above than 6.8, the majority of the rhamnolipid carboxyl groups have been dissociated and formed carboxylate groups. At pH 5 or lower, the protonated form reign in the solution and compete with the heavy metal at adsorption site [20].

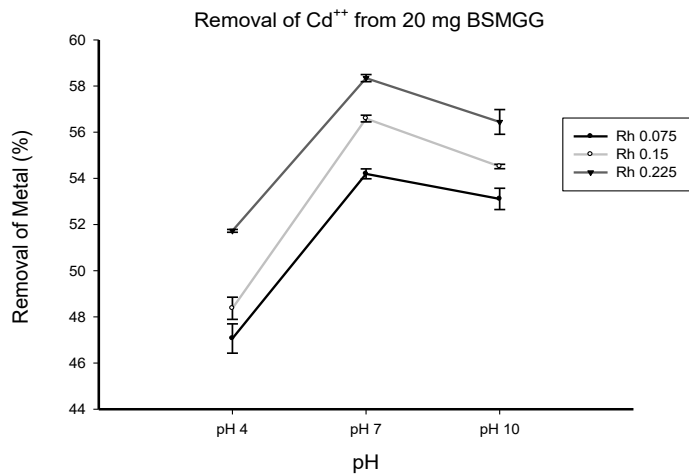


Fig. 2. Effect of pH and concentration on the Removal of the Cd⁺⁺ through 20 mg BSMGG.

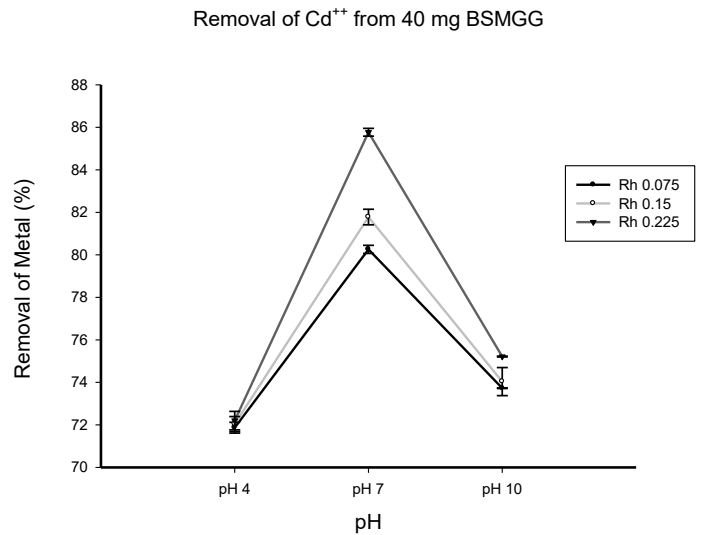


Fig. 4. Effect of pH and concentration on the Removal of the Cd⁺⁺ through 40 mg BSMGG.

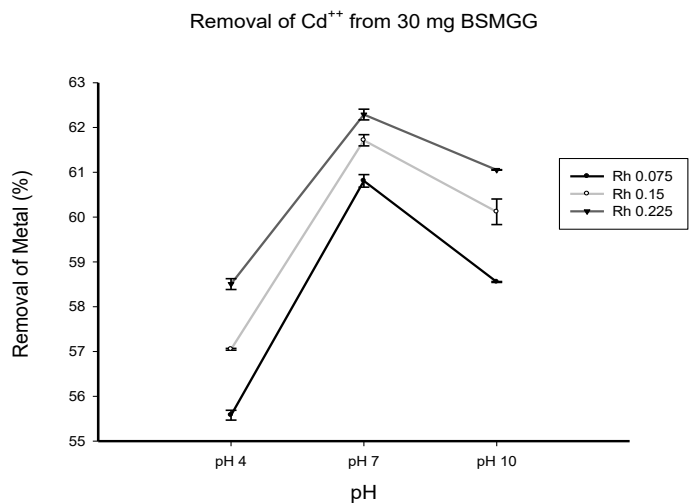


Fig.3. Effect of pH and concentration on the Removal of the Cd⁺⁺ through 30 mg BSMGG.

Another study done by Zhang and Miller in 1992 [19] also supports this effect of pH on the rhamnolipid. They reported that the surface activity of the rhamnolipid is greatly affected by the pH due to the change in the surface tension of the solution. Surface activity of the rhamnolipid was quite high between the pH 7 to 7.5 however, as the pH was raised from 7.5, a slight decrease in the activity of rhamnolipid was found due to the increase in the surface tension from 30 to 32 mN/m. The surface tension of the solution was relatively stable up to a pH of 11. Furthermore, as the pH was decreased from 7.0 to 5.0, surface tension was increase from 30 to >40 mN/m resulting in a significant decrease decrease in the surface activity.

