Studies on the Removal of Heavy Metals Copper (II) and Cadmium (II) from Aqueous Solutions by *Annona squamosa* L. Leaf Powder as an Adsorbent

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ABSTRACT

Heavy metals are major pollutants in the environment due to toxicity and threat to creatures and human being at high concentrations. Copper is highly toxic due to its non biodegradable and carcinogenic. Cadmium causes hypertension anemia, paint join hence to study the removal of these heavy metals from waste water by batch adsorption process. *Annona squamosa L.* leaf powder (ASLP) use as a natural adsorbent for effective removal of copper (II) and cadmium (II) ions. The main parameters influence the adsorption of copper (II) and cadmium (II) as an effect of adsorbent dosage, effect of pH, effect of contact time, effect of temperature and effect of metal ion concentration was studied in batch process. The adsorption study was carried out isothermally at different temperatures. Freundlich isotherm and Langmuir isotherm were used to describing the equilibrium data and the results 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 *Annona squamosa L.* leaf powder (ASLP). This values showed that the adsorption of copper (II) and cadmium (II) ions on *Annona squamosa L.* fruit coat (ASFC) was a spontaneous and endothermic process. *Annona squamosa L.* leaf powder (ASLP) was successfully employed for the removal of copper (II) and cadmium (II) ions from waste water and the techniques will be applicable at low cost.

INTRODUCTION

Environmental pollution is the major serious problem today. Environmental pollution causes due to the heavy metals. These heavy metals effect on human. The term "heavy metal" is collectively applied to a group of metals with density greater than 5 g/cm^3 and atomic number above 20[1]. Electroplating, battery manufactures, painting, paper, pigments, fuels, photographic materials, explosive manufacturing and metalworking industries discharge large amounts of heavy metals. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and storage batteries industries[2]. Heavy metals pollution occurs in much industrial wastewater such as that produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. This waste water commonly includes Cd, Pb, Cu, Zn, Ni and Cr[3] including copper (Cu), and cadmium (Cd) ions, in their effluent[4,5]. Heavy metals are major pollutants in the environment due to their toxicity and threat to creatures and human being at high concentrations[6]. Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries[7]. The other major industries discharging copper in their effluents are paper, pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal waste[8].

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[9]. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and drink. Copper has been reported to cause neurotoxicity commonly known as "Wilson's disease" due to deposition of copper in the lenticular nucleus of the brain and kidney failure[10]. Copper is an essential trace element necessary for plant and animal growth. Copper ion in small amounts is used in agriculture and is an essential element for health of plants, animals and humans. In humans, it helps in the production of blood haemoglobin. High concentration of copper creates a kind of disease, which is similar to flu. It has been proved that drinking water, including 30 grams of copper ion is fatal and the

concentration of 1.3 mg/l of this ion could be a reason for the relatively common diarrhea, abdominal cramps and nausea[11,12].

Copper as lead can damage the health of all living organisms; therefore heavy metals should be prevented from reaching the natural environment[13]. In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever[14]. Moreover, continued inhalation of copper-containing sprays is linked to an increase in lung cancer among exposed workers. Cadmium hypertension or high blood pressure dulled sense of smell, anemia[15]. And cadmium exposure causes hypertension or high blood pressure, dulled sense of smell, anemia[15], joint soreness, hair loss, dry scaly skin, loss of appetite, decreased production of T cells and, therefore, a weakened immune system, kidney diseases and liver damage, emphysema, cancer and shortened lifespan. When people breathe in Cadmium it can severely damage the lungs. This may even cause death. Animals eating or drinking Cadmium sometimes get high blood-pressures, liver disease and nerve or brain damage. A maximum acceptable concentration of 0.005 mg/L (5μg/L) for cadmium in drinking water has been established on the basis of health considerations[16]. Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and co-precipitation/adsorption. Studies on the treatment of effluent bearing heavy metals have revealed adsorption to be a highly effective technique for the removal of heavy metals from waste stream and activated carbon has been widely used as an adsorbent[17].

