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**Research Article**

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# Absorption of Cr(III) and Cr(VI) metals in aqueous solution using Mangosteen Rind (*Pithecellobium jiringa*(*jack*) *prain*.)

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## ABSTRACT

*Jengkol shells (Pithecellobium jiringa (jack) prain.) a agricultural waste from typical Indonesian plant has been investigated for its ability to absorb Cr(VI) and Cr(III) heavy metal ions. Effect of pH , concentration , contact time , mass and the speed of stirring on biosorptivity was studied by the method of Batch . The concentration of Cr(VI) and Cr(III) metal ions was measured using Atomic Absorption Spectrophotometer (AAS) . The optimum conditions for metal ions uptake of Cr(VI) occurs at pH 4 , the concentration of 7000 mg / L , contact time of 60 minutes , 0.1 g biosorbent mass and stirring speed 100 rpm . As for Cr(III) metal ions is obtained optimum conditions at pH 5 , the concentration of 1500 mg / L , contact time of 60 minutes , 0.1 g biosorbent mass and stirring speed 100 rpm . Functional groups contained in the jengkol shells analyzed using Fourier Transform Infra Red (FTIR) . Data equilibrium uptake of Cr(VI) and Cr(III) metal ions by the jengkol shells analyzed using two isotherm models , namely Langmuir and Freundlich isotherm models . The absorption of both the metal ions tend to follow the Langmuir isotherm models in which the absorption capacity of metal ions obtained for Cr(VI) and Cr(III) is 24 , 9376 mg / g and 39 , 0625 mg / g . The optimum condition was applied to study the Batang Arau river water in Padang city obtained a capacity of 15 , 065 mg / g with 45 efficiency , 94 % for the uptake of metal ions Cr (total ) .*

**Keywords**: Jengkol Shells, Metal Ions Cr(VI), Metal Ions Cr(III), Biosorption, Isotherms

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## INTRODUCTION

Chrome is a contaminant which is generally found in textile waste, paint, ink, colorant. Aluminium and electroplating industry. Chrome(III) and Chrome(IV) belongs to metal which is reported as potentially carcinogenic reported, which cause liver and kidney cancer.[1]. Chrome distributed in oxide from between Cr(III) to Cr(IV). However only chrome with oxidation number 3 and 6 which leave similar biological behavior. of Chrome(III) is the most distributed in nature. Chrome(III) is less poisonous compared to chrome(VII) [2]. One of the method used to reduce chrome content in industry waste is treatment sorption. The sorption method occur through interaction between analyst and solid surface (adsorbent). Sorbent used are from organic materials [3]. Various organic materials such as Kayu Apu [4], nutshell [5], mangosteen rind [6], algae [7], flour hyacinth [8] and mesocar coco palm [9] reported to absorb heavy metal from the environment efficiently and have been investigated their role as biosorbent and bioaccumulator of heavy metals. The role due to the presence of secondary metabolites such as flavonoids with amino, carboxyl, thiol, hydroxyl-carbonyl and phosphate which form complex compounds with heavy metal ions.

Jengkol belongs to plant which distributed in South East Asia, especially in Indonesia. Jengkol is well known in Indonesia due to the fruits used as a food, especially in West Sumatera. However the jengkol shell grab shows templeasant view in many towns in West Sumatera such as in Pasar Raya Padang and Pasar Sawah in Bukittinggi. Jengkol shells contain alkaloid, flavonoid, glycosides, anthraquinone glycosides, taurine, triterpenoids and saponin [10]. Based secondary metabolites contained in the shell previous research reported that jengkol shell can be used for bioherbicides and biolarvacides [11], anti bacteria [12], and acid base indicator. Literature review conducted showed there is no reports on the use of jengkol shells as biosorbent. The aim of this research is to investigate the ability of jengkol shells as biosorbent for Chrome(III) and Chrome(VI).

## EXPERIMENTALSECTION

### Chemicals

Jengkol shells were collected in Pasar Raya Padang, West Sumatera. $K_2Cr_2O_7$, $CrCl_3$, $HNO_3$, NaOH were from Merck..

### Preparation of jengkol shells as biosorbent

Jengkol shells were washed with water and cut into small size and dried at room temperature. The dry jengkol shells were crushed and filtered through 150 μm particle filter. Jengkol shell powder were soaked in 0.01 mole/L $HNO_3$ for two hours, then filtered and washed with water and dried at room temperature. The powder was kept in special bottle and used as biosorbent.

