Adsorption of Hexavelent Chromium, Cr (VI) by Using Leucaena Leucocephala Pods

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***Abstract*- Industrialization and urbanization were the most factors of large amount of heavy metals and other pollutants presents in the wastewater. One of the heavy metals that presents in the wastewater is hexavalent chromium Cr (VI). The present studies have been done by using Leucaena Leucocephala Pods (LLP) as adsorbent in the removal of heavy metals present in the waste water. In the experiment, LL was used in the removal of hexavalent chromium Cr (VI) ions. Thermo Gravimetric Analysis (TGA), Point of zero charge (pHpzc) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterise the pods of LL. The experimental adsorption parameters investigated include effect of pH, adsorbent dosage and contact time. The best condition of parameters such as 0.25 g of LLP dosage, time of contact of 120 min, pH of 2 indicated the maximum Cr (VI) uptake. This study shows that LLP is an efficient and cost-effective adsorbent for removing Cr (VI) and it can be a solution for Cr (VI) discharging industries.**

Keywords: Leucaena Leucocephala Pods (LLP), Hexavelent Chromium, Adsorption, Characterization

1.0. Introduction

Industrialization and urbanization were the most factors of large amount of heavy metals and other pollutants presents in the wastewater. This wastewater containing all the heavy metals and pollutants were then released into the aquatic ecosystem [1]. Both human and aquatic lives were affected due to the high release amount of heavy metals present in the wastewater[2]. One of the heavy metals that presents in the wastewater is hexavalent chromium Cr (VI). Due to its harmful effects to the human, hexavalent chromium was listed as one of top sixteen most pollutants heavy metals. Malaysia encountered quick expansions in terms of industrialization and urbanization to become one of the most advanced country by 2020. However, the activities conducted to make the country advanced have affected in water pollution around the areas of the country [3]

Electroplating, fertilizer, textile mill, paint and dye were the industry that generates hexavalent chromium as their effluent[4]. Disease such as kidney and liver damage, lungs and digestive tract cancer were reported when exposed to high dosage amount of hexavalent chromium[5]. Skin irritation and ulceration were also reported if a person were exposed to the metals in a low concentration.

The amount of these heavy metals that presents in the wastewater can be reduced by many applications such as membrane filtration, biological methods, ion exchange, reverse osmosis, solvent extraction, reduction and precipitation[6]. However, by using these types of applications, further disposal will be needed as the toxic sludge was formed. These methods or application cannot be used to extract a too low or too high concentration of hexavalent chromium. The costs of these applications also were high due to the equipment maintenance and supervision.

More effective methods in the removal of heavy metals were introduced which is by adsorption using biomaterials, carbons, carbo nanotubes and polymeric resins. This method is more favourable due to low operation cost, simple operation design and sludge free environment[7]. Bio adsorption is also more advantageous due to the local availability compared to other methods[8].

Many researches had been done in adsorption process by using different types of adsorbent of raw and modified agricultural waste such as persimmon[9], orange waste[10], banana peel[11], orange peel[12], peanut hull[13], peanut husk[14], rice husk[15] and coconut fibre[16]. When using plant wastes for wastewater treatment, it provides other advantages such as cheap and simple technique, requiring little processing and equipment, higher capacity of adsorption, selective adsorption of heavy metal ions, abundance of plant waste and can be recycled[12]. Recently some agricultural wastes have been developed as adsorbents and the cost of these biomaterials lower compared to the adsorption by using activated carbon.

The present studies have been done by using LLP as adsorbent in the removal of heavy metals present in the waste water. Cellulose, hemicellulose and lignin were presents LLP[17]. These chemical components present in LLP contains hydroxyl, carbonyl and carboxyl groups. These functional groups act as a binding site and thus can be used to adsorb metals ion such as hexavalent chromium[18]. The objectives of the paper were to determine the cellulose, hemicellulose and lignin content present in LLP and to study the effect of pH, effect of time and dosage of adsorbent in the adsorption of hexavalent chromium Cr (VI) ion by using modified LLP.

