

Finger Millet (Ragi) Husk as a Low Cost Adsorbent for Removal of Cu(II) from Electroplating Effluents

Rudre Gowda, A.G. Nataraj and N. Manamohan Rao

Abstract--- This experimental study was focused on finger millet husk as an alternative adsorbent for the removal of Cu(II) from electroplating effluents. Batch experiments were conducted at room temperature 28^oC to determine the various parameters such as contact time, adsorbent dosage, pH and initial concentration. The maximum removal efficiency of Cu(II) was 86.86% for 1.0g/50ml of ragi husk at pH 2.0 and equilibrium contact time of 4hours with the initial concentration 6.24mg/l. The experimental data was analysed to use the Langmuir and Freundlich adsorption isotherm models. The data fitted well to both Langmuir and Freundlich isotherms. The results indicate that the ragi husk was having high potential adsorption and technically feasible, biodegradable, eco-friendly low cost and locally available materials for the treatment of Copper bearing aqueous solution.

Keywords--- Adsorption, Ragi Husk, Copper, Electroplating Effluent

I. INTRODUCTION

INDIA is one of the development countries which is having world second highest population. Increase in population growth with urbanization and industrialization growth has generated large volume of industrial wastes containing toxic heavy metals. Electroplating operation is widely practised either to enhance the engineering properties of material or modification of properties or also to improve the appearance of the end product. These industries are part of rapidly growing industrial sector which is being operated on a job work basis or as a direct plating unit. In India, more than 50,000 large medium and small scale electroplating industries have been housed [9] and there are about 79 electroplating industries housed in Karnataka state, out of which 71 industries are in and around Bangalore city only [10]. The water consumption is less in electroplating industries when compared to other industries, and the effluent is more toxic than other wastes. These industries produce toxic hazardous waste containing heavy metals approximately 78,000kg/annum which adversely effect on environment, especially on biotic components.

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When waste water containing heavy metals flows on the surface of the ground, it loses fertility and the discharge of waste water containing chemicals and metallic ions nearby water courses is well documented. Heavy metals lead to health hazards, if the concentration exceeds allowable limits. Therefore, before waste water flows through waterbodies or land it should be treated [4]. Effluents from industrial processes such as electroplating, mining, nuclear power operations, manufacturing of batteries, dye and pigments have been identified to contain high level of heavy metals. According to the World Health Organisation, the metals of most immediate concern are Cr(III), Cr(VI), Zn, Cd, Cu, Ni, Hg, Pb, Al, Mn [13]. These metals cause direct toxicity to biotic ecosystem.

Copper can be found in many kinds of food, in drinking water and air, long-term exposure to copper can cause irritation of the nose, mouth, and eyes and it causes headaches, stomachaches, dizziness, vomiting, and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Industrial exposure to copper fumes, dusts, mists may result in metal fume fever with atrophic changes in nasal mucous membranes, chronic copper poisoning results in Wilsom's disease characterised by a hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea.

The methods adopted are ion exchange, electrochemical reduction, evaporation, solvent extraction, reverse osmosis, chemical precipitation, membrane filtration, and adsorption [6]. Adsorption is one of the important and effective economical methods for removal of heavy metals. Many researchers have identified the low cost adsorbent like Saw dust[7], Rice husk[3], Coir pith[17], Coconut shell, Waste Tea powder, Coconut husk[16], Sugar cane bagasse[8], etc... Even though the industries are not keen to adopt these adsorbents, all industries are adopting chemical processes only, due to difficulty in disposing of adsorbent materials after use.

Therefore, it is important to identify low cost adsorbent material like ragi husk for removal of copper(II) in electroplating industrial effluents. Ragi husk is having a high potential of adsorption of Cu(II) and can be easily available and decomposable adsorbent material.

The main objective of this study aims at providing economically viable treatment methodology of electroplating wastes using an agro based origin like ragi husk as a low cost adsorbent material for removal of Copper (II) from selected electroplating effluents.

II. RAGI HUSK (ADSORBENT)

Ragi Husk is a by-product derived at the time of harvesting of ragi crop. It is a bio-degradable agricultural waste.

