THERMAL ACTIVATED *Casuarina equisetifolia* WOOD BARK FOR HEAVY METAL ADSORPTION

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ABSTRACT: *The thermal activation has been used with better results for increase the adsorption capacity of some materials and the thermally modified wood might be a better adsorbent than untreated wood. Wooden materials or wastes are cheap sorbent materials. The useful of application of wooden by-products or wastes for wastewater treatment are determined by their high removal selectivity, good adsorption capacity and possibility of regeneration. In order to, present studies suggest this hypothesis for several criteria. The powdered Casuarina equisetifolia wood bark heat treated at 2, 6 and 8 hours were obtained and the maximum adsorption was evaluated in pH 5 and pH 8 for the unheated and heated series respectively. In spite of that, all heat treated wood samples showed a significant higher adsorption capacity than compared to unheated wood for cadmium and chromium adsorptions. Although this reported that the Langmuir model gave a better fit than the Freundlich model, whereas adsorption capacity is optimum in Cr (III) ion in pH 5 and the maximum monolayer adsorption capacity reported for Cd (II) ion in pH 5. This can be a better benefit of heat treated wood in the end of its life.*

Keywords: Thermal activation, Adsorbate, Freundlich model, Adsorption capacity

1. INTRODUCTION

With the fast development of industry, water pollution is a global problem threatening the entire biosphere and affecting the life of many millions of people around the world (Esteves et al, 2017) (Bolisetty et al, 2019). Heavy metals are very common pollutants in some industrial wastewaters. The most dangerous heavy metals are chromium and cadmium which exists in very high concentrations in wastewater mainly from the leather, metal cleaning plating and electroplating industries. The removal of chromium from these waters is usually done by precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange and adsorption (villaescusa et al, 2004). When adsorption is used, activated carbon and ion-exchange resins are preferred. The main disadvantage of these method is the high cost for the chromium removal, and therefore several studies have been made on low cost adsorption materials, most of them lignocellulosic materials like agro industrial residues, wood sawing powders or barks. Present work is the removal of heavy metals by using Casuarina equisetifolia wood bark as a natural tool (Kamble et al., 2009). Wood bark, a relatively inexpensive adsorbent, is crucial for removing metal ions, some types of acid and basic dyes, and other undesirable chemicals from wastewaters. The primary sites for metal binding are found in lignin, cellulose and hemicellulose, polysaccharides, and phenolic compounds, which contain carboxyl, hydroxyl, sulphate, phosphate, and amino groups.

There are numerous advantages to using wood bark to remove contaminants for the preservation of the environment and the timber sector (Demcak et al. 2017). In this project, summarize the current state of research on the removal of heavy metals with low-cost adsorbent as a wood bark that are realistic in the context of the developing world (Joseph et al, 2019). In order to enhanced the adsorption capacity of some materials, thermal activation was used with better output results and so thermally modified wood might be a better adsorbent than untreated wood. The thermal modification strengthens the wood, sustainability and durability. Which the Process heat may have many influences on product quality. Thermal activation could be prepared through the process of heat treatment of woods by using autoclave. In the process the dried raw materials should be heated under autoclave in sterilized conditions (Bourgois et al, 1989). Here in this study, the heavy metal absorption concentrations are determined by Atomic Absorption Spectrometer with respect to the pH Values and thermal activations (Chubar et al, 2004). The aim of this research is to recognize the adsorption efficiency of thermally treated and untreated wood. Reports have looked into the impact of different experimental conditions like concentrations. Using the Langmuir and Freundlich adsorption isotherms, equilibrium modeling was done. (SenthilKumar et al, 2011).

2. METHODOLOGY

The Casuarina equisetifolia wood bark were treated at atmospheric pressure inside an autoclave for 2, 6 and 8 hours at 190 ºC. Heating was performed by admission of steam into the autoclave. After the treatment, the samples were milled, sieved and the 40 mesh fraction was used for the adsorption tests. To determine the best pH for adsorption 25 ppm of Cadmium chloride hydrate $(CdCl_2(H_2O)_x)$ and Chromium (III) chloride hexahydrate $(CrCl_3.6H_2O)$ solutions were prepared and titrated to pH 5 and 8. Milled samples (unheated, 2h, 6h, 8h) were dried and 100 mg of each sample was placed in a conical flask with 10 mL solution separately for the Cd (II) and Cr (III) and agitated in a rotary mixer at 250 rpm for 18 h. Afterwards the samples were filtered in a Buchner funnel. Chromium and cadmium concentrations in the solutions of unheated, 2h, 6h, 8h for pH 5 and pH 8 were determined by atomic absorption spectroscopy. In order to plot Langmuir isotherms, adsorption tests were made with varying chromium concentrations from 15 ppm to 35 ppm at pH 5 and pH 8 and cadmium concentrations from 18 ppm to 42 ppm at pH 5 and 4.2 ppm to 9.8 ppm at pH 8 respectively during 24 h. (Esteves et al, 2017).