2.0. Methodology

2.1. Materials and Chemicals.

Leucaena Leucocephala pods were collected at Section 7, Shah Alam, Selangor (3.087244,101.498005). Then, hexavelent chromium, Cr (VI) solutions of 1000 mg/L were produced by dissolving 2.8286 g potassium dichromate powder (MERCK Chemicals), $K_2Cr_2O_7$ into deionized water. The stock solution was diluted with distilled water as per the requirement of the experiment. The solution pH was arranged using 0.1 (M) HCl (Fisher Scientific Sdn. Bhd.) and 0.1 (M) NaOH solutions (R&M Chemicals) for the experiment purposes.

2.2. Preparation of Lucaena Leucocephala Pod Adsorbents.

Samples of LLP were washed by using water and dried in an oven at 100°C for 72 hours. Then, the samples were grinds into powder and sieved using ENDECOTTS Octagogon 2000 Digital Sieve Shaker to remove uneven particle size to the size of 400 µm.

2.3. Modification of LLP

2.3.1. Removal of Chlorophyll Content

200 mL of distilled water in the 250 mL of beaker was boiled until it reached 100 °C. 100 g of dried LLP biomass of 400 µm was added into the beaker. LLP samples were boiled with hot water to kill a leaf, to softer the cuticle, and to kill any interruptions of the cell membrane. Thus, this step makes it possible to eliminate the chlorophyll with hot ethanol. Then, the mixture was stirred at 220 rpm and at 200 °C for 10 minutes. Next, the sample was filtered after cooling and the residue was oven dried overnight until it reached constant weight at 105 °C.

After dried, 100 g of dried biomass that has been free of silica content was transferred into a 1000 mL beaker. 500 mL of 95% of Ethanol (Fisher Scientific Sdn. Bhd.) was added into the beaker. The selection of the ethanol used due to the researcher before found the most efficient of extraction with methanol and acetone was about the same with commercial 95% (by volume) aqueous ethanol and prepared 80% (by volume) aqueous acetone [19]. The mixture was then stirred at 300 rpm at 60 °C for 3 hours. After cooled the sample, it was then filtered. The residue obtained after filtration was oven dried overnight to a constant weight at 105 °C.

2.3.2. Removal of Lignin in LLP

100 g of dried LLP biomass that has been free off silica and chlorophyll contents was transferred into a 1000 mL beaker. 500 mL of 0.1 N HCL solution was added. The mixture was agitated for 3 hours at 50 °C in a hot plate using magnetic stirrer. Afterwards, the remains were filtered and washed repeatedly with distilled water until the pH of the sample become neutral. Lastly, the samples were oven dried at 80 °C for 48 h until reached constant weight [20].

2.4. Physical Characterization of Adsorbent.

Fourier Transform Infrared Spectroscopy were used to study the functional groups inside the sample of adsorbent that is used for the removal of hexavelent chromium, Cr (VI) within the range of 500 to 4000 cm^{-1}. FTIR were conducted by using Perkin Elmer Spectrum One FT-IR Spectrometer

Thermo Gravimetric Analysis (TGA) was used to determine chemical components inside the adsorbent by heating the biomass. TGA was conducted using Mettler Toledo TGA851/1600. TGA was conducted by using nitrogen gas. The heating rate used in TGA was 10 °C/min and the temperature ranging from 0 to 1000 °C. was done to evaluate the specific surface area of adsorbent. First, degassed the adsorbent at 200 ◦C in nitrogen environment for 1 h.

The point of zero charge (pH_{PZC}) of the LLP adsorbent was determined. The LLP adsorbents were arranged by weighing 0.1 g of LLP sample. Then, the sample were inserted into conical flask containing 25 ml of 0.01 M KNO_3 solution. The pH of the solution range from 2 to 12 were adjusted and the samples were agitated at 120 rpm in a shaker for 24 h [5].

2.5. Adsorption experiments

For biosorption experiment, a few parameter or variables such as different pH (2, 4, 6, 8, 10 and 12), adsorbent dosage (0.05, 0.25, 0.5, 0.75, and 1 g) and different adsorption time (10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 min) were conducted [20].

For the experiment of biosorption, 25 ml of 50 mg/L of Cr (VI) solution was inserted into conical flask. Then, the flask was covered with aluminium foil and the was placed in the rotating shaker with 120 rpm shaking rotation. Make sure the shaking was constant throughout the experiment.

After shaked, the solutions were filtered using filter paper. The filtrate was stored into bottles to determine the amount of Cr (VI) remains in the solution. Then, the concentration of Cr (VI) before and after experiment were determined by using ThermoFisher iCP 6000 Series to determine the removal of Cr (VI) in the solution.