Agricultural waste is one of the rich sources of low-cost adsorbents besides industrial by-product and natural material. Due to its abundant availability agricultural waste such as peanut husk, rice husk, wheat bran and sawdust offer little economic value and, moreover, create serious disposal problems[18]. Activated carbons derived from peanut husk and rice husk have been successfully employed for the removal of heavy metals from aqueous solutions[19]. The use of peanut hull carbon for the adsorption of Cu(II) from wastewater was studied by Periasamy and Namasivayam[20].

In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research low cost agricultural waste by-products such as sugarcane bagasse[21-25], rice husk[26-30], sawdust[31-33], coconut husk[34], oil palm shell[35], neembark. A number of physicochemical protocols are being used worldwide to depollute water loaded with heavy metals. However, these methods are inherently problematic in their

application and are not economically feasible[36-38]. Biological processes like bioaccumulation, biosorption have acquired due attention owing to number of advantages and engaged the scientists from all over the world to identify the potent biomass type[39-41]. The term, biosorption is used to describe the passive non metabolically mediated process of metal binding to living or dead biomass[42-43]. Since most conventional methods are neither effective nor economical, especially when used for the reduction of heavy metal ions to low concentrations, new separation methods are required to reduce heavy metal concentrations to environmentally acceptable levels at affordable cost. A variety of low-cost biomass has been studied by various workers for controlling pollution from diverse sources in different parts of the world[44].They include anaerobically digested sludge[45-48]. Agricultural materials have also been used. These include rice bran, soybean and cottonseed hulls, crop milling waste[49], groundnut husk, maize cob meal, coir, jute and sawdust[50], canola meal, coconut shell[51] and spent tea leaves[52-53]amongst others. Fruit waste of Gular used for the removal of Cr (VI)[54], *Foeniculum vulgaris* for Cd[55]. Most cellulosic materials investigated have been found to be good adsorbents for heavy metals[56]. Diverse plant parts such as coconut fiber pith, coconut shell fiber, plant bark (*Acacia arabica*, Eucalyptus), pine needles, cactus leaves, neem leave powder have also been tried for chromium removal showing efficiency more than 90–100% at optimum pH[57-61].

The main objective of the work is to investigate the adsorption properties of *Annona squamosa L.* leaf powder (ASLP) for the removal of copper (II), cadmium (II), The study includes adsorption as an effect of contact time, effect of adsorbent dose, effect of concentration of metal ion solution, effect of pH of the solution, effect of temperature of the system. The isotherm studies were fitted for Freundlich and Langmuir adsorption isotherm.

MATERIALS AND METHODS

Adsorbent

The adsorbent used in the present investigation were leaves of *Annona squamosa L.* plants collected from the garden Nil-Lohit, Saishradhanagar, Sangamner, Ahmednagar District of Maharashtra state (India). The leaves of *Annona squamosa L.* were thoroughly rinsed with water to remove dust. Then it was allowed to dry in shadow avoiding direct sunlight on them. The dried plant leaves were grinded into powdered were boiled in distilled water to remove the suspended dust for one hour and filtered. Left residue was treated with formaldehyde and

finally washed with the dilute solution of sulphuric acid. It was stirred vigorously by using mechanical stirrer at room temperature about 1 hr. Then it was filtered and washed with distilled water three times to remove free acid. After chemical treatment residue was dried first in air and finally in oven at 110ºC for 12 hrs and was then stored in desiccators for final study.

Preparation of Adsorbate solution

All the chemicals used were of analytical reagent (AR) grade. Stock solution of 1000 mg/L of copper (II), was prepared from copper sulphate and cadmium (II) from cadmium sulphate by distilled water. Desired test solutions of copper (II) & cadmium (II) ions were prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of copper (II) & cadmium (II) ions prepared from standard solution varies between 10 and 50 mg/L. Before mixing the adsorbent, the pH of solution was adjusted to the required value with 0.1 M NaOH.

