

# Study of Removal of Heavy Metal Copper (II) from Aqueous Solutions by Punica Granatum Seed Powder by Adsorption

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## ABSTRACT

Heavy metals contribute to a variety of adverse health environmental effects due to their acute and chronic exposure through air, water and food chain. Heavy metal toxicity can result indamaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease. Copper is highly toxic due to its non biodegradable and carcinogenic. Punica granatum seed powder use as a natural adsorbent for effective removal of copper (II). The main parameters influence the adsorption of copper (II) as percentage recovery, initial metal concentration, effect of adsorbent dosage, metal ion concentration, effect of time and effect of pH was studied in batch process. The adsorption study were carried out isothermally at different temperatures. Freundlich isotherm and Langmuir isotherm were used to describe the equilibrium data and the result were discussed in details. The kinetic data well described by the pseudo first order kinetic model. The thermodynamic parameters such as standard free energy change, entropy change and enthalpy change were studied for Punica granatum seed powder. This values showed that the adsorption of copper (II) ion on Punica granatum seed powder was a spontaneous and endothermic process. The removal of copper (II) ion from waste water and the techniques will be applicable at low cost.

**Keywords:** Adsorption, Punica Granatum Seed, Langmuir Isotherm, Freundlich Isotherm, Kinetic, Thermodynamics Data.

## I. INTRODUCTION

Environmental pollution causes due to the heavy metals. Heavy metals are major toxic pollutants with severe health effects on humans. They are released into the environment from a variety of industrial activities. Cadmium, lead, zinc, chromium and copper are the most toxic metals of widespread use in industries such as tanning, electroplating, electronic equipment manufacturing and chemical processing plants. Heavy metals contribute to a variety of adverse health environmental effects due to their acute and chronic exposure through air, water and food chain The international community is beginning to recognize the adverse health effects of heavy metals [1]. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease,

Parkinson's disease, muscular dystrophy, and multiple sclerosis. Heavy metals are associated with myriad adverse health effects, including allergic reactions (e.g., beryllium, chromium), neurotoxicity (e.g., lead), nephrotoxicity (e.g., mercuric chloride, cadmium chloride), and cancer (e.g. arsenic, hexavalent chromium). Humans are often exposed to heavy metals in various ways mainly through the inhalation of metals in the workplace or polluted neighborhoods, or through the ingestion of food (particularly seafood) that contains high levels of heavy metals or paint chips that contain lead [2]. It is therefore essential to remove heavy metals from industrial waste water and drinking water. Conventional treatment methods of metal removal are often limited by their cost and ineffectiveness at low concentrations. Adsorption has emerged as promising technique for metal removal. It is one of the most popular purification methods due to its high selectivity, low cost, high efficiency and easy post-treatment after adsorption. Adsorption can be a potential alternative to traditional treatment processes of metal ions removal [3-

5]. The process can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, or liquid-solid interfaces [6]. Recently, a series of low-cost adsorbents derived from agricultural waste or natural materials [7-8] have been investigated for toxic substances like fluoride removal from aqueous solutions, such as apple and orange juicing residue, waste tea, peanut hull, rice straw, and coconut shell. Adsorption can be a potential alternative to traditional treatment processes of metal ions removal [6-8]. The phenomenon of adsorption has been described in a wide range of non-living biomass like potato peel waste [9], untreated *Cocos Nucifera* [10], orange peel [11], crab shell [12], untreated coffee grounds [13], as well as of living biomass like, microbial cell [14], moss [15], yeast [16], fungi [17-18], algae [19-20]. Adsorption has been proved to be an excellent way to treat industrial waste effluents, offering significant advantages like the low-cost, availability, profitability, easy of operation and efficiency [21-22]. There is a large volume of literature relating to the performance of different biosorbents for the removal of variety of heavy metals [23-26].

Copper is highly toxic because it is non biodegradable and carcinogenic. The effect of copper, liver disease, renal dysfunction, fibromyalgia symptoms, muscle and joint pains, depression, chronic fatigue symptoms, irritability, tumor, anemia, learning disabilities and behavioral disorders, stuttering, insomnia, niacin deficiency, leukemia, high blood pressure [27].

The objective of this work is to study the adsorption behavior of respect to copper ion. The batch method was employed parameters such as percentage recovery, initial metal ion concentration, effect of addition of dose of adsorbent, effect of time, effect of pH, effect of temperature, Freundlich and Langmuir adsorption isotherm, Kinetic study and also thermodynamic were studied.