3.0. Results and Discussion

3.1. Adsorption Characterization

3.1.1. Point Zero Charge

Point of zero charge (pH_{pzc}) can be defined as the pH at which the adsorbent has zero value of surface charge. Point zero of charge also indicates the sites of adsorbent surface has equal amount positive and negative charges. The pH_{pzc} is found to be 6.0. This can be seen from Figure 1 where the determination of pH_{pzc} were plotted. When the solution pH higher than pH_{pzc}, the adsorbent has a positive surface charge. The adsorbent has a negative surface charges when the pH were lower than pH_{pzc}, Adsorbent with negative surface charge could interact with metal positive species while adsorbent with positive charge at the surface could interact with negative species [21]. From Fig. 1, the adsorbent surface is positively charge below pH 6 while the surface of the adsorbent is negatively charged above pH 6.

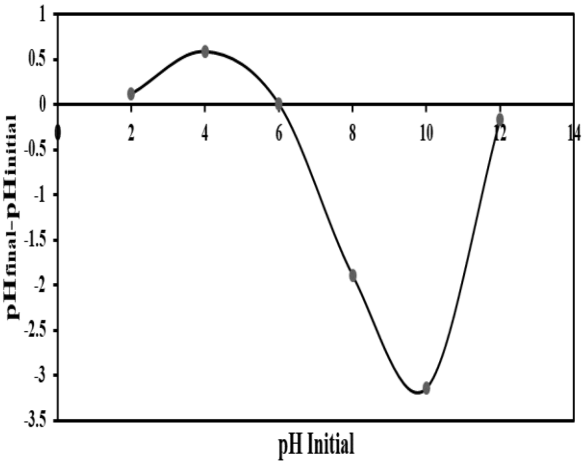


Fig. 1: Point Zero Charge

3.1.2. FTIR

To determine the functional group that exists on the surface of LLP, FTIR was conducted. These active functional groups that present in the surface of LLP might involve in the adsorption process of Cr (VI). The wavelength of adsorbents was set within 500 cm^{-1} to 4000 cm^{-1}. The FTIR spectra of LLP for raw (A), modified (B) and after adsorption (C) were shown in Fig. 2 below. From Fig 2 below, there are few adsorptions peak present. These peaks indicate the functional groups that presents in the surface of LLP such as hydroxyl, carbonyl and carboxyl groups.

For modified LLP, a large wide peak at 3331 cm^{-1} wavenumbers corresponds to the vibrations of the OH stretching bonds apparently due to the cellulose present in the LLP. For raw LLP, the band at 2924 cm^{-1} attributed to the vibrations of asymmetric elongation of CH_2 and the symmetrical elongation of $-CH_3$ of the aliphatic acids. The band about 1600 cm^{-1} for all samples indicates the elongation vibration of the carboxylic groups. The band at 1319 cm^{-1} originates from the elongation vibration of the -OH groups of the phenolic compounds [22].

The vibration of aromatic bonds C=C can be seen at the peaks between 1500–1650 cm^{-1}. These peaks reveals that lignin exist in LLP. It can be seen that the lignin content inside LLP decreases as the peak present in Fig 2 shows the decreasing in peaks for raw, modified and after adsorption process [16]. COO^{-} of carboxylate group and intervention of hydroxyl group exist and it can be seen at peak of 1323 cm^{-1} [23].

