

## RESEARCH ARTICLE



### EFFECTIVE REMOVAL OF CR(VI) AND CU(II) FROM AQUEOUS SOLUTION USING FORMALDEHYDE TREATED *ALBIZIA PROCERA* LEGUMES SUBSTRATE AS AN ADSORBENT

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#### Abstract

Adsorption capacity of Cr(VI) and Cu(II) onto formaldehyde treated *Albizia procera* legume substrate was investigated in a batch system by considering the effects of various parameters like contact time, initial concentration, pH, temperature, agitation speed, column studies and absorbent dose. The adsorption was solution pH dependent and the maximum adsorption was observed at solution pH of 4.5 to 5.5. The amounts of Cr(VI) and Cu(II) adsorbed increased with increase in dose of both adsorbents and their contact time. A contact time of 30 min was found to be optimum. Experimental results show low cost biosorbent was effective for the removal of pollutants from aqueous solution. Experimental data showed a good fit with the Freundlich isotherm model. The method could be successfully employed for removal of toxic metals from industrial effluents.

**Keywords:** Chromium, Copper, Freundlich adsorption model, *Albizia procera*, Low Cost Absorbent. Column studies.

#### Introduction

Due to enormous growth of industrial activities, the problem of removing pollutants from wastewater is growing daily. Heavy metal pollution is of great concern, owing to their potentially hazardous effects at elevated levels in the environment. Toxic metals like Cr, Cu, Ni, Zn, Cd, and Pb make their way into water bodies via wastewater from metal plating industries, leather industries, pulp and paper mills, refineries and steel work foundries, etc. Chromium, a highly reactive metal, is widely used in electroplating, leather tanning, metal finishing, textiles, dyes, cement and photography industries (Ajmal M. et al 1996). Normally, industrial waste contains both hexavalent and trivalent forms of chromium; however, Cr (VI) is more hazardous to biological activities. Cr(VI) compounds are carcinogenic and corrosive on tissue and long-term exposure causes nausea, ulceration, skin sensitization and kidney damage (Metcalf and

Eddy. 2003., McKee J. E, et al 1963, Camp T. R, 1963., Baral A., et al 2002., Costa M., 2003., Lach J., et al 2007., Schneider R., et al 2007) and is reported to be bio-accumulated in to flora and fauna, creating ecological problems (Sing V K, et al., 1997; Thio M. et al .,2007). It is important to note that water pollution by both heavy metals and organic compounds is considered a serious environmental problem because these pollutants modify the chemical properties of water and are toxic to aquatic flora, animals and human beings (Demirbas A., 2008; Fu F. et al., 2011; Guezquez et al., 2009; Zhang et al., 2008). The recommended limit of Cr(VI) in waste water is only 0.05 mg/L (Daneshvar et al., 2002) . But the industrial and mining effluents contain much higher concentrations compared to the permissible limit. Therefore, the concentrations of Cr(VI) must be reduced to levels that satisfy environmental regulations for various

bodies of water. Copper find its way to water bodies through wastewater from Cu wire mills , coal burning industries, elecroplating, tanning, smelting and refining, insecticides, fungicides and iron and steel producing industries (Zuane 1996). According to the IS:2296-1974 the maximum permissible limit of copper in inland surface water used for public water supply and bathing is 1.0 mg/L and according to IS:3306-1974 and IS:7968-1976, the tolerance limit of copper for industrial effluent discharge is 3.0 mg/L. A viable and safe disposal of copper sludge has not yet been identified world over. Some important methods used are ion –exchange, reduction and precipitation, evaporative recover, electrolysis, ion flotation and reverse osmosis. Many of these method required high capital and recurring expenditure and consequently are not suitable for industrial use (Kapoor et al., 1999).