## II. MATERIALS AND METHODS

### Materials

#### Adsorbent

The *Punica granatum* seed common name, Pomegranate, was purchased from market. Then the material was washed with doubly distilled water to remove the free

acid and then dried at 200 K for 12 hours. The resulting product was cooled to room temperature and grind into fine powder and sieved to the desired particle size. Finally, the product was stored in air tied bottle for use as a adsorbent.

### Preparation of copper (II)

Copper (II) prepared by dissolving copper sulphate in double distilled water. The chemicals used were of analytical grade and used without further purifications. The solutions were prepared in distilled water. The prepared solutions were standardized as per literature.

### Absorption Study ( Batch Process)

The dried powder of *Punica granatum* seed powder of 1.0 gm was taken in stoppered bottle. The Copper (II) with initial concentration of 10 mg/dm<sup>3</sup>, 20 mg/dm<sup>3</sup>, 30 mg/dm<sup>3</sup>, 40 mg/dm<sup>3</sup>, 50 mg/dm<sup>3</sup>. The mixture were well stirred on a shaker at 100 rpm at the temperature 298 K, 303 K, 308 K and 313 K for 20, 40, 60, 80, 100 & 120 minutes until the equilibrium condition were reached. The content was filtered. The adsorbate and adsorbent were separated by filtration. The filtrate in the aqueous solution after adsorption was measured by using pH values of Copper (II) solution were determined by using pH 5 using pH meter. The percentage of adsorption was determined from initial and equilibrium concentration respectively.

The percentage of Copper (II) removal was calculated as

$$\text{The \% of Metal ion removal} = \frac{C_i - C_f}{C_i} \times 100$$

$C_i$  &  $C_f$  = Concentration of metal ion before and after the treatment.

The adsorption isotherm studies and kinetic studies were also carried out and the calculation were performed to get the appropriate result as well as thermodynamic parameters were calculated.

## III. RESULTS AND DISCUSSION

### Effect of Adsorbent Dose

The effect of adsorbent on copper (II) removal was studied by batch adsorption process. The percentage of removal of copper (II) reaches about 86-87 % each. The dose required is nearly about 160 mg/ 25 ml for the initial concentration of 25 mg/L at pH 4.

### Effect of pH

Effect of pH solution is very important in adsorption process of metal ion. pH of solution affect on the surface of adsorbent, solubility of metal and also the speciation of metal ion. Effect of removal of copper (II) ion using *Punica granatum* seed powder as an adsorbent. With increasing pH from 2 to 8 the percentage of copper (II) also increases.

### Effect of Temperature

Temperature is very important factor for adsorption. Higher temperature increases the rate of the adsorbate and decrease in the viscosity of the solution. Change in the temperature changes the equilibrium capacity of the adsorbent for the particular adsorbate. A series of experiments were conducted at 298 K, 303 K, 308 K, 313 K and 335 K to study the effect of temperature on the adsorbate time rate for 20, 40, 60, 80, 100 & 120 minutes. **Figure 1.**

### Freundlich Adsorption Isotherm

Freundlich plot for the adsorption of copper (II) ion with *Punica granatum* seed powder shows that the values of adsorption intensity  $1/n$  is less than 1. Indicates the applicability of Freundlich adsorption **Table 2.**

### Langmuir Adsorption Isotherm

The value of  $Q_0$  of Langmuir adsorption isotherm found to be comparable with commercial activated carbon. Value of  $b$  lies between 0 to 1 it indicate that the adsorption is favourable. It indicate that the applicability of Langmuir adsorption isotherm **Table 3.**

### Adsorption Kinetics

Adsorption rate of copper (II) ion on *Punica granatum* seed powder was studied by first order kinetic rate equation. It is found that the initial concentration of copper (II) ion increases rate constant decreases it indicate that the adsorption does not follow the first order kinetics **Table 4.**

### Thermodynamics Parameters

Adsorption depends on temperature. Increasing temperature mass of copper (II) ion per unit mass was increased. Thermodynamics parameters like change in Gibb's free energy, change in enthalpy and change in entropy was calculated. The change in enthalpy indicate the process is endothermic nature **Table 5.**