3. DISCUSSION AND RESULTS

Cd (II) adsorption studies

Table 4. Effect of heat and pH for Cd (II) metal ions Adsorption efficiency (%)

sample	C_i Initial concentration of ion (ppm)		C_e Final concentration of ion (ppm)		$C_i - C_e$ adsorbed concentration of ion (ppm)		$\frac{C_i - C_e}{C_i} \times 100\%$ Adsorption efficiency (%)	
	P^H 5	P^H 8	P^H 5	P^H 8	P^H 5	P^H 8	P^H 5	P^H 8
unheated	24.538	24.538	2.283	4.704	22.255	19.834	90.6960632	80.8297335
2h	24.538	24.538	1.463	3.948	23.075	20.59	94.0378189	83.9106692
6h	24.538	24.538	0.284	2.994	24.254	21.544	98.8426115	87.7985166
8h	24.538	24.538	0.102	1.918	24.436	22.62	99.5843182	92.183552

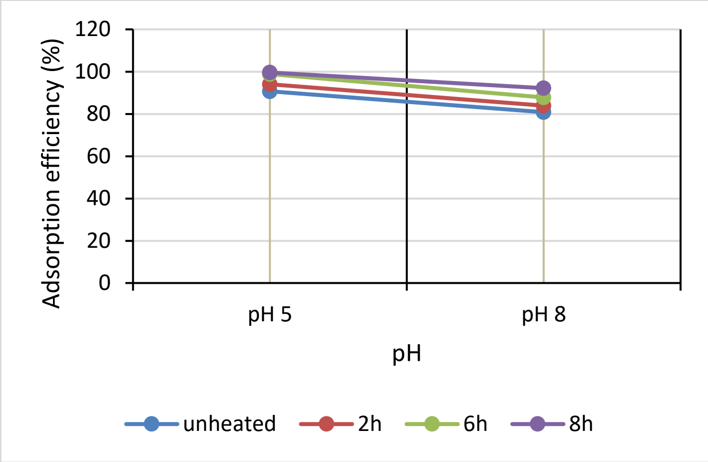

Figure 1. Adsorption efficiency (%) of cadmium as a function of pH for untreated and for treated wood at 2h, 6h, 8h

According to Table 1 and Figure 1, 8h heat treated wood had highest adsorption efficiency and was observed in pH 5 (99.5843182%).

Figure 1 shows the adsorption variation with pH for untreated and heat treated wood. When compared the pH 5 and pH8, the maximum adsorption was obtained at pH 5 for which a clear increase in adsorption with the treatment woods. The detected differences for the results might be more acidic nature of the wood treated for longer times, which can lower the initial pH of the solution. With pH decrease, adsorption increases at pH 5, decreasing afterwards (Esteves et al, 2017). At pH 5 there is no more difference between wood treated at 2, 6 or 8 hours with highest adsorption efficiency, but all showed a higher adsorption compared to untreated wood (90.6960632%). Most of the adsorption has been made during the 8 hours for heat treated wood.

Cr (III) adsorption studies

Table 5. Effect of heat and pH for Cr (II) metal ions Adsorption efficiency (%)

sample	C_i Initial concentration of ion (ppm)		C_e Final concentration of ion (ppm)		$C_i - C_e$ adsorbed concentration of ion (ppm)		$\frac{C_i - C_e}{C_i} \times 100\%$ Adsorption efficiency (%)	
	p^H 5	p^H 8	p^H 5	p^H 8	p^H 5	p^H 8	p^H 5	p^H 8
unheated	24.538	24.538	0.709	0.823	23.829	23.715	97.1106039	96.6460184
2h	24.538	24.538	0.151	0.448	24.387	24.09	99.3846279	98.1742603
6h	24.538	24.538	0	0.285	24.538	24.253	100	98.8385361
8h	24.538	24.538	0	0.067	24.538	24.471	100	99.7269541