The conventional methods for removing heavy metal ions from water and wastewater include chemical precipitation, ion exchange, electrochemical deposition, solvent extraction, membrane filtration and adsorption. However, most of these methods have drawbacks including high operational costs or the challenges associated with residual metal sludge disposal. Among these, adsorption is more effective and economical technique (Ahmad et al., 2009) has received a great deal of attention for the removal and recovery of heavy metals from solution as it has been found to be an inexpensive, highly effective and simple method for the treatment of effluents bearing heavy metals. Several low-cost adsorbents such as rice husk carbon (Srinivasan, et al.,1988), coconut-shell based activated carbon (Alaets, J. et al., 1989), fertilizer waste slurry (Srivastava et al., 1989), sphagnum moss peat (Sharma et al., 1993), bark remnants of eucalyptus and *Cassia fistula* (Tiwari et al., 2000), rice straw (Samanta, et al., 2000), saw dust (Shrivastav R. et al .,2000), agricultural byproducts, bidi leaves, composite chitosan (Boddu et al 2003), polymer chitin and deacetylated chitin ( Satish N. et al., 2004) and Japanese cedar bark Aoyama et al., 2004) have been used previously for the removal of Cr(VI) from aqueous solutions and industrial wastes at solid-solution interface. Phosphate treated sawdust (Ajmal M. et.al 1996) has been used for the removal of Cr(VI) from electroplating wastes.

In this present study, formaldehyde treated *Albizia procera* legume substrate was investigated as a potential and low cost adsorbent for the removal of Cr(VI) ions from aqueous solutions. The objective of

the present work was to investigate and explore the possibility of utilizing formaldehyde treated *Albizia procera* legume substrate as a sorbent for removing Cr(VI) ions from aqueous solutions. The effect of various experimental parameters such as adsorbent dose, initial Cr(VI) concentration, contact time, stirring rate, temperature and pH were investigated. Freundlich adsorption isotherms was also evaluated and reported. The results are quite encouraging and efficient removal is possible and is comparable with high cost activated charcoal and alumina

## Materials and methods

### Preparation of metal ions aqueous solution

All the chemicals, diphenylcarbazide, acetone, sulfuric acid, formaldehyde, disodium salt of EDTA, citric acid sodium diethyldithiocarbamate, n-butyl acetate, cupric sulfate and potassium dichromate used were of analytical grade purchased commercially and were used without further purification. The metal ion solutions of Cr (VI) and Cu(II) were prepared respectively from potassium dichromate and cupric sulfate in double distilled water. The glass wares used were leached with conc. HNO<sub>3</sub> and dried in an oven at 50 °C. The pH of potassium dichromate and cupric sulfate solutions was adjusted to 4.5 using buffer solution to prevent hydrolysis.

### Adsorbent Material Development

The *Albizia procera* legumes were collected from Chandrapur district (India) and dried at room temperature in the air, further grinded using a grinding machine and sieved through a 500 µm mesh. Adequate mass of the *Albizia procera* legumes substrate were mixed with 0.25 N sulfuric acid and 39% v/v formaldehyde. The mixture was continuously agitated for 6 h using commercial shaking machine. The mixture was then filtered and washed, several times with double distilled water until the pH of filtrate was attained to 5. The residue was dried in an oven at 50 °C for 24 h. The formaldehyde treated *Albizia procera* legume substrate was used as adsorbent for batch adsorption experiments.

### Batch adsorption studies

Batch experiments were carried out by agitating a known weight of *Albizia procera* legumes substrate placed in contact with 100 ml of metal ion solutions of different concentrations. The suspension was continuously stirred in a shaker, the effect of pH and

initial metal ion concentration have been studied for pH range 2.5-9.5 and for initial metal ion concentrations ranging from 30-90 mg/L of Cr(VI) and Cu(II). The pH of the solution was adjusted by the addition acidic buffer. The contact time was varied from 5 min to 240 min, The concentration of Cr(IV) and Cu(II) was determined by spectrophotometer (Vogel A. I. 1961).

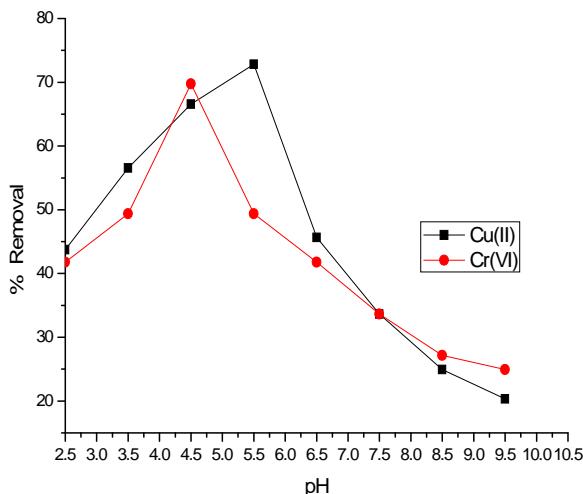
### Preparation of Column for adsorption