### Solution of Cr(IV) and Cr(III)

First, the solution of 8000 mg/L was prepared by dissolving 11.32 g of $K_2Cr_2O_7$ in 500 mL of water. The solution was diluted to obtain solution of 20, 100, 300, 900, 1200, 1500, 2000, 3000, 4000, 5000, 6000, 7000 and 8000 mg/L.

### The Effect of pH on metal absorption

The experiments were conducted at pH of 2,3,4, 5, 6 and 7. To each Erlenmeyer 0.3 g of biosorbent of 150 μm was placed and 25 ml solution of Cr(VI) ion of 20 mg/L was added. The solution was stirred with speed of 100 rpm for 90 minutes. The solution was filtered and the concentration of metal ion in the filtrate was analyzed with atomic absorption spectrophotometry. Thus was applied to Cr(III).

### The effects of the beginning concentration of metal on metal absorption.

The experiments were conducted at optimal pH. Into Erlenmeyer 0.3 g of biosorbent with 150μm of particle size was placed and 25 ml of Cr(VI) solution with optimal concentration was added. The solution was stirred with 100 rpm of speed. The experiments conducted with various contact time (i.e, 14, 30, 60, 90 and 120 minutes). The same procedures were also applied to Cr(III).

### The effects of biosorbent mass on metal absorption

25 ml of Cr(VI) solution with optimal concentration was added into absorbent mass of 0.1, 0.3, 0.6, 0.9 and 1.2 g. the experiment was conducted at pH and optimal contact time with the stirring speed of 200 rpm. The filtrates were analyzed with atomic absorption spectrophotometry. The same procedure were also applied to Cr(III).

## RESULTS AND DISCUSSION

### The effects of pH on metal ion absorption

For the absorption of heavy metal ions, the pH was the most important factor. The high pH of a solution will affect the dissociation of biomass surface. Picture 1 showed the absorption of the Cr(VI) and Cr(III) by jengkol shells. The ability of biosorbent to absorb Cr(VI) ion increased at pH 2-5, which the absorption ability decreased at pH 6-7. At acidic condition the jengkol shell surface were saturated by hydrogen ions, since $[H^+]$ is high in the solution. At low pH electrostatic bond formed between protonated sorbent surface and Cr(VI) ion of negative charge when the pH increased most of the biomass surface will be on the negative charge. So that it will decrease the ability of jengkol shells to absorb metal ion. The ability of biosorbent to absorb Cr(III) ion kept increase with the increase of pH at 2-5.

At pH 6-7 the decrease of absorption capacity ability occurred. The decrease of pH marked the charge of biosorbent surface became more negative, so the Cr(III) ion more absorbed, because the attraction between cation and functional groups on biosorbent. Meanwhile, if the pH was higher than 5, some of Cr(III) ion would precipitate to from $Cr(OH)_3$ and it will disturb the absorption of metal ion . The maximal absorption capacity occurred at pH 4 and 5 for Cr(VI) and Cr(III) ions, i.e. 1.4064 and 0.822 mg/g respectively. The absorption capacity of Cr(VI) ion was higher than Cr (III), this showed that negative charge functional groups such as –OH, -NH2 and –COOH were more on biosorbent surface [5.8]

**The effect of metal ion concentration on metal absorption**

The effect of metal ion concentration was investigated by varying the concentration both metal ion. The results of biosorption by varying concentrations were shown in figure 2. The pictures showed that absorption capacity increased by increasing the concentrations of Cr(VI) and Cr(III) ions. This condition was consistent to the previous research reported. The metal ion concentration was closely related to the total of active sides on the surface of biosorbent which be able to bind the metal. If the total of active sides found much more than the total of metal ion, consequently the absorption capacity was high. The absorption capacity of Cr(VI) ion was higher than Cr(III) ion. This was because Cr(VI) in the solution decomposed to give $Cr_2O_7^{-2}$ anion. This anion formed coordination with functional groups on jengkol shells, especially amino groups (- NH2).

**The effect of contact time on metal absorption**

The determination of contact time was aimed to gain the information about the minimal time required by biosorbent of jengkol shell powder to absorb maximal, in figure 3 showed that optimal absorption capacity of Cr(VI) was obtained at 60 minutes, i.e. 488.333 mg/g. Optimal absorption of Cr(III) at contact time of 60 minutes was 71.481 mg/g. The same results were shown by metal ions Cr(VI) and Cr(III) when different biomaterials were used [13]. The more interactions between absorbates and absorbents, this more metal ions Cr(VI) and Cr(III), absorbed on the jengkol surface, so that the active sides which were available before became less. The absorbates formed thin layers on the surface of biosorbants and covered the biosorbant surface, consequently decreased the absorption capacity [14]. The decrease of total metal ion absorbed may becaused by metal particles released [15].