- The main physical and chemical compositions of the ragi husk are:

Table 1: Physical Characteristics of Ragi Husk

Density of Ragi husk used	0.7014g/cm ³
pH of Ragi husk	6.58

Table 2: Chemical Composition of Ragi Husk

Parameter, mg/l, Max	Percentage
Nitrogen (Ni)	28
Calcium (Ca)	49
Phosphorous (P)	14
Silicon di-oxide (SiO ₂)	12.52
Total Aluminium dioxide(Al ₂ O ₃) + Iron oxide (Fe ₂ O ₃), percent by mass (minimum)	1.68
Magnesium oxide (MgO), percent by mass (maximum)	0.29
Loss on ignition	80.6

(Source: K.Saguna -1997, Civil Aid Bangalore-2011)

A. Preparation of Adsorbents

Ragi husk was obtained from Mandya district, sieved with I.S.sieve (600-300 μ). Sieved sample was washed with distilled water and dried at room temperature (28 $^{\circ}$ C \pm 10 $^{\circ}$ C) for 24 hours, and then the sample was dried in hot air oven at a temperature 42 $^{\circ}$ C for 8 hours and later cooled at the room temperature and preserved in air tight plastic container.

A stock solution containing 1000mg/l of Cu(II) was prepared by dissolving the pure copper metal in 1:1 hydrochloric acid solution and then diluting the same up to 1000ml in a volumetric flask with double distilled water and 5ml of HNO₃.

B. Batch Experiments

Batch equilibrium adsorption experiments were conducted by adding 0.1g to 1.0g for ragi husk to erlenmeyer flasks containing 50ml of industrial effluent at different concentrations of Cu(II) at pH 2.42. Initial pH solution was adjusted by adding 0.1M HCl or 0.1M NaOH. The flasks were agitated 150 rpm in rotary shaker. The experiments were conducted for contact time of 30minutes to 300 minutes and pH ranging from 2 to 12. Initial concentration of Cu(II) was 6.24mg/l. The adsorbents were separated from the solution by filtration. The removal efficiency of Copper was determined using Chemito AA-203 Atomic Adsorption Spectra Photometer depending upon the wavelength and working standards. The percentage removal efficiency and equilibrium concentration were determined.

III. RESULTS AND DISCUSSIONS

A. Effect of Contact Time on Cr removal using Ragi Husk

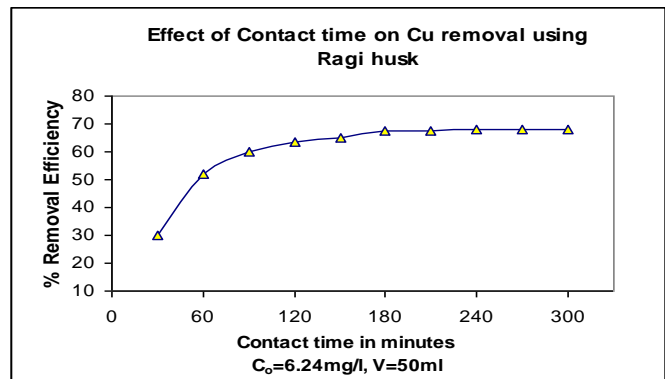


Figure 1

The results for the effect of contact time on adsorption of Cu(II) removal are shown in Fig (1). 0.1g to 1.0g adsorbent was used for this experiment in contact time of 30minutes to 300minutes.

The percentage removal efficiency of Cu(II) ions increases with increase in contact time and reached equilibrium after 240 minutes and which was considered as optimum time.

At initial stage, the rate of removal of Cu(II) was higher due to availability of more number of active sites on the surface of the adsorbent and became slower at the later stages due to decreased or lesser number of active sites. Fig (1) reveals that the curve is single, smooth and continuous, leading to saturation suggesting, the possible mono layer coverage of Cu(II) ions on the surface of the adsorbent.

Similar results have been reported in literature [13], [14], [18].

B. Effect of adsorbent dosage on Cu(II) removal using Ragi husk

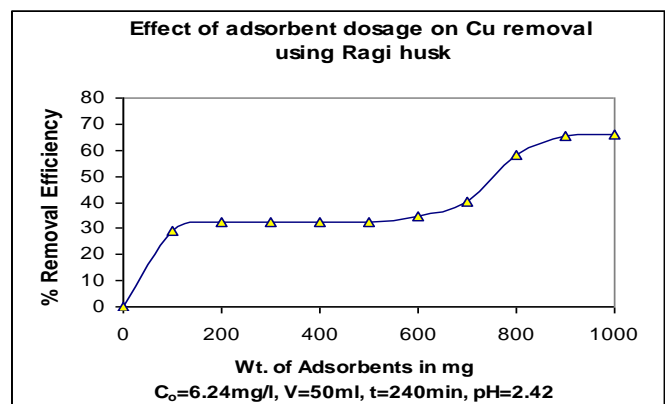


Figure 2

The experiment was conducted over adsorbent dosage range of 0.1g to 1.0g and with the partial size was between 600-300 μ , at an equilibrium contact time of 4 hours. The removal efficiency varies from 29.16 to 66.18% as shown in Fig (2). The percentage of adsorption increased with increase in the adsorbent. This could be due to increased surface area and the availability of more and more adsorption sites. Similar

results have been reported in literature [6], [13], [18].