Column studies were carried out in a column made of Borosil glass of 1.5 cm internal diameter and 15 cm length. The two columns were filled with 1 g of dried formaldehyde treated *Albizia procera* legume substrate by tapping so that maximum amount of adsorbent was packed without gaps for adsorption of Cr(VI) and Cu(II) respectively. The influent aqueous solution of Cr(VI) and Cu(II) containing known concentration were filled in the two different reservoir of large cross sectional area. The height of the liquid level was adjusted so as to maintain constant flow rate of effluent. The influent solution was allowed to pass through the packed column at constant flow rate of 2 mL/min. All the experiments were carried out at room temperature. The effluent solution was collected at every 5 minutes intervals and the concentration of the Cr(VI) and Cu(II) solution was determined by Beer's law (Vogel A. I. 1961) using spectrophotometer.

## Result and Discussion

### Effect of pH

**Fig.1.** Effect of  $p^H$  on adsorption of Cr(VI) and Cu(II)



The effect of pH on the adsorption of Cr(VI) and Cu(II) ions on formaldehyde treated *Albizia procera* legume substrate has been studied in the pH range

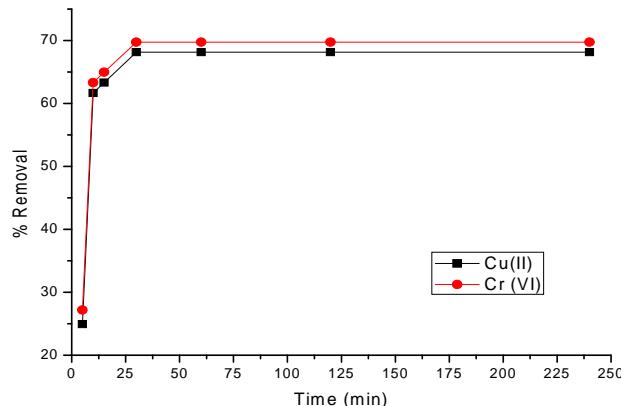
of 2.5 – 9.5 at room temperature and at fixed initial sorption concentration of  $1.0 \times 10^{-4}$  M shown in Fig. 1.

In each case 1 g of the substrate at the desired pH was agitated for 30 min. The percentage removal was found to increase up to certain extent and then decrease. The decrease may be due to precipitation of metal hydroxide. The data showed that adsorption of Cr(VI) and Cu(II) is optimum at 4.5 and 5.5 pH respectively. The physicochemical characteristics of the adsorbent may also play an important role. It was reported that free metal ions are adsorbed better than hydroxides of metal ions (Anima et al., 2004). Hence, pH 4.5 and 5.5 for Cr(VI) and Cu(II) respectively was selected for all studies.

### Effect of time of agitation

The adsorption of metal ion by substrate for different interval of time was studied. The time of agitation was varied from 5 min to 24 hrs. It was observed in all cases that up to 30 minutes, adsorption increases at a fast rate and attains saturation (Figure 2). Hence, 30 minutes time was fixed for all batch experiments.