3. Effects of concentration of rhamnolipid on Cd⁺⁺ adsorption

The concentration of the rhamnolipid has a great effect on cadmium ions adsorption. Figure 2; shows that the increase in the rhamnolipid concentrations increases the Cd⁺⁺ removal of the aqueous solution. This is attributed to the reduction in the surface tension of the solution. High concentration of the rhamnolipid also provides more anionic character to the biosorbent and increases the active sites for the Cd⁺⁺.adsorption

3.4 Effects of bio-sorbent dosage on Cd⁺⁺ adsorption

The effect of the bio-sorbent dosage was investigated and shown in the figure 5. The percentage of removal of the Cd⁺⁺ was increased as the concentration of the bio-sorbent was increased. Initially, the rate of the removal of the Cd⁺⁺ was very high but after that, the rate of the removal percentage has dropped down and the change in the removal ratio was little.

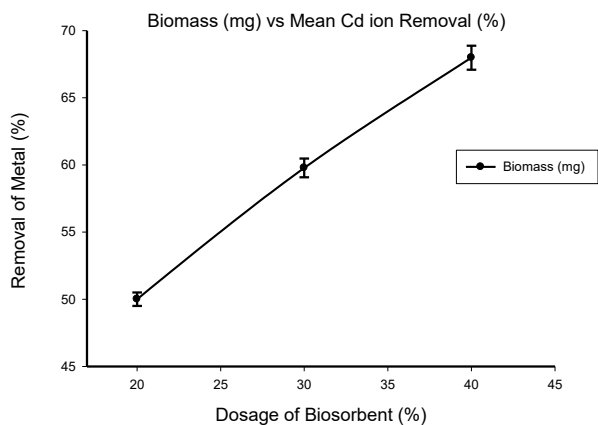


Fig.5. Effect of bio-sorbent dosage on the removal of the Cd²⁺ at natural pH.

Primarily, the formation of the complex between active sites on the surface and the Cd²⁺ was high due to the presence of a high amount of Cd²⁺. The adsorptions at the higher dosage of bio-sorbent need more Cd²⁺ ion to increase the rate of removal whereas, it is maintained at constant level at constant concentration amount of the Cd²⁺ ion. the complex formation rate between Cd²⁺ and active site decrease when the dosage of the bio-sorbent increase.

3.5 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Figure 6, shows the FTIR spectra of the grass before and after the adsorption process. The broad adsorption peak at 3281.61 cm⁻¹ is due the O-H stretching vibration from dissociating hydroxyl groups. Peaks at 2918.48 cm⁻¹ and 2850.53 cm⁻¹ are attributed to the C-H stretching vibration of methyl groups. Peak at 1730 cm⁻¹ is due to the presence of carbonyl (C=O) stretching vibration of ketone group, while the peak at 1587.11 is attributed to N-H stretching vibration and N-H bending vibration. The peak at 1400 cm⁻¹ is due to the presence primary amides, this peak shows the N-H stretching vibration. 1264.80 cm⁻¹ was caused by C-O stretching vibration of carbonyl and it may cause for O-H and C-N stretching vibration. Peak at 1158.68 cm⁻¹ may result from C-N. The absorption peak at 1034.81cm⁻¹ is caused by phosphate functional groups such as P-OH and PO₄³⁻. Those peaks may also represent the presence of alcoholic and polysaccharide compounds exist in native grass. The FTIR spectrum of the grass after the adsorption of the cadmium is changed from the spectra of grass before adsorption [21].

The FTIR spectrum of the biomass before the adsorption is different from the FTIR spectrum of the biomass after the cadmium ion adsorption as shown in figure 6-B. Hydroxyl, amide and carbonyl groups are the highest functional groups that are involved in the metal ion adsorption [6]. At 15345.68 cm⁻¹, the new peak may be due to C=C symmetric stretching or may be due to N-H stretching vibration of secondary amide. The peaks at 1587.11 cm⁻¹, 1397.02 cm⁻¹, 1264 cm⁻¹ are slightly shifted.

Polysaccharides, proteins and lipids are the main components of grass that act as the basic adsorption sites for the metal ions [22]. Many scientists have reported that carboxyl group and amine group are important compound groups that are involved in heavy metals absorption of the [7 &19].

According to the Zeng et al., [23] the cadmium adsorption through the biomass is due to the presence of O-H (hydroxyl group), C-N (cyanide), C=O (carbonyl), P=O (phosphate) and N-H (amide) functional groups. The FTIR analysis indicates the presence of these functional groups, which proves that the bio-surfactant modifies ground grass, is more potential biomass that can use for the bio-sorption for the cadmium ion from the wastewater.