**Table 1.** Summary of % Recovery of Adsorbent Capacity of adsorbent  
Initial concentration 10 mg/L Adsorbent dose 1 mg/L

Sr.No.	Adsorbent	Heavy Metal	Final Conc (mg/L)	% Recovery	Q (mg/L)
1	<i>Punica granatum</i> seed powder(PGSP)	Copper (II)	57.48	87.04 %	26.43

**Table 2.** Freundlich Adsorption Isotherm of Copper (II) on PGSP

		Concentration	Freundlich Constant	
			K	1/n
1	Copper (II)	10 mg/L	2.9401	1.001
		20 mg/L	4.9265	1.632
		30 mg/L	7.3527	2.115
		40 mg/L	8.2573	3.920
		50 mg/L	9.2104	4.026

**Table 3.** Langmuir Adsorption Isotherm of Cu (II) on PGSP

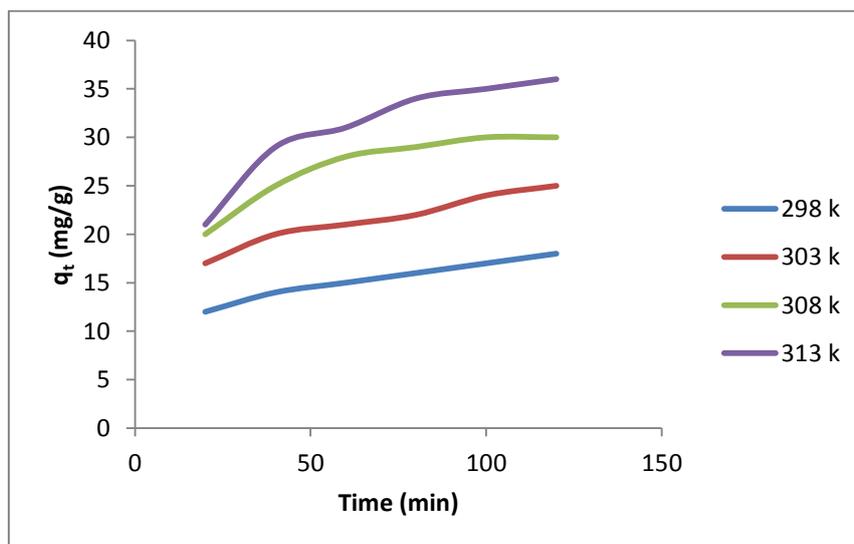
Sr.No.	Heavy Metal	Concentration	Langmuir Constant	
			Q <sub>0</sub>	B
1	Copper (II)	10 mg/L	42.18	0.041
		20 mg/L	52.89	0.059
		30 mg/L	67.23	0.072
		40 mg/L	71.25	0.091
		50 mg/L	74.09	0.099

**Table 4.** Adsorption Kinetics of Copper (II) on PGSP

Sr.No.	Heavy Metals	Concentration	First order rate constant (K <sub>1</sub> )
1	Copper (II)	10 mg/L	4.382 x10 <sup>-3</sup>
		20 mg/L	5.032 x10 <sup>-3</sup>
		30 mg/L	6.193 x10 <sup>-3</sup>
		40 mg/L	7.374x10 <sup>-3</sup>
		50 mg/L	8.215 x10 <sup>-3</sup>

**Table 5.** Thermodynamic parameters for the adsorption of Copper (II) on PGSP

Sr.No.	Heavy Metals	T (°K)	Change in Gibb's free energy (KJ/mole)	Change in enthalpy (KJ/mole)	Change in entropy (KJ/mole)	R <sup>2</sup>
1	Copper (II)	298 K	-32.84	55.31	0.4892	0.0945
		303 K	-41.03			
		308 K	-50.11			
		313 K	-54.28			
		335 K	-67.36			



**Figure 1.** Effect of temperature on adsorption of copper (II) on PGSP

#### IV. CONCLUSION

Adsorption process is rapid at the starting and a becomes slow at the standard stage. It dependent on initial concentration of adsorbate and also time for adsorption. This adsorption is good agreement with Freundlich adsorption isotherm and also for Langmuir adsorption isotherm Adsorption process is good at pH 5. The cost of adsorbent is very low & is easily available

#### V. ACKNOWLEDGMENT

The author are grateful to the Principal of S.M.B.S.T.College, Sangamner, Ahmednagar.

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