**Fig. 2.** Effect of agitation time on removal of Cr (VI) and Cu(II)

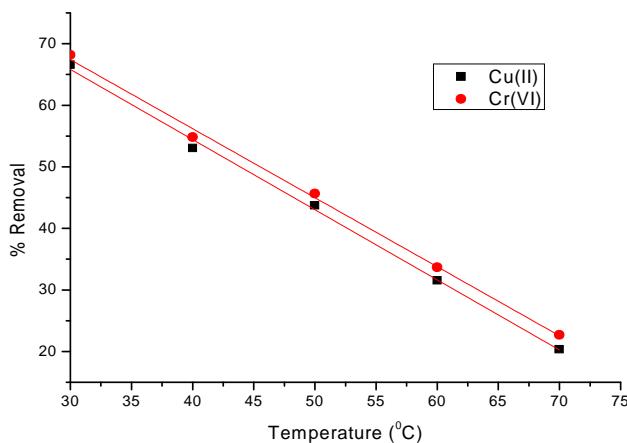


### Effect of temperature

The effect of temperature on adsorption of Fe (II) and Cu(II) ions by formaldehyde treated *Albizia procera* legume substrate has been investigated by conducting set of experiments at variable temperature ranging from 30 to 70 °C at a step of 10 °C. The initial concentration of precursor Cr(VI) and Cu (II) ions in the solution was kept at  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> at 4.5 and 5.5pH respectively. It was observed that with the increase in temperature the uptake of metal ions decreased from 68.16 to 22.66

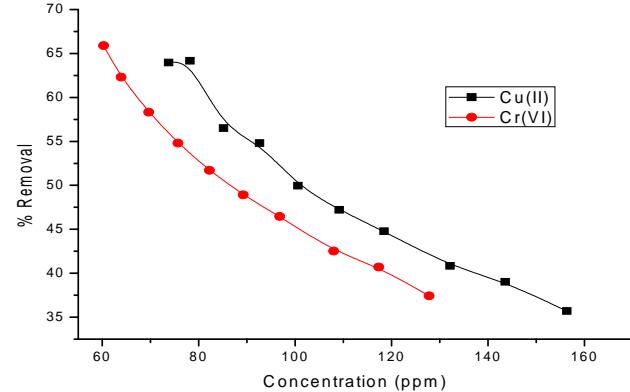
% at the equilibrium as shown in Figure 3. This fact is supported by Freundlich model of adsorption isotherm.

**Fig. 3.** Effect of temperature on removal of Cr (VI) and Cu(II)

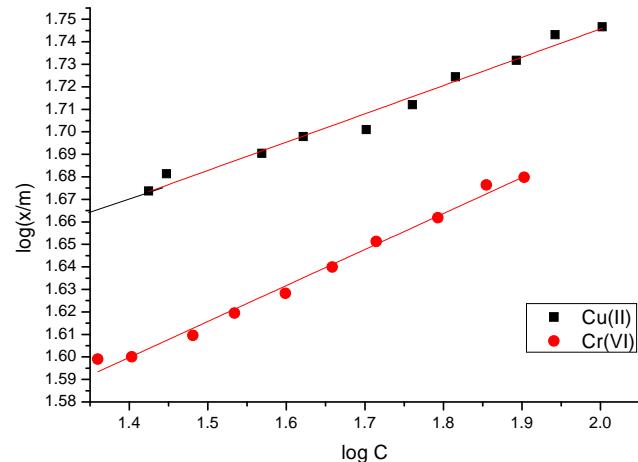


stronger bond between adsorbate and adsorbent (Faust 1987). The higher numerical values of  $K$  confirm the significant affinity of Cr(VI) and Cu(II) ions for formaldehyde treated *Albizia procera* legumes substrate.

**Fig. 4.** Effect of concentration on removal of Cr (VI) and Cu(II)



**Fig. 5.** Freundlich adsorption isotherm for Cr(VI) and Cu(II)



**Table 1.** Freundlich Isotherm Constant for Cr(VI) and Cu(II)

Metal ions	$1/n$	$K_f$	$R^2$
Cr(VI)	0.1597	30.8673	0.9972
Cu(II)	0.1256	23.7684	0.9896

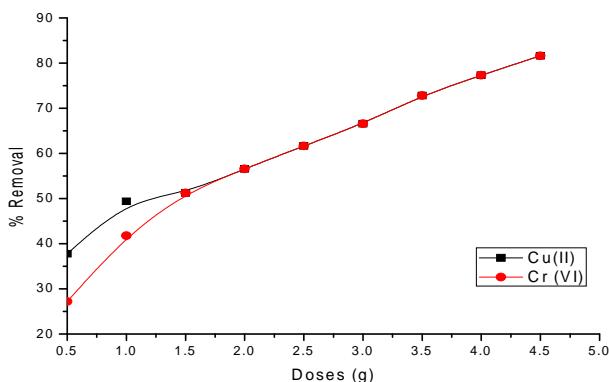
### Effect of adsorbent doses

The effect of adsorbent doses on removal of Cr(VI) and Cu(II) are depicted in figure 6. It was observed that removal of Cr(VI) and Cu(II) ions increases with increase in the adsorbent dose in all experimental runs. Cr(VI) and Cu(II) concentration was fixed at 75.70 and 92.60 ppm respectively. An adsorbent dose was varied from 0.5 g/100ml to 4.5 g/100ml in aqueous solution at their optimum pH value.