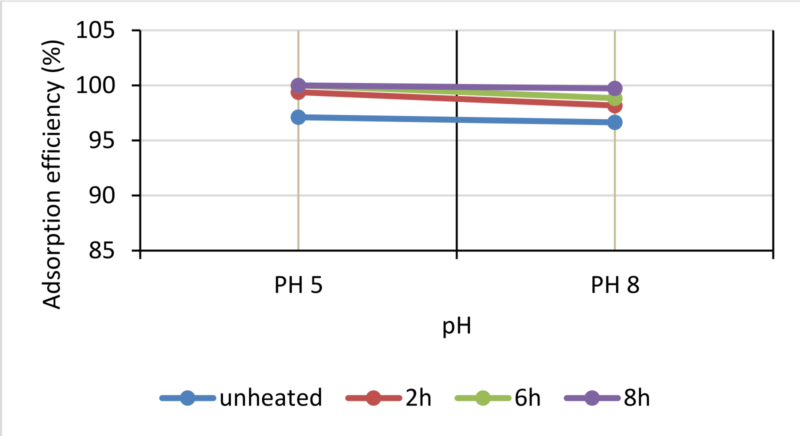

Figure 2. Adsorption efficiency (%) of chromium as a function of untreated and for treated wood at 2h, 6h, 8h for pH

According to Table 2 and Figure 2, 8h and 6h heat treated wood had the highest adsorption efficiency and was observed in pH 5 (100.00%).

Figure 3.2 shows the adsorption variation with pH for untreated and heat treated wood. When compared the pH 5 and pH 8, the maximum adsorption was obtained at pH 5 for which a clear increase in adsorption with the treatment woods. The detected differences for the results may give more acidic nature of the wood treated for longer times, which can lower the initial pH of the solution. With pH decrease, adsorption increases at pH 5, decreasing afterwards (Esteves et al, 2017).

At pH 5 there is no more difference between wood treated at 2, 6 or 8 hours with highest adsorption efficiency, but all showed a higher adsorption compared to untreated wood (97.11060396%). Most of the adsorption has been made during the 8 hours for heat treated wood.

Adsorption Isotherms

Langmuir Isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases (Tan et al, 2009)

The linear form of Langmuir isotherm equation is given as:

$$\frac{1}{q_e} = \frac{1}{K_L Q^0}\frac{1}{C_e} + \frac{1}{Q^0} \qquad 1$$

The equilibrium concentration of the adsorbate (ppm), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg), Q^0 is the Langmuir constant for adsorption capacity or maximum monolayer adsorption capacity (mgg^{-1}) and K_L is the Langmuir constant for energy of adsorption (Lg^{-1}). The values of Q^0 and K_L can be obtained from the slopes and intercept of the linear plot of 1/q_e versus1/ C_e (Tan et al, 2009).

Langmuir adsorption isotherm for Cd (II)

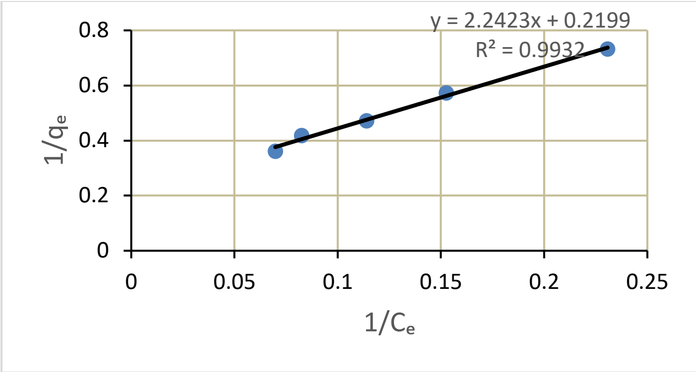

Figure 3. Relationship between $1/q_e$ versus $1/C_e$ of Cd (II) ion in pH5

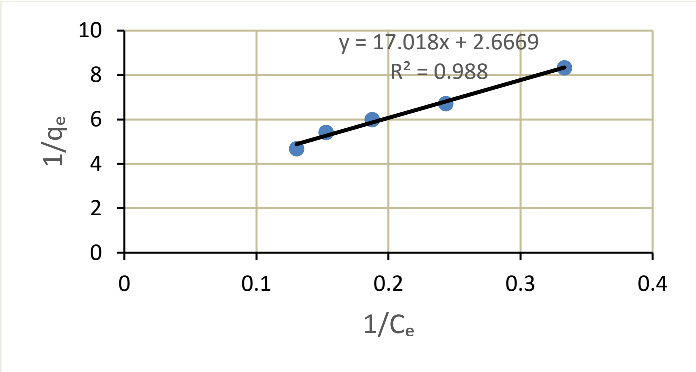

Figure 4. Relationship between $1/q_e$ versus $1/C_e$ of Cd (II) ion in pH 8

Langmuir adsorption isotherm for Cr (III)