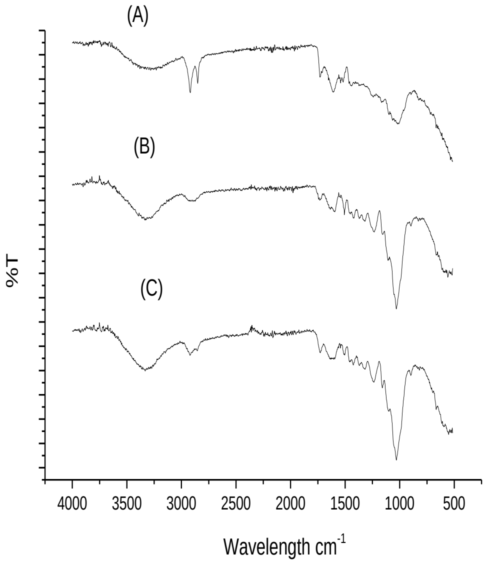
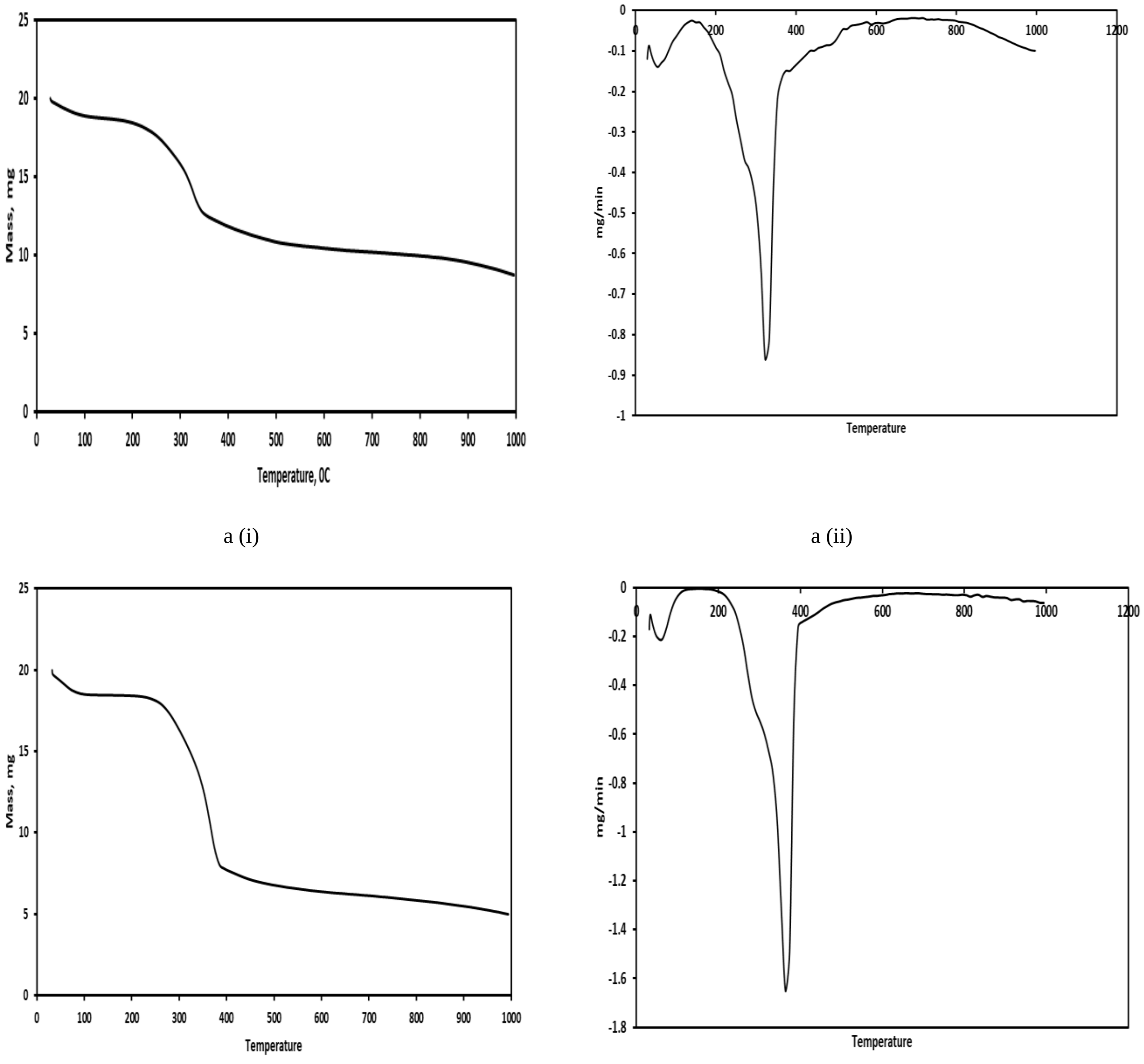