The fractional value of  $1/n$  indicates the surface of adsorbent is of heterogeneous type with an exponential distribution of energy sites. Since the value of  $1/n$  is less than 1, it indicates favorable adsorption. A smaller value of  $1/n$  indicates better adsorption mechanism and formation of relatively

However, with the further increase in adsorbent doses, there was no appreciable change in Cr(VI) and Cu(II) removal.

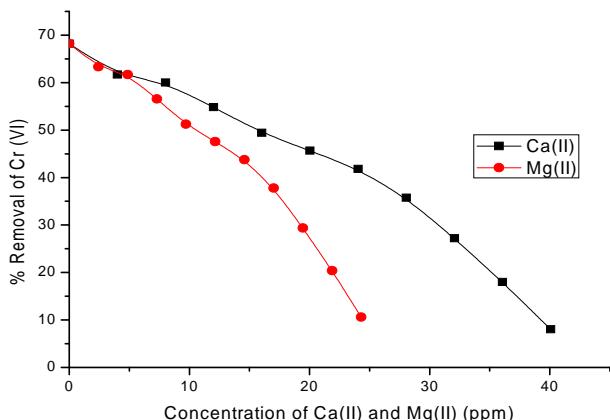
**Fig. 6.** Effect of adsorbent doses on removal of Cr (VI) and Cu(II)



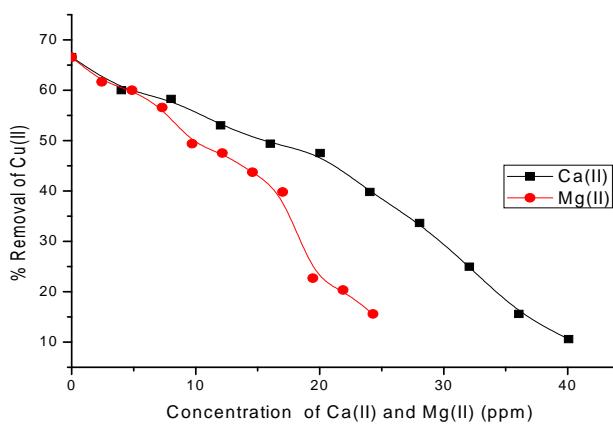
### Effect of co-metal ions

The effect of co-metals Ca(II) and Mg(II) on adsorption of Cr (VI) and Cu(II) ions by formaldehyde treated *Abizia procera* legumes substrate has been investigated by conducting set of experiments at variable concentration of Ca(II) and Mg(II) ranging from 2 mg/L to 40 mg/L at 30°C. In first set of experiment variable concentration of Ca(II) ions mixed with fixed concentration of Cr(VI), later on variable concentration of Mg(II) ions was homogenized with the same initial concentration of Cr(VI) ions for adsorption study. Similar adsorption was studied for Cu(II) ions. The initial concentration of precursor Cr(VI) and Cu (II) ions in the solution was kept at  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> at 4.5 and 5.5 pH respectively. It was observed that with the adsorption of Cr(VI) and Cu(II) decreases with increasing in the concentration of co-metal ions (Fig. 7 & 8).

**Fig. 7.** Effect of co-metals Ca<sup>2+</sup> and Mg<sup>2+</sup> on Cr (VI) adsorption by formaldehyde treated *albizia procera* legumes substrate



**Fig. 8.** Effect of co-metals Ca<sup>2+</sup> and Mg<sup>2+</sup> on Cu (II) adsorption by formaldehyde treated *albizia procera* legumes substrate

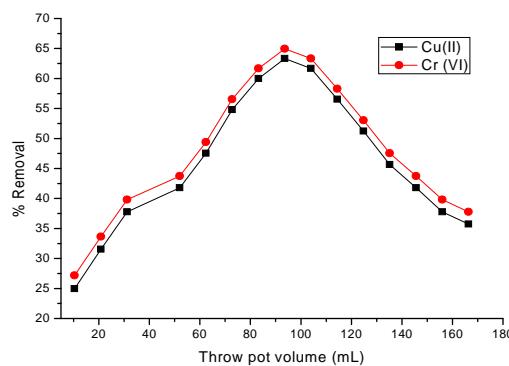


This proves that *Albizia procera* legumes substrate effectively removes heavy metal ions and co-metal ions as well.