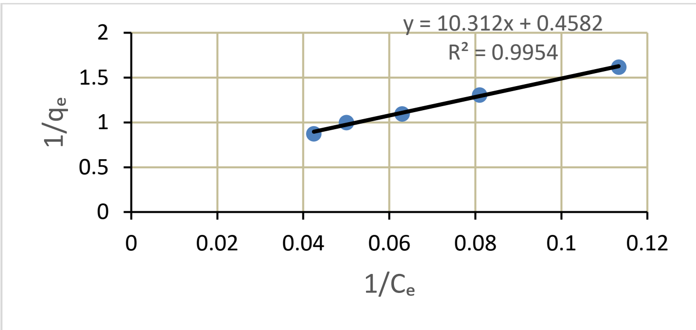

Figure 5. Relationship between $1/q_e$ versus $1/C_e$ of Cr (III) ion in pH 5

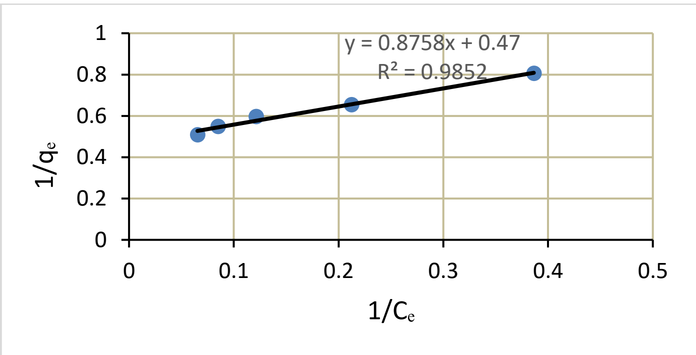

Figure 6. Relationship between $1/q_e$ versus $1/C_e$ of Cr (III) ion in pH 8

Freundlich adsorption isotherm

Freundlich adsorption isotherm, equation 2 is a reliable model for interpreting adsorption beyond one layer (Tan et al, 2009).

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \qquad 2$$

Freundlich adsorption isotherm for Cd (II)