C. Effect of pH on Cu(II) Removal Using Ragi Husk

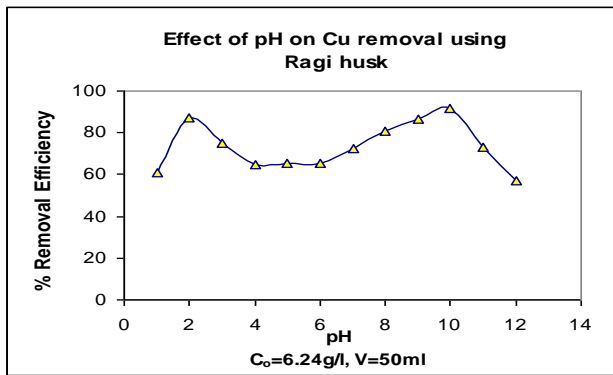


Figure 3

The effect of pH on the percentage of adsorption is significant. It was observed that, the Cu(II) ions adsorbed at a faster rate at low pH ranges compared to alkaline ranges. The percentage of Cu(II) ion adsorbed at pH 2 is 86.86%, pH 4 is 65.05%, however a maximum of 72.33% of Cu(II) ion adsorption occurred at pH 6 and 80.49% at pH 8. At higher pH ranges a maximum of 97.97% in pH 10, as shown in Fig(3)

This indicates that, the strong force of interaction between the metal ion and the adsorbent, that either H⁺ or OH⁻ ions could influence the adsorption capacity. Here the interaction is more at below pH 6, the competence of acidic H⁺ ion with metal cation for the sorption sites. The percentage of sorption increased at the above pH values due to the presence of ionic COOH groups. By increasing the pH values, the metal removal due to enhanced chemical precipitation as hydroxides thus high removal efficiency obtained.

D. Effect of initial concentration on Cu(II) removal using Ragi husk

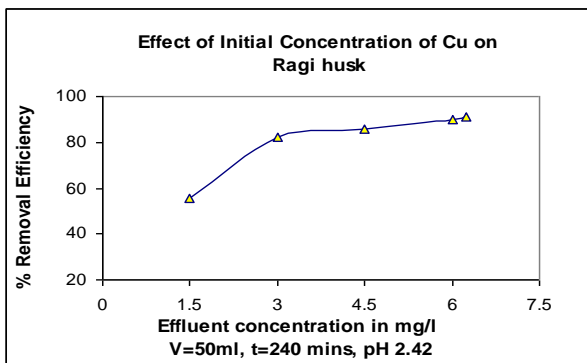


Figure 4

The effect of initial concentration of Cu(II) is shown in Fig (4). The result shows that, as the initial concentration increases, the percentage removal efficiency is increases. The percentage removal efficiency varied from 55.63% at 1.5mg/l to 91.18% at 6.24mg/l with contact time of 4hours and 1.0g adsorbent. It is observed that, as the initial concentration increases, the percentage removal efficiency is increases because at low concentration number of active sites is more in the surface of adsorbent as the concentration increases the number of metal ions increases and hence adsorption

increases, but higher concentration more and more sites are covered by metal ions leading to unavailability of adsorption sites for further adsorption.

Similar result have been reported in literature [13], [18].

E. Langmuir isotherm and Freundlich isotherm for Ragi husk

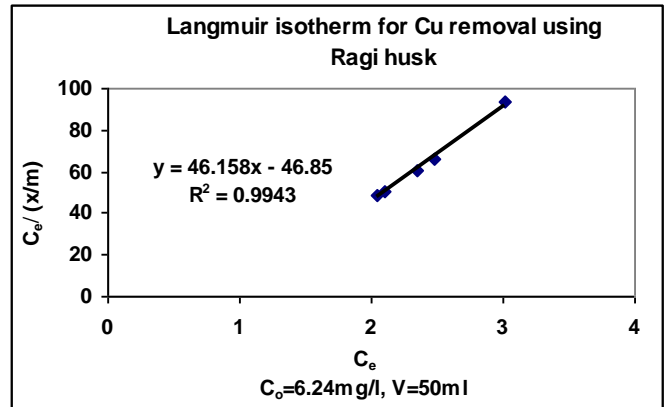


Figure 5(a)