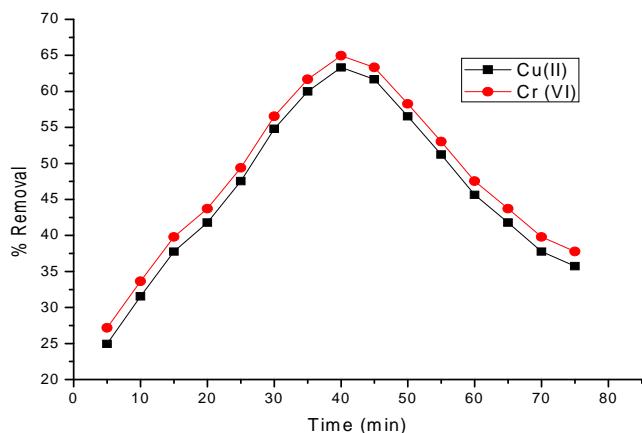
### Column studies

Column adsorption studies of Cr(II) and Cu(II) on *Abizia procera* legume substrate at room temperature are investigated using aqueous solution of 70 mg/L influent concentrations at the optimal 4.5 and 5.5 pH value respectively for Cr(VI) and Cu(II). Faster and effective adsorption of Cr(IV) and Cu(II) occurs during the initial phase. Adsorption reaches to the optimum value at 45 min and upto the 100 mL effluent. Subsequent adsorption decreases as a consequence of the progressive saturation of the binding sites. It was observed that the column gets saturated after passing 160 mL of Cr(VI) and Cu(II) solutions (Figure 9). Optimum adsorption of Cr(VI) and Cu(II) observed between 40 - 45 min in a packed column of *Albizia procera* legume substrate (figure 10).

**Figure 9:** Optimum adsorption of Cr(VI) and Cu(II) observed at 90 mL of throw pot volume.



**Figure 10:** Optimum adsorption of Cr(VI) and Cu(II) observed between 40 - 45 min in a packed column



## Conclusions

*Albizia procera* legumes are available in abundance in the Vidarbha region of Maharashtra state, India. It was studied for its ability to adsorb the heavy metal ions Cr(VI) and Cu(II) from aqueous solution.. Detailed studies were carried on the adsorption of Cr(VI) and Cu(II)using *Albizia procera* legumes substrate as an adsorbent. Adsorption studies show that equilibrium was attained in 30 min and the adsorption of Cr(VI) decreases with an increase in initial Cr(VI) and Cu(II) concentration. The experimental data well fitted the Freundlich isotherm in the Cr(VI) and Cu(II) concentration range of 60 to 128 mg L<sup>-1</sup> and 73 to 157 mgL<sup>-1</sup> respectively. The adsorption of Cr(VI) and Cu(II)are pH dependent and maximum removal occurs at pH 4.5 and 5.5. The material can thus be used effectively at pH range of 4.5-5.5 for the removal of Cr(VI) and Cu(II) from wastewater. The study of adsorbent efficiency for Cr(VI) and Cu(II) removal in the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> showed that the presence of Ca<sup>2+</sup>and Mg<sup>2+</sup> ions leads to an insignificant decrease in Cr(VI) adsorption. Thus it effectively removed co-metals as well.

The substrate materials are not only cheap, inexpensive, and easily available but needs simple processing for effective removal of metal ion and co-metal ions like Ca(II) and Mg(II) without use of any sophisticated equipment or expert attention. It could be effective alternative to conventional adsorbents like activated charcoal or alumina and expensive ion exchange resins. Application of this adsorbent to wastewater treatment is expected to be economical and efficient.

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