**The effect of biosorbent mass on metal absorption**

The effect of jengkol shell mass on the absorption capacity of metal ion was shown on picture 4. The total of Cr(VI) and Cr(III) ion attached per g of biosorbant decreased with the increase of total of biosorbant. The absorption of metal ions Cr(VI) and Cr(III), were 1382.25 mg/g and 210.277 mg/g respectively. Both the absorption capacity of metal ions decreased when biosorbant was optimal. The decrease of absorption capacity caused by solution of metal ion start saturating to bind with biosorbant. The more the active sides unsaturated during the absorbance process meant total of active sides available for binding increased with the increase of total biosorban [16]. If the more biosorbant used, it will form coagulations which cause the decrease of biosorbant surface area [17].

**The effect of stirring speed on metal ion absorption**

The effect of stirring speed on the absorption capacity was shown on figure 5. It was shown that the absorption capacity increased on the stirring speed of 30-100 rpm and decreased when the speed of 150-200 rpm. The maximal absorption capacity for both metals occurred when the speed of 100 rpm. When the stirring speed of 150-200 rpm desorption of metal ion occurred, so that the absorption capacity decreased.

Absorption varied depending on the characteristic of biomass [18]. Biosorption equilibrium model is important to be prepared, because it will describe the representatives of the equilibrium test conducted. Biosorption equilibrium model describes absorbate distribution between liquid phase and solid phase and analyzed with Langmuir and Freundlich isotherm equation [19] Table1. Qm describes capacity of maximal absorption of Cr(VI) and Cr(III) ions per unit of jengkol shell (mg/g) total of active sides which are available for absorption. K1 describes affinity between sorbent and sorbate.

Table 1 showed that maximal absorption (Qm) of Cr(VI) ion was less than Cr(III) ion. However, it did not means that the absorption of Cr (III) metal ion was better than Cr(VI) metal ion because K1 value of Cr(III) ion was lower described the affinity between Cr(III) ion with jengkol shell was lower than affinity of Cr(VI) ions in Cr2O7-2 anion form [18]

Determination coefficient value R2 both isotherm model (table 1) showed that the experiment tend to follow Langmuir isotherm equation than Freundlich isotherm equation. This showed that active sides distributed homogeneously on jengkol shell in which Cr(VI) and Cr(III) ion covered the sorbent surface leg forming monolayer and found to active sides of jengkol shell chemically [14] Table parameters of Langmuir and Freundlich isotherm on the absorption of Cr(VI) and Cr(III) ions on jengkol shell.

Figure 7 described Freundlich isotherm plot with various concentrations of Cr(VI) and Cr(III) ions constant Kf and l/n were described in table 1. Table 1 showed l/n value for Cr(VI) and Cr(III) were 0.9109 and 0.8445 respectively. As value of $0.1 < l/n < 1$ can be concluded that Cr(VI) and Cr(III) finely absorbed in this experiment. R1 value for both metals (figure 8a) were in range 0-1. This showed that jengkol shell was effective bisorben for Cr(VI) and Cr(III) ion absorption in low concentrations. R1 value became less at higher concentrations. This mean that Cr(VI) and Cr(III) metal ions in higher concentrations were finely absorbed on jengkol shell. θ value became higher by increasing the concentrations of both metal ion (figure 8b). the increase of concentrations for both metal ion caused more jengkol shell surface coated by metal ion. In higher concentrations, θ value underwent a little bit increase.

**FTIR Analysis**

The FTIR spectrum of jengkol shell before and after absorption with Cr(VI) metal ion was used to determination functional groups present in jengkol shell as well as obtaining the value of such functional groups after absorption with Cr(VI). OH absorption appeared as broadening band at 3448.41 cm-1 (figure 8a) and 3447,41 cm-1 (figure 8b). Band at 2360,61 cm-1 (figure 8a) and 2360.41 cm-1 and 2342.87 cm-1 (figure8) identified as NH2+, NH3+ amines. Sulphonate group 1383.93 cm-1 (picture 8a) and 1384.06 cm-1 (figure 8b). Band at 1032.93 cm-1 (figure8a) and 1058.79 cm-1(picture 8b) identified as –C-O group of alcohol. Carboxyl group showed –C- O absorption appeared at 1629.15 cm-1, 1459.00 cm-1 (figure 8a) and 1508.01 cm-1, 1459.00 cm-1 (figure 8b). The presence of functional groups of carboxyl, hydroxyl, amine, sulphonyl, which underwent wave number shift, this showed the participation of these groups in bound formation with Cr(VI) metal ion.