Fig 2: FTIR Spectra for LLP

3.1.3. Thermo Gravimetric Analysis (TGA) and Derivative Thermogravimetric (DTG).

Thermo gravimetric analysis (TGA) illustrated thermal degradation of different components of LLP with rising temperature while DTG indicates the zones in which there were various steps of reaction occurs[24]. Thermo gravimetric analysis (TGA) illustrated thermal degradation of different components of LLP with rising temperature. The thermal parameters of the adsorbent present two stages of thermal degradation. TGA and DTG curve for raw LLP were represented in Fig 3a(i) and (ii). Weight loss about 5.43 % when the temperature increases until 61 ^{o}C apparently due to the moisture content in the samples evaporates. The second stages apparently due to the decomposition of cellulose and hemicellulose which can be overlapped when the temperature increases from 61-512 ^{0}C. A maximum reduction of the mass sample were obtained at this stage and the residual weight of the biomass after this phase was 53.36 %[25]. A further loss of weight continued until 1000 ^{0}C decomposing lignin[13]. From the TGA analysis it shows that the major component presents in raw LLP is hemicellulose and cellulose and it was easily degraded. The component of cellulose presents in raw LLP was the second most abundant after hemicellulose. Most stable components present in the raw LLP is lignin compared to cellulose and hemicellulose. Lignin is stable as it is the last to degrade compared to other components.

TGA and DTG curve for modified LLP were represented in Fig 3 b(i) and (ii). From Fig 3 b(i) and (ii), weight loss about 6.7 % when the temperature increases until 55 ^{o}C apparently due to the moisture content in the samples evaporates. The moisture content can be seen increases from 5.43 % to 6.7 % for raw and modified LLP due to the increases in H$^+$ ions during the modification process of LLP. The second stages apparently due to the decomposition of cellulose and hemicellulose which can be overlapped when the temperature increases from 55-547.74 ^{0}C. A maximum reduction of the mass sample were obtained at this stage and the residual weight of the decreases to 32.8% compared to raw LLP which was 53.6%. From the analysis, the cellulose and hemicellulose present in the modified LLP increased compared to raw LLP. A further loss of weight continued until 1000 ^{0}C decomposing lignin [24]. The composition of lignin can be seen decreased from 10.77 mg to 6.52 mg. This result obtained shown that the amount of lignin present in the LLP decreased after it was modified. As a result, a higher amount of Cr (VI) can be adsorbed into modified LLP.



a (i)

a (ii)

b (i)

b (ii)

Figure 3:TGA [a(i)] and DTG [a(ii)] for Raw LLP, TGA [b(i)] and DTG [b(ii)] for Modified LLP

3.2. Effect of various adsorption parameter

Adsorption of Cr (VI) were influenced by various process parameters like the pH of the solution, the contact time of adsorbent and dosage of the adsorbent.

3.2.1. Effect of pH

The effect of pH on the adsorption behaviour of Cr (VI) was evaluated over a pH range from 2 to 12. The results (Fig. 4 and Fig. 5) showed that the adsorption capacity of Cr (VI) was maximum which 6.89 mg/g (92.11 %) for LLP at pH = 2 at an initial concentration of 50 mg/L. With the increasing of pH of the solution from 2 to 12, the efficiency and Cr (VI) adsorption decreases as a result. According to this result, an important adsorption was observed at very acidic pH medium for LLP.

At pH lower than 6, the surface charge for LLP is mainly positive. Since there is no competition to chromium ions in solution leading to this significant adsorption capacity through electrostatic forces of attraction. This behaviour is explained by the functional groups present on the surface of LLP (amino, carboxyl and sulphonate groups) that undergo a strong protonation, which gives the adsorbent positive global charge.

Chromium exists as $HCrO_4^{-1}$, $Cr_2O_7^{-2}$ when the pH was higher than 2. At pH of 7 and higher, chromium exists in the form of CrO_4^{-2}. At lower pH, chromium was repeatedly adsorbed in the form of $HCrO_4^{-1}$ on adsorbent surface as the surface contained positive charges. Then, electrostatic forces were produced between adsorbent surface and chromium ions. So, adsorption can be seen higher at low pH. When pH of the solution increased, $HCrO_4^{-1}$ ions of chromium start to reduce, and surface charge of the adsorbents change from positive to negative. As a result, adsorbent surface became repellent against chromium ions and thus the adsorption decreased[1].

When pH of the solution was increases up to 10, the concentration of hydroxyl (OH^-) in the solution increases. Those radicals compete with the anionic Cr (VI) species, causing a decrease in the amount of chromium adsorbed at higher pH values since, so the active sites number drops significantly. As pH of the solution increases, the surface charge of LLP becomes negative which also can reduces adsorption rate of Cr (VI)[27].