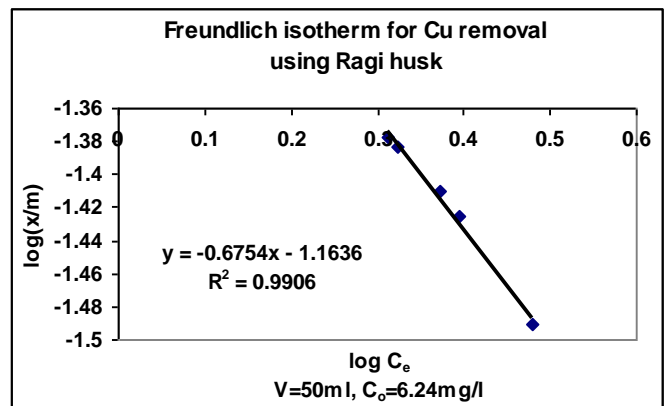


Figure 5(b)

By plotting Langmuir and Freundlich isotherms (Fig 5.a and 5.b), the mean value of Regression co-efficient (R^2) is found to be 0.99578 in Langmuir isotherm and 0.98644 in Freundlich isotherm. The result shows that the experimental data best suits for both the isotherms. The results are shown in the table (5). This indicating that the strong binding of Cu(II) ions to the surface of the ragi husk. Similar result has been reported in [7], [18].

Table 5: Adsorption isotherms for Copper using Ragi husk

Concentration in mg/l	Langmuir Isotherm		Freundlich Isotherm	
	Equation from Graph	R ² value	Equation from Graph	R ² value
1.5	y = 1567.4x - 265.8	0.9923	y = 0.5036x - 3.1596	0.9843
3.0	y = 58.437x - 9.0782	0.9936	y = 0.2882x - 1.6928	0.9694
4.5	y = 31.561x - 3.4987	0.9993	y = 0.1856x - 1.4511	0.9931
6.0	y = 26.445x - 5.954	0.9994	y = 0.2453x - 1.3062	0.9948
6.24	y = 46.158x - 46.85	0.9943	y = 0.6754x - 1.1636	0.9906

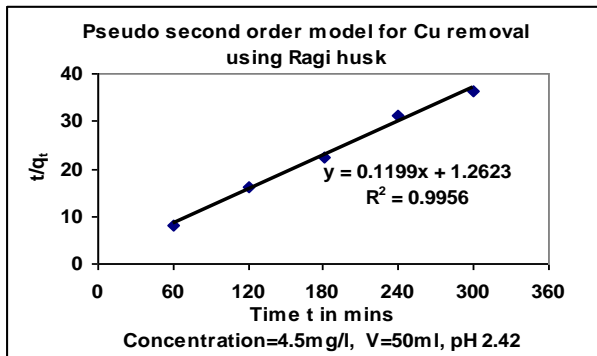
6.0	y = 0.0003x + 1.1878	0.4975	y = 0.1183x + 0.9806	0.9060
6.24	y = 0.0003x + 0.7141	0.3509	y = 0.4123x + 7.7478	0.9773

The objective of this paper was to use ragi husk as a low cost adsorbent material for Copper(II) ion removal. The following conclusions have been drawn from the investigation

- i. The maximum removal efficiency of Cu(II) ion through adsorption on to Ragi husk was found to be 86.86% and 97.97% with pH 2.0 and 10.0 respectively at room temperature 28^oC.
- ii. The initial pH of the aqueous solution affects the Cu(II) ion solution. On the other hand, percentage removal efficiency of copper is increasing with the increasing concentration and increasing with the increase in adsorbent dosage.
- iii. Both Langmuir and Freundlich isotherm equations were well fitted to the adsorption isotherm
- iv. Adsorption kinetics is well described by pseudo-second order model.

Hence, ragi husk has high potential adsorption of Cu(II) removal, economical and ecofriendly adsorption of low cost adsorbent material

F. Pseudo Second Order Kinetics for Ragi Husk



The experimental data fitted to pseudo first and second order kinetics, the result is more favourable to pseudo second order. In pseudo first order and second order, the R2 value lies from 0.3245 to 0.6041 and 0.906 to 0.9956 respectively. The results are tabulated in table (6). Similar observations have been reported [19].

Table 6: Adsorption Kinetics for Pseudo First and Second Order

Concentration in mg/l	Pseudo first order equation	R ² value	Pseudo second order equation	R ² value
1.5	y = 0.0007x + 0.8058	0.6041	y = 0.2306x + 5.97408	0.9204
3.0	y = 0.0006x + 0.8255	0.492	y = 0.1904x + 4.8614	0.9341
4.5	y = 0.0001x + 1.3044	0.324	y = 0.1199x + 1.2623	0.9956

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