**Application on water sample**

For this application, water of Batang Arau River was used as sample. Before examined on jengkol shell, this concentration of metal ion in water was measured.

**Table 2 . the data of total concentration of Cr metal in water of Batang Arau River and the concentration after trailed with jengkol shell**

| Metal ion | The beginning Conc (mg/l) | The Last Conc (mg/l) |
|---|---|---|
| Cr (Total) | 127.16 | 68.74 |

Since the optimal condition for Chrome total and ion was obtained , the results of this research was applied on water of Batang Arau River to reduce the total ion concentration which were available in such sample. Jengkol shell absorbed total Cr metal ion 45.90 % with absorption capacity was 15.605 mg/l. total of concentration of chrome heavy metal in water waste was quiet high.

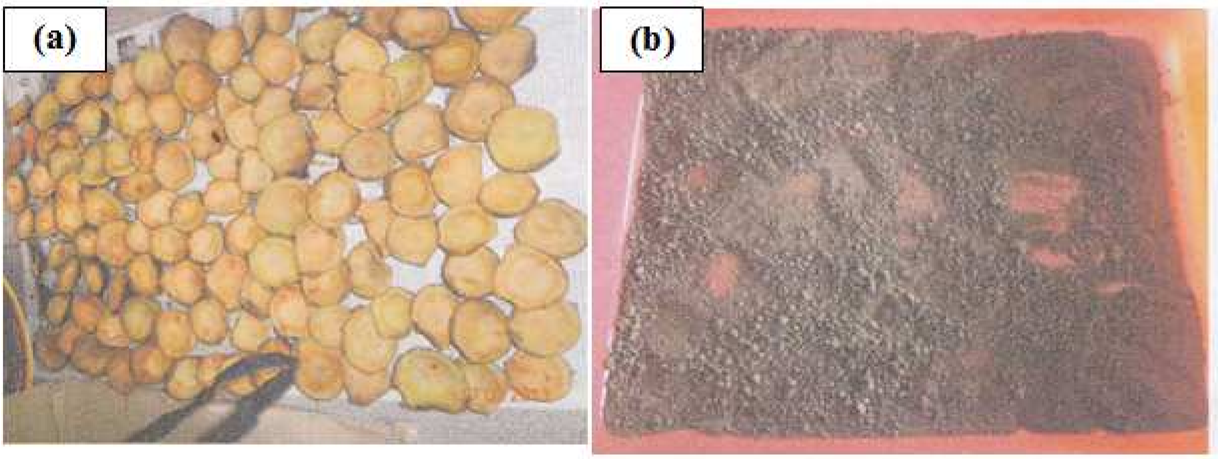


**Figure. (a) Magosteen (b) Magosteen powder**

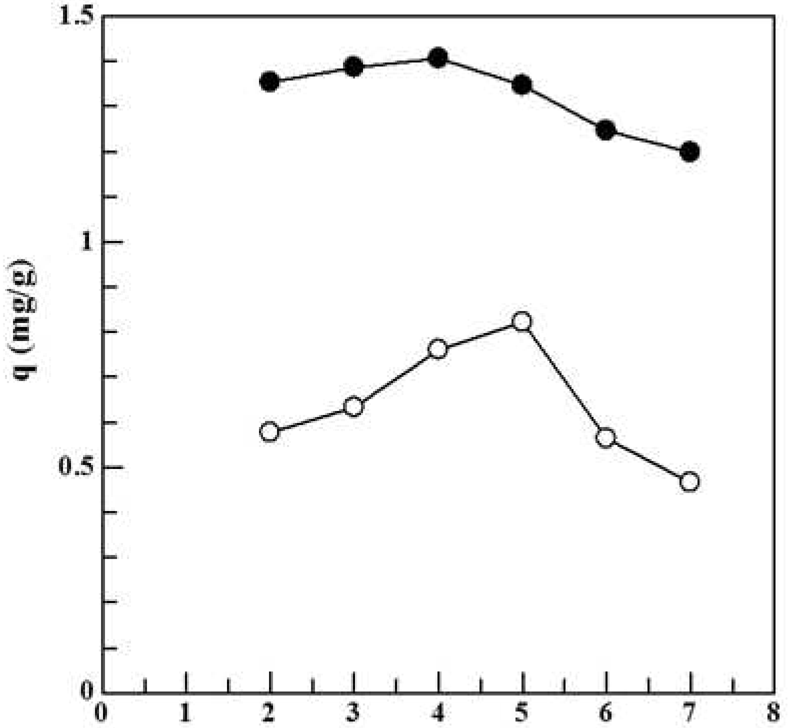


**Figure. 1 Effect of pH on Cr adsorption**

Cr(III) Cr(VI)