Absorption Study (Batch Process)

The dried *Annona squamosa L.* leaf powder (ASLP) was taken in a stoppered bottle of various amount and standard 200 ml containing various concentration of copper (II) & cadmium (II) was added in the bottle and shake well. The equilibrium by shaking the contents of the solution at room temperature. The content was filtered. The adsorbate and adsorbent were separated by filtration. The filtrate was determined by spectrophotometrically. It measures the concentration of copper (II) & cadmium (II). Effect of adsorbent dosage, effect of pH, effect of contact time, effect of temperature and effect of metal ion concentration was also studied. The percentage of adsorption was determined from initial and equilibrium concentration respectively. The batch adsorption studies were carried out by varying the experimental conditions.

The percentage of copper (II) & cadmium (II) removal was calculated as

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

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

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

RESULTS AND DISCUSSION

Effect of adsorbent dose

The effect of amount of adsorbent on the adsorption of copper (II) & cadmium (II) as shown in **Fig 1.** It was observed that the copper (II) & cadmium (II) removal efficiency increases with increase in the amount of adsorbent added. After which it becomes nearly constant with 0.9 mg/L and 1.2 mg/L adsorbent copper (II) & cadmium (II) ions. Increase the adsorbent dosage more binding sites will be vacant for the complexation of copper (II) & cadmium (II) ion and there will be an increase in the rate of adsorption. But there will be very slow increase in the percentage of removal after an optimum dose which is due to the equilibrium state between the adsorbate and adsorbent.

Effect of pH

A given concentration of metal ion solution was taken along with a fixed amount of solvent and the pH was set from 1 to 10 using 0.5 M HNO$_3$ and 0.1 M NaOH. The change in pH was observed in **Fig 2**. The minimum adsorption was observed at pH 3 for copper (II) & pH 6 for cadmium (II).

Effect of contact time

The time of contact of the adsorbent with copper (II) & cadmium (II) ions were changed from 10 minutes to 360 minutes and the variation observed is shown in **Fig 3.** It was observed that the time is increased the amount of metal ion is adsorbed by the sorbent increases but after 140 minutes the solution of copper (II) and 180 minutes cadmium (II) attain equilibrium. It explains that at starting stage large number of vacant sites may be available for adsorption but after that it slows down as the vacant sites may be exhausted. It is due to repulsion between the solute molecules and bulky phase.

Effect of time

The variation in adsorption of copper (II) & cadmium (II) ions was studied at 6 different temperatures. 25ºC, 30ºC, 35ºC, 40ºC, 45ºC, 50ºC. As the temperature increased the % of recovery also increased with a maximum of 92 % at 45ºC for Copper (II) and 87 % at 40ºC for cadmium (II). This indicates that the adsorption process is a chemisorption process.

Effect of Metal ion concentration

Varying the concentrations of 15 mg/L -300 mg/L of copper (II) & cadmium (II) was taken and keeping the adsorbate dose fixed. The effect is as given in **Fig 4.** It was observed that the adsorption of metal ion increases as the metal ion concentration increases. At lower concentrations, all the metal ions interact with the binding sites and thus gives the maximum adsorption at lower concentration. But at higher concentration metal ions will has free binding sites but due to lack of binding sites for complexation, the adsorption lowers at greater concentrations. It indicates that % removal of metal ions decreases with increase in concentration.

Freundlich Adsorption Isotherm

Freundlich plot for the adsorption of copper (II) & cadmium (II) with *Annona squamosa L.* leaf powder (ASLP) shows that the values of adsorption intensity 1/n is less than 1, indicates the applicability of Freundlich adsorption **Table 1.**

Langmuir Adsorption Isotherm

The value Q_0 of Langmuir isotherm found to be comparable with commercial activated carbon. Value of b lies between 0 to 1 it indicates that the adsorption is favourable. It indicates that the applicability of Langmuir adsorption isotherm **Table 2.**

Adsorption Kinetics

Adsorption rate of copper (II) & cadmium (II) on ASLP was studied by first order kinetic rate equation. It is found that the initial concentration of copper (II) & cadmium (II) increases. Rate constant decreases it indicates that the adsorption does not follow the first order kinetics **Table 3.**