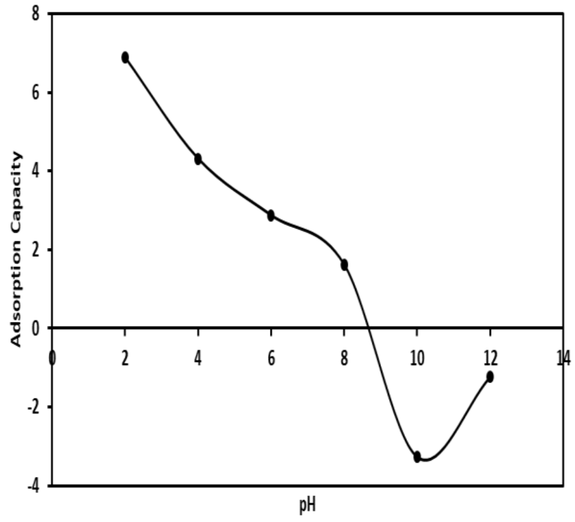


Fig.4: Adsorption capacity against pH

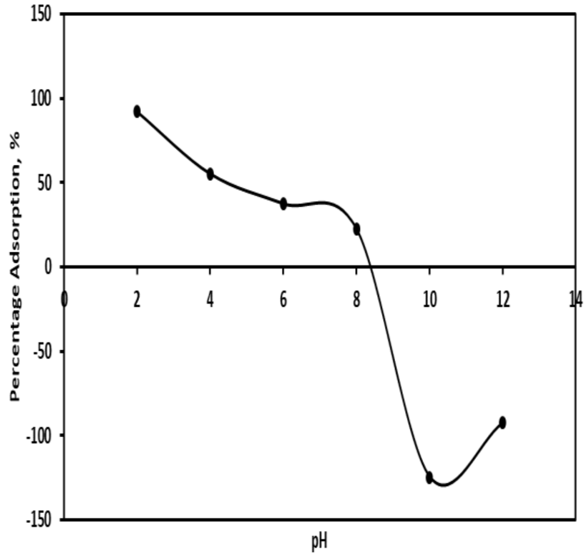


Fig 5: Effect of pH on the biosorption of Cr (VI) by LLP: Co = 50.00 mg/L, particle size 400 µm, contact time = 24 h, temperature = 25 °C, pH = 2-12 for Cr (VI)

3.2.2. Effect of Adsorbent Dosage

The effect of adsorbent dose on the adsorption capacity of the Cr (VI), was studied. The influence mass of LLP on the adsorbed amounts of Cr (VI) is represented in Fig. 6. An increase in adsorbent dosage leads to an increase of removal efficiency from 94.79 % to 98.68 % when varying adsorbent amount from 0.05 g to 1.0 g. This result can be obtained probably due to the higher number of active sites presents when the adsorbent dosage is high[28].

However, the adsorption capacity can be seen decreases as the dosage of the adsorbent increases from 0.05 g to 1.0 g. Figure 7 shows that the adsorption capacity decreases as the adsorbent dosage increases. At 0.05 g, the adsorption capacity is high which was 35.46 mg/g while when the amount of adsorbent was 1.0 g, the adsorption capacity decreases to 7.38 mg/g. This might due to the saturation that occurs quickly at accessible sites and needed less energy. However, chromium adsorption in accessible sites that require larger energy, do not achieved and lead to greater adsorption rate of chromium but its capacity declining [29]. Thus, choosing a reasonable adsorbent amount in the removal of Cr (VI) ion with a comprehensive deliberation is essential.

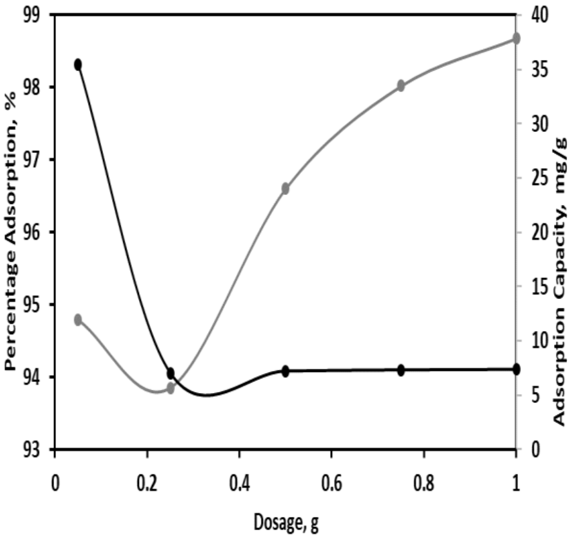


Fig. 6: Effect of dosage on the biosorption of Cr (VI) by LLP: Co = 50.00 mg/L, particle size 400 µm, contact time = 24 h, temperature= 25 °C, pH = 2 for Cr (VI)