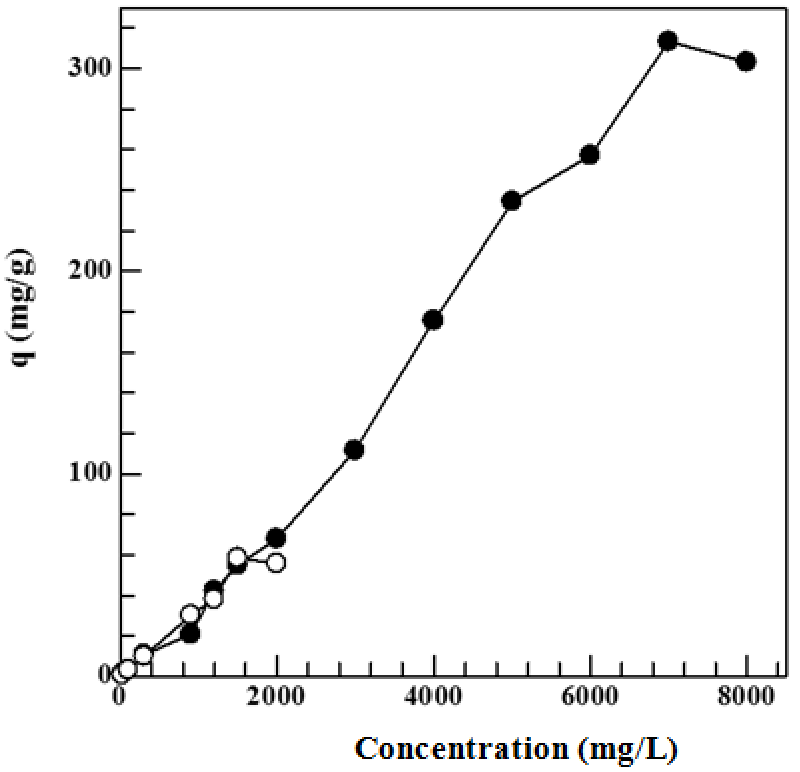


**Figure.2 Concentratioeffect on adsorption of Cr**

Cr(VI) Cr(III)

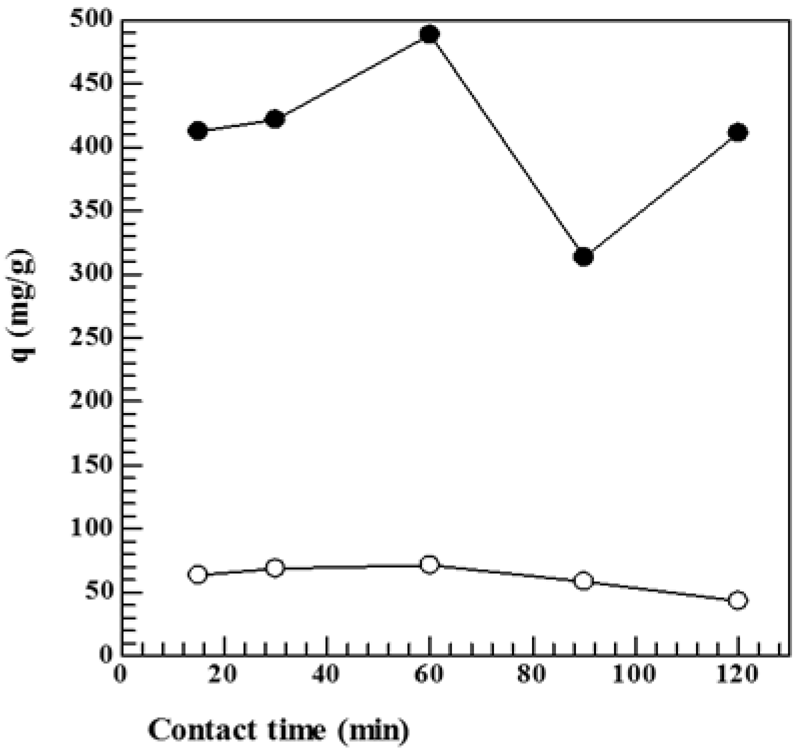


**Figure 3. Effect of cotact time on adsorption of Cr (VI) and Cr (III)**

Cr(III) Cr(VI)