Thermodynamic Parameters

Adsorption rate depends on temperature was investigated at 25^0C, 30^0C, 35^0C, 40^0C, 45^0C, 50^0C. It concludes that increasing temperature mass of copper (II) & cadmium (II) adsorbed per unit mass of the adsorbent was increased. At above temperature, the change in Gibb's free energy, change in enthalpy and change in entropy was calculated. Change in Gibb's free energy shows negative value it indicates that the adsorption of copper (II) & cadmium (II) on ASLP is spontaneous and feasibility. The change in enthalpy value indicates endothermic nature of copper (II) & cadmium (II) on ASLP. The change in entropy shows positive value indicates increase randomness during the adsorption process of copper (II) & cadmium (II) on ASLP. **Table 4**

Table 1 Freundlich Adsorption Isotherm of copper (II) & cadmium (II) on ASLP.

Sr. No.	Concentration of Metal Ion	Freundlich constant			
		K		b	
		Cu(II)	Cd(II)	Cu(II)	Cd(II)
1	10 mg/L	4.8754	5.2016	1.7348	1.6302
2	20 mg/L	5.8091	4.9532	1.7732	1.4569
3	30 mg/L	3.5687	4.0354	1.3604	1.2834
4	40 mg/L	6.0345	5.8790	1.7976	1.6021
5	50 mg/L	5.9159	5.0324	1.8421	1.9473

Table 2 Langmuir Adsorption Isotherm of copper (II) & cadmium (II) on ASLP.

Sr. No.	Concentration of Metal Ion	Langmuir constant			
		Q_0		b	
		Cu(II)	Cd(II)	Cu(II)	Cd(II)
1	10 mg/L	36.91	38.05	0.0321	0.2910
2	20 mg/L	10.83	32.55	0.0196	0.0362
3	30 mg/L	36.88	35.40	0.0173	0.0173
4	40 mg/L	38.04	33.55	0.0280	0.0391
5	50 mg/L	30.85	32.87	0.0331	0.0274

Table 3 Adsorption Kinetics of copper (II) & cadmium (II) on ASLP.

| Sr. No. | Concentration of Metal Ion | First order rate constant | |
| | | K_1 | |
		Cu(II)	Cd(II)
1	10 mg/L	6.9402×10^{-2}	5.8041×10^{-2}
2	20 mg/L	4.9436×10^{-2}	7.3504×10^{-2}
3	30 mg/L	3.3842×10^{-2}	4.5561×10^{-2}
4	40 mg/L	7.2436×10^{-2}	6.7820×10^{-2}
5	50 mg/L	6.2435×10^{-2}	7.2436×10^{-2}

Table 4 Thermodynamic Parameters of copper (II) & cadmium (II) on ASLP.

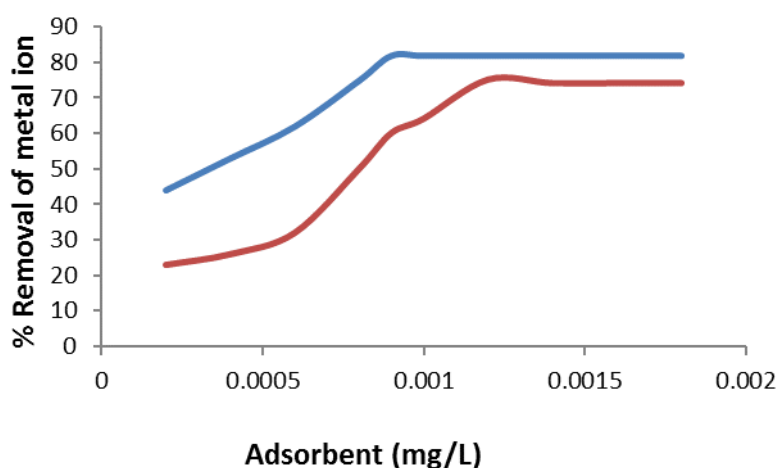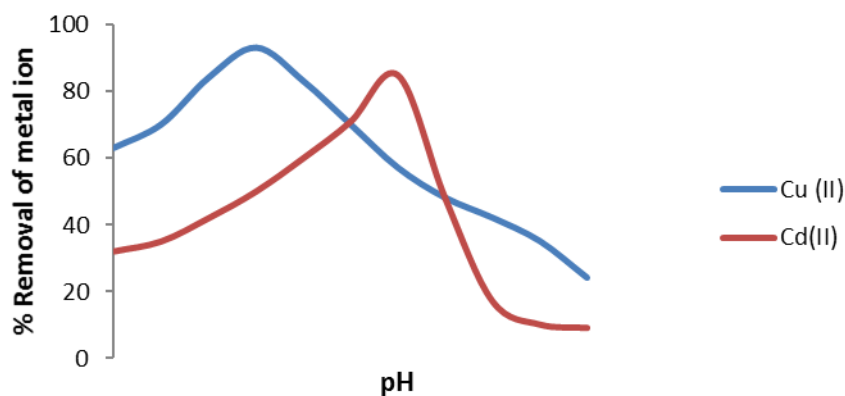| Sr. No. | Temperature | ΔH | | ΔG | | ΔS | |
		Cu(II)	Cd(II)	Cu(II)	Cd(II)	Cu(II)	Cd(II)
1	25ºC					-19	-12
2	30ºC					-17	-16
3	35ºC					-23	-27
4	40ºC	8.94329	9.25374	0.079356	0.082410	-20	-17
5	45ºC					-18	-20
6	50ºC					-26	-24