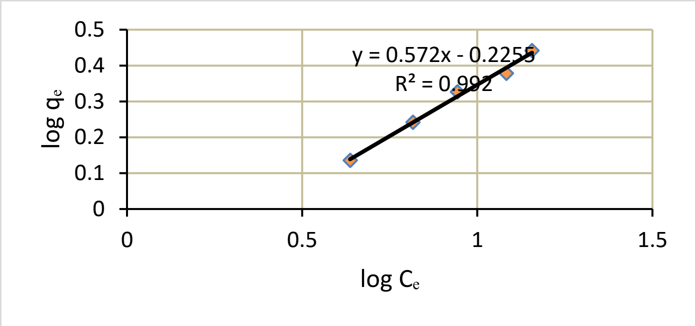

Figure 7. Relationship between log q_e versus log C_e of Cd (II) ion in pH5

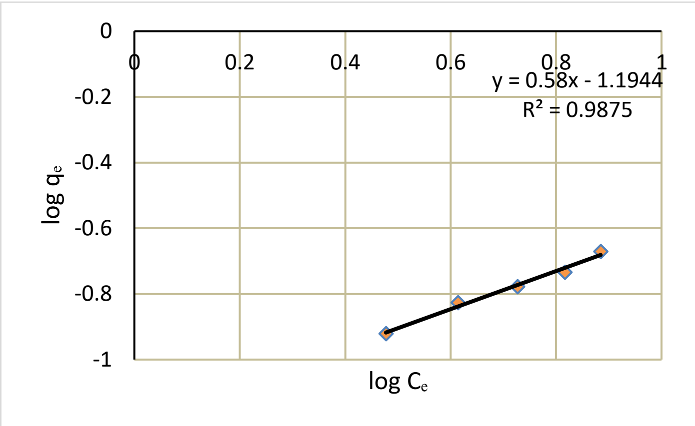

Figure 8. Relationship between log q_e versus log C_e of Cd (II) ion in pH8

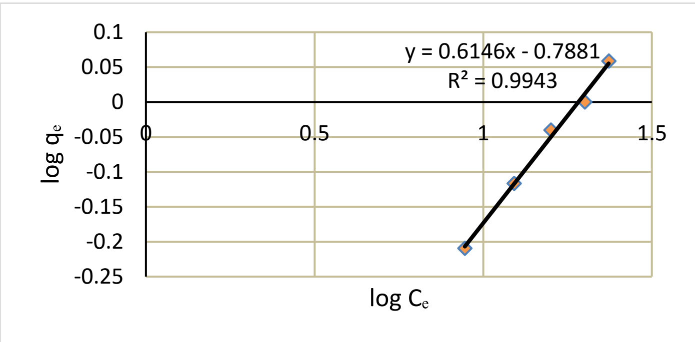

Figure 9. Relationship between log q_e versus log C_e of Cr (III) ion in pH5

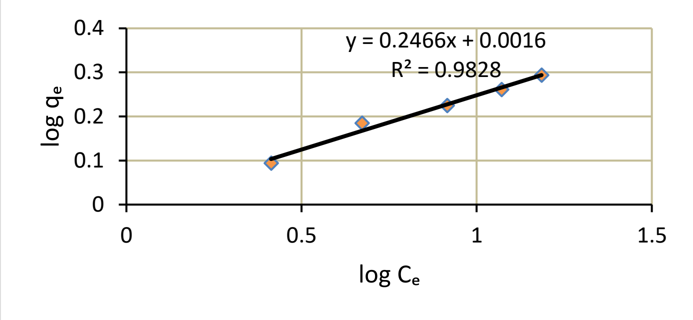

Figure 10. Relationship between log q_e versus log C_e of Cr (III) ion in pH8

According to the above data, comparison between correlation co-efficient of Langmuir adsorption isotherm (R^2) value for Cd (II) ion in pH 5 is 0.9932 and Freundlich adsorption isotherm (R^2) value for Cd (II) ion in pH 5 is 0.992. Therefore, the results agreed with the works carried out for Cd (II) ion in pH 5 which reported that the Langmuir model give a better fit than the Freundlich model. Then, comparison between correlation co-efficient of Langmuir adsorption isotherm (R^2) value for Cd (II) ion in pH 8 is 0.988 and Freundlich adsorption isotherm (R^2) value for Cd (II) ion in pH 8 is 0.9875.

Therefore, the results agreed with the works carried out for Cd (II) ion in pH 8 which reported that the Langmuir model give a better fit than the Freundlich model. Then, comparison between correlation co-efficient of Langmuir adsorption isotherm (R^2) value for Cr (III) ion in pH 5 is 0.9954 and Freundlich adsorption isotherm (R^2) value for Cr (III) ion in pH 5 is 0.9943. Therefore, the results agreed with the works carried out for Cr (III) ion in pH 5 which reported that the Langmuir model give a better fit than the Freundlich model. Then, comparison between correlation co-efficient of Langmuir adsorption isotherm (R^2) value for Cr (III) ion in pH 8 is 0.9852 and Freundlich adsorption isotherm (R^2) value for Cr (III) ion in pH 8 is 0.9828. Therefore, the results agreed with the works carried out for Cr (III) ion in pH 8 which reported that the Langmuir model give a better fit than the Freundlich model.

According to Langmuir model, maximum monolayer adsorption capacity (mgg^{-1}) Q^o for Cd (II) ion in pH 5 is 4.547567 where as in pH 8 is 0.374973. Maximum monolayer adsorption capacity (mgg^{-1}) Q^o for Cr (III) ion in pH 5 is 2.182258 where as in pH 8 is 2.127708. So the optimum value for Q^o reported in Cd (II) in pH 5.

Then, Langmuir constant for energy of adsorption (Lg^{-1}) K_L for Cd (II) ion in pH 5 is 0.098066 where as in pH 8 is 0.156705. Langmuir constant for energy of adsorption (Lg^{-1}) K_L for Cr (III) ion in pH 5 is 0.044439 where as in pH 8 is 0.536628

Cadmium is a naturally occurring metal, used primarily in batteries, paints, pigments and some jewelry, which is a noxious metal enters to the human body through the food chain and caused defects to the organisms. In recent years, Cadmium is increasingly used as an electrode component, plastic stabilizer in PVC-related products and several alloys, tobacco smoke, phosphate fertilizers and sewage sludge applied to the crops. The incineration of Cd containing waste contaminates the environment massively. Cadmium in drinking water is safe if the level is lower than 0.005mg/L (Friberg, 2017).