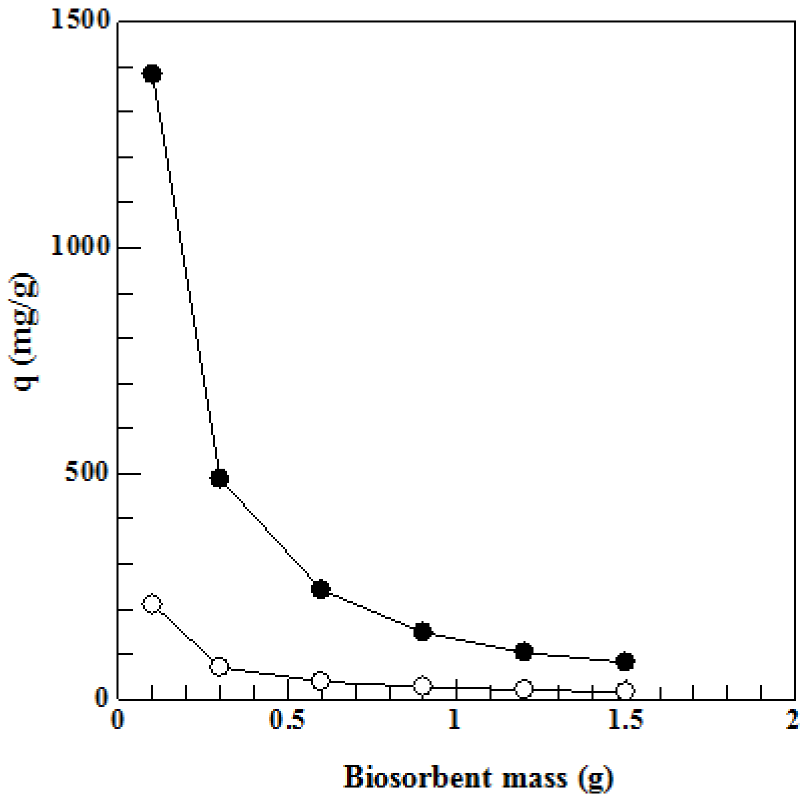


**Figure 4. Biosorbent effect on adsorption**

Cr(VI) Cr(III)