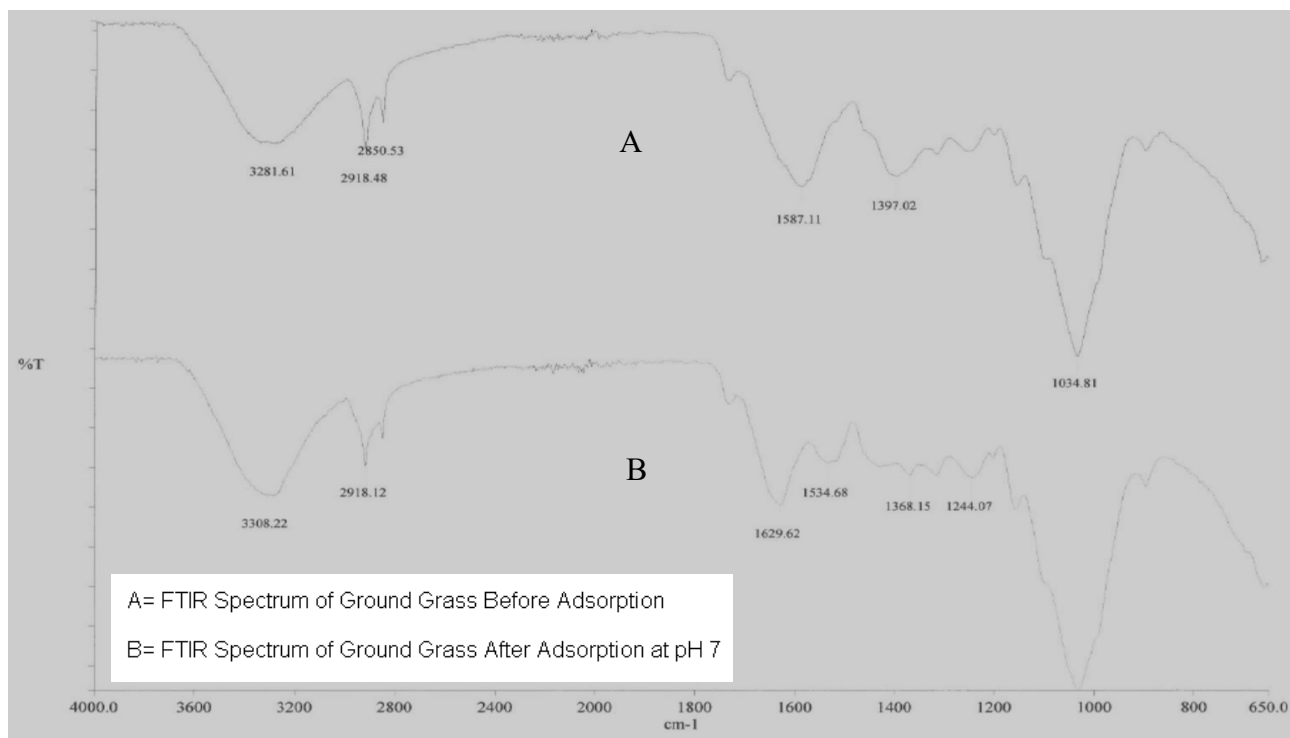


Fig. 6. FTIR spectrums of the grasses (A) before and (B) after adsorption at pH 7.

IV. CONCLUSION

The current study explores a new and economical bio-sorbent for the adsorption of the Cd^{++} ions from the wastewater. This bio-sorbent is a cheaper alternative solution as compared to the costly synthetic adsorbent process for Cd^{++} ions removal. The use of bio-surfactant can be a better candidate for the treatment of heavy metals or contaminated wastewater due to its high heavy metals removal capability, low toxicity and high biodegradability. In Addition, the main advantages of the rhamnolipid modified bio-sorbent are that its rapid attachment, high sorption ability and low cost. SEM analysis reveals that the surface of the BSMGG is highly porous and rough structure of the material whereas, the EDX analysis (data not shown) confirmed the absorption of Cd^{++} on the rough and porous surface of ground grass is an essential process element in the adsorption of the Cd^{++} from the waste water.

AAS observations showed that the adsorption of the Cd^{++} by the ground grass is strictly dependent on concentration of rhamnolipid and pH level. the optimum pH was recorded at pH 7.0. FTIR analysis of the surface of the BSMGG has indicated the presence of characteristic functional groups showing the complexity nature of the ground grass. The results from AAS has shown that an increase in the concentration of rhamnolipid results in an increase the adsorption of the Cd^{++} .

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