3.2.3. *Effect of Contact Time*

The effect of contact time on the adsorption capacity of LLP was studied. As shown in Fig. 7, the amount of adsorbed Cr (VI) onto LLP increased when the contact time increased from 10 to 180 min. Fig. 7 shows that the amount of Cr (VI) adsorbed onto LLP at contact time of 10 min are 11.85 mg/g. As the contact time between LLP and Cr (VI) solution increases to 120 min, the amount of Cr (VI) adsorbed onto LLP increases to 19.73 mg/g, respectively.

From Fig.7, a quick or fast uptake of solid-liquid contact had occurred within the first 60 min. After that, subsequent slow uptake of solid-liquid contact occurs from 60 to 180 min [22]. At the beginning the removal rate was high because of the accessibility of abundant active groups for Cr (VI) adsorption[30]. By increasing the contact time, it produced enough time for Cr (VI) in solution to look for free site to be adsorbed into LLP. This can be seen on Fig. 7 where percentage adsorption of Cr (VI) onto LL increased from 63.34 % to 87.92 % from 10 to 120 minutes respectively. After 120 minutes, the adsorption rate reach equilibrium and becomes slow. This is as the result of declining in the number of active sites after this time[31].

The fast or quick uptake of Cr (VI) during early phase can be described due to higher striking possibility and abundant porous active sites presents on the outer layer of adsorbents. These active sites were filled up rapidly by the action of adsorbates ions. As soon as outer layer of adsorbent reached saturation level, then adsorbates molecules forcefully adsorbed into internal pores of adsorbent.

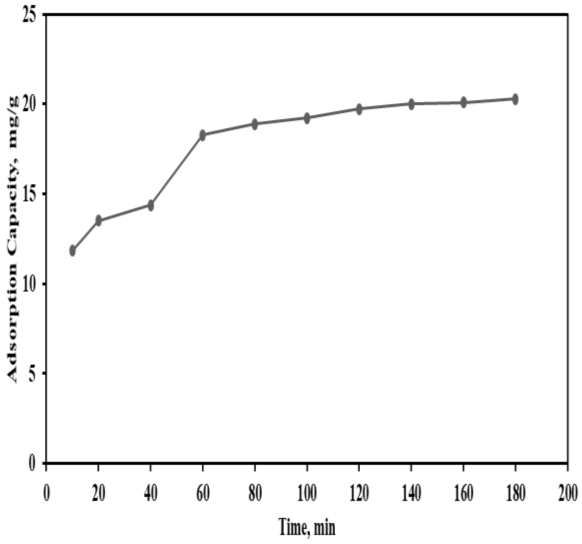


Fig. 7: Effect of contact time on the biosorption of Cr (VI) by LLP: Co = 50 mg/L, particle size 400 µm, contact time = 180 min, temperature = 25 °C, pH = 2 for Cr (VI)

4.0. Conclusion

The pods of Lucaena Leucocephala has a potential as a green adsorbent for Cr (VI) adsorption. Adsorption of Cr (VI) onto LLP would preferably occur in mostly acidic conditions as the adsorbent as the adsorbent has positive surface charge at pH ≤ 6. Based on the experimental analysis, it appears that the best condition for adsorption of Cr (VI) would be (13.85 mg g-1) at pH 2 with concentration of 50 mg/L for an adsorbent dose of 250 mg and contact time of 120 min at 27 °C.

This study was conducted to illustrate the viability of sustainable management of LLP in a way that is friendly to environment but offers economic incentive. Thos study also shows that this material should be used for the elimination one of the common carcinogens. From the results obtained, it can be seen clearly that LLP can be utilized as an option as adsorbent that can be used in a comprehensive wastewater and water treatment plant for the elimination of Cr (VI) from contaminated water.

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