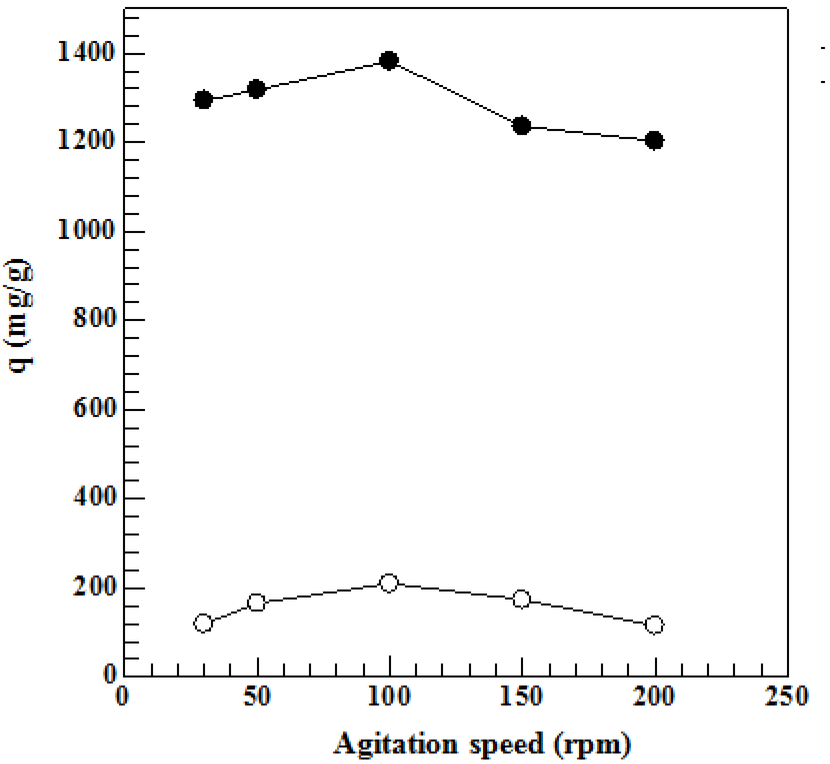


**Figure 5. Agitation speed effect on adsorption of Cr**

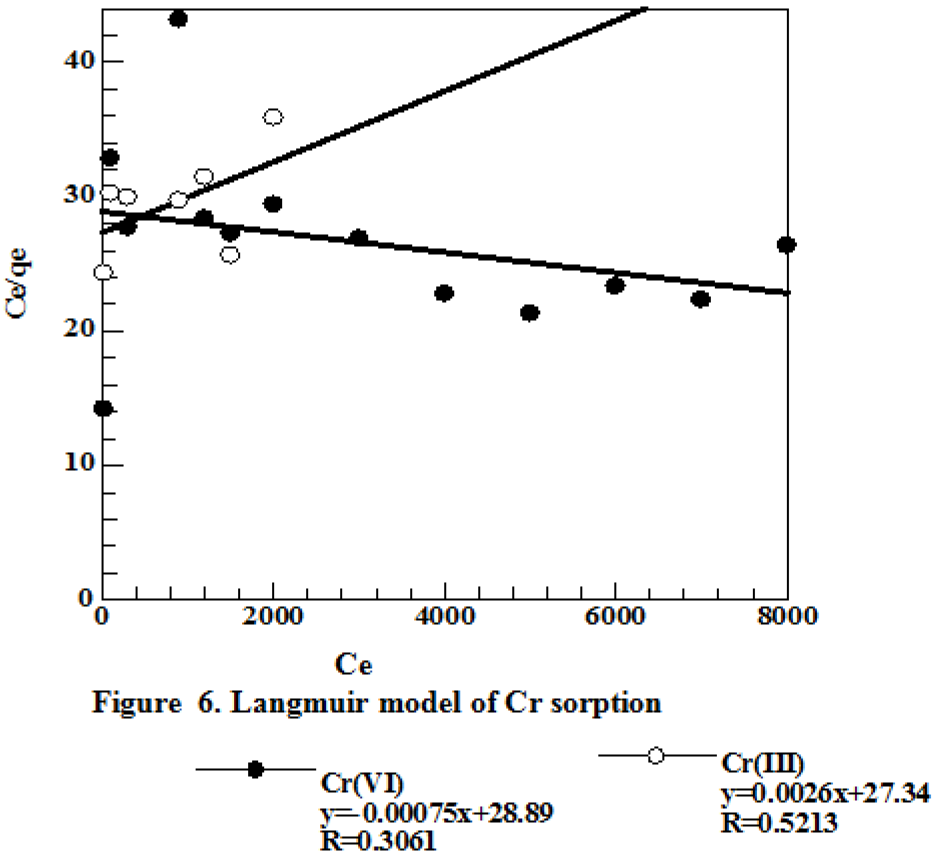


**Figure 6. Langmuir model of Cr sorption**

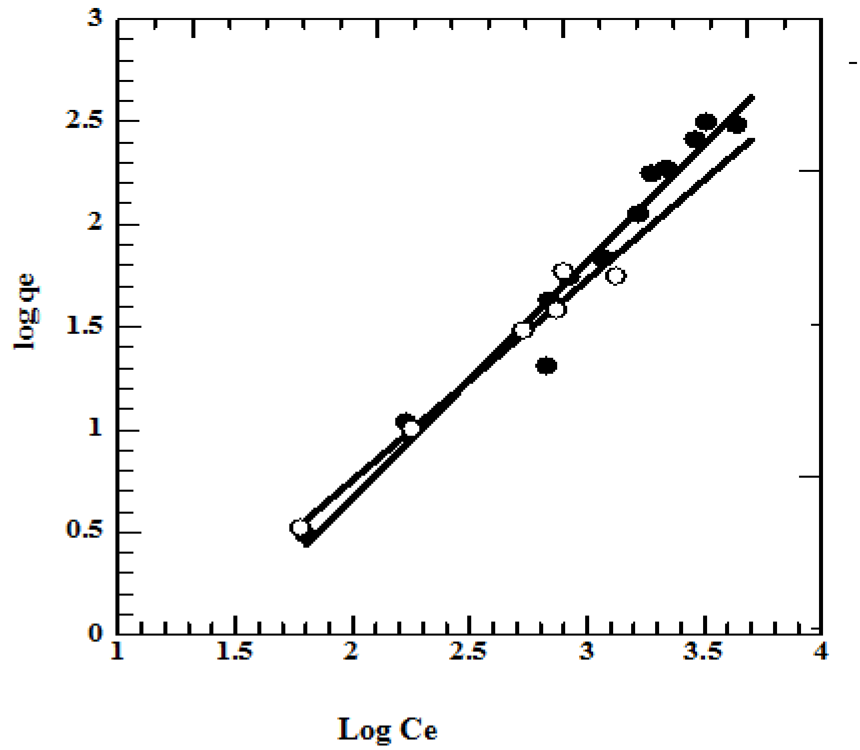


**Figure 7. Freundlich model of Cr adsorption**



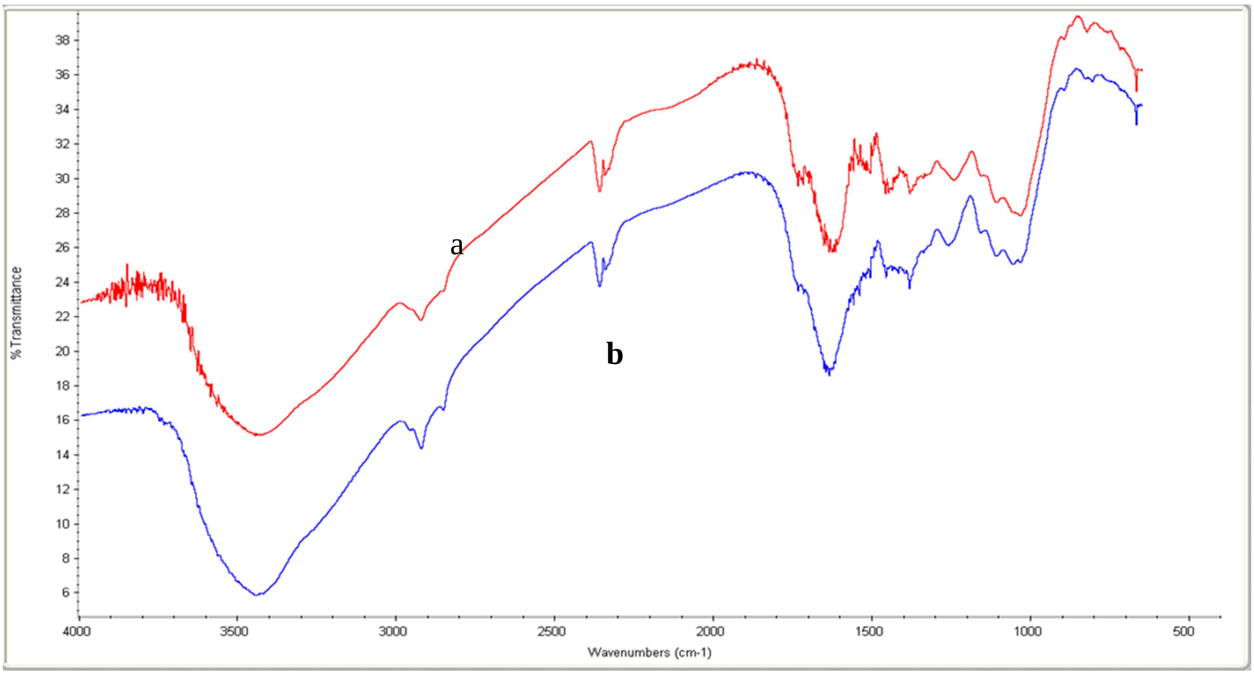


**Figure 8. FTIR spectrum before (a) and after (b) Cr ions biosorption**

## CONCLUSION

From this research inducted the conclusions were as follow:

1. Jengkol shell proved to be effective to absorb Cr(VI) and Cr(III) metal ions

2. Optimal condition for Cr(VI) and Cr(III) metal ions absorption on jengkol shell occur at pH 4. Concentration of Cr (VI) was 7000 mg/l, contact time was 60 minutes, biosorben mass was 0.1 mg and the speed was 100 rpm with absorption capacity was 1382.25 mg/g. Whereas for Cr(III) ion optimal condition obtained at pH 5, concentration 1500 mg/l, contact time was 60 minutes, biosorbent mass was 0.1 g and the speed was 100 rpm with capacity was 210.277 mg/g.
3. According to Langmuir Isotherm, optimal absorption capacity (Qmax) for Cr(VI) metal ion was 24.9376 mg/g and 39.0625 mg/g for Cr(III) metal ion. Langmuir Isotherm described that metal ion bound chemically on jengkol shell.
4. Based on Freundlich Isotherm, l/n value was 0.8445 for Cr(VI) and 0.9109 for Cr(III). The Value 0.1 <l/n<1 showed that both metal ion bound physically on jengkol shell.
5. The application of research results in water sample of Batang Arau River showed that capacity was 15.065 mg/g with efficiency of absorption was 45.94 % for total Cr metal i

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