Cadmium has been recognized as one of the toxic heavy metals that enters the water through disposal of waste from industries. The increasing technological use of cadmium has raised the concern for its removal from water/wastewater. This experimental procedure provides an overview of use of heat treated *Casuarina equisetifolia* wood bark as adsorbents for removal of cadmium from water/wastewater. This study necessitates the identification of environmentally friendly, low-cost and efficient heat treated wood bark sorbents for water/wastewater purification (Kumar & Chawla, 2013).

The elemental Chromium (Cr) does not occur in nature, but is present in ores. Chromium, two oxidation states, Cr (III) and Cr (VI) are stable and predominant in the environment. Chromium plays an essential role in glucose and cholesterol metabolism and is an essential element to living organisms but at higher levels is toxic (Arunakumara & Zhang, 2008).

The waste water released from the dyes and pigments, film and photography, metal cleaning, plating and electroplating, leather and mining industries contains disagreeable amounts of chromium ions. Chromium in drinking water is safe to use if the maximum allowed concentration is 0.05 mg/L.

The US EPA allows solutions containing heavy metals to be discharged if the concentration is usually less than 5.0 mg/L. There are several conventional methods for removing chromium from waste water include chemical reduction, electrochemical treatment, ion exchange, and evaporative recovery. Such processes may be ineffective or extremely expensive when the initial heavy metal concentrations are high. So, an alternative process which use heat treated *Casuarina equisetifolia* wood bark as adsorbents for removal of chromium from water/wastewater has been proposed recently (Nourbakhsh et al, 1994).

During the study for the determination of Cadmium and chromium concentration, the series of solutions were prepared and the absorbance were measured using the Atomic Absorption Spectrophotometer. In this experimental procedure, the absorbance were measured for the unheated and heat treated samples. From the data obtained, the graphs were plotted. And hence, respective concentrations of cadmium and chromium were calculated.

Here for the cadmium adsorption, 8h heat treated wood had highest adsorption efficiency was observed in pH 5 (99.9918494%). Where, for the chromium adsorption, 8h and 6h heat treated wood had highest adsorption efficiency was observed in pH 5 (100.00%). For this it is very clear heat treated woods had higher adsorption than the untreated woods.

In this report, heat treated wood samples showed a significant higher adsorption capacity than compared to unheated wood for cadmium and chromium adsorptions. According to the above data, comparison between correlation co-efficient of Langmuir adsorption isotherm (R^2) value for Cr (III), Cd (II) ion in pH5 and pH8 and Freundlich adsorption isotherm (R^2) value for Cr (III), Cd (II) ion in pH5 and pH8, which reported that the Langmuir model gave a better fit than the Freundlich model, whereas adsorption capacity is optimum in Cr (III) ion in pH 5 and the maximum monolayer adsorption capacity reported for Cd (II) ion in pH 5. This can be a better benefit of heat treated wood in the end of its life.

4. CONCLUSION

The research was carried out to determine the Cadmium and Chromium concentrations and their adsorption efficiency (%) by using thermal activation. The main intention of this research is to determine thermally modified wood might be a better adsorbent than untreated wood. To carry out this research heat treated Casuarina equisetifolia wood bark used as an adsorbents. It was discovered that the adsorption of all cations, including Cd (99.5843182%) 8h heat treated wood and Cr (100.00%) 8h, 6h heat treated wood for pH 5 ions, were greatly increased by the addition of Casuarina equisetifolia wood bark sample. The effectiveness of the adsorption process was verified by the study using Freundlich and Langmuir adsorption isotherms. The Langmuir adsorption isotherm was found to be well fitted to the experimental data for Cd (II) and Cr (III) respectively.

The maximum monolayer coverage (Q^o) for the Cd (II) in pH 5, pH 8 and Cr (III) in pH 5, pH8 were determined to be 4.547567 mgg^{-1}, 0.374973 mgg^{-1}, 2.182258 mgg^{-1}, and 2.127708 mgg^{-1} respectively from the Langmuir isotherm model.

According to the results obtained from above data, adsorption capacity is optimum in Cr (III) ion in pH 5 and the maximum monolayer adsorption capacity reported for Cd (II) ion in pH 5 by enhancing the thermal activation give better results for adsorption efficiency.

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