Fig 1 Effect of adsorbent dose
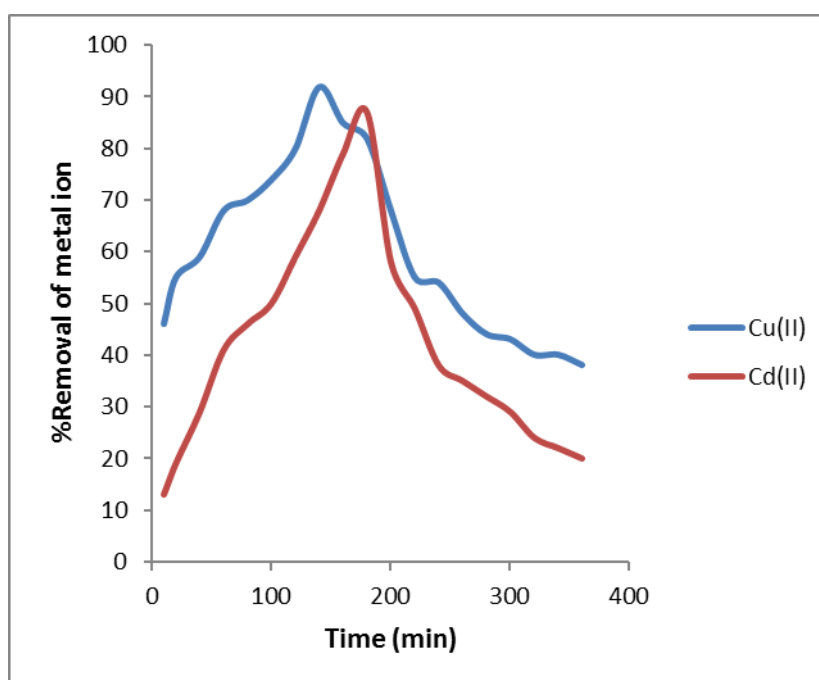
Fig 2   Effect of pH

Fig 3   Effect of contact time

CONCLUSION

From the above study, it can be concluded that ASLP are very effective adsorbent for the removal of copper (II) & cadmium (II) ions from a given water sample. It gave a maximum adsorption at pH 3 for copper (II) & pH 6 for cadmium (II) and adsorbent time of 140 min for copper (II) & 180 min for cadmium (II). The adsorbent dose of 0.9 mg/L for copper (II) & 1.2 g/L for cadmium (II). The maximum % removal of copper (II) & cadmium (II) was found to be 92 % & 87 %. Adsorption studies show that the Freundlich model fits better than the Langmuir model for the experimental data. Thermodynamic values showed that the process was spontaneous and exothermic.

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