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Removal of Cu (II) ion from Ezana (Meli) Gold Mining Wastewater Using Eucalyptus Bark as Adsorbent

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Abstract

This study investigated the potential use of Eucalyptus Bark (EB) powder as an adsorbent in batch mode experiments for removal of Cu^{2+} from Ezana (Meli) wastewater. The discharge of untreated gold mining wastewater contaminated by Cu (II), which is threatening ecosystems and carcinogenic to the human. Since the removal by using adsorption method is cost effective and environmentally friendly, it has been widely studied by many researchers. Characterizations of Eucalyptus Bark were analyzed using proximate analysis, Fourier transform infrared (FTIR) and X-ray diffractometer (XRD). Various characterization techniques showed that the effluent discharged from the factory contains: total suspended solid (TSS), turbidity, Electrical conductivity (EC), Total dissolved solid (TDS), COD, Temperature, pH, cyanide WAD with $<11^{\circ}\text{C}$ (ppm). Atomic absorption spectroscopy study indicated that heavy metals found in the wastewater were in the order $\text{Fe}^{2+} > \text{Cu (II)} > \text{Pb (II)} > \text{Mn} > \text{Cr (VI)} > \text{Zn} > \text{Co} > \text{Ni} > \text{Cd}$ in ppm. The selected parameters were pH, adsorbent dosage and contacting time. The highest percentage of Cu (II) removal achieved was 92%. In this study, the adsorption data were well-fitted to the Langmuir isotherm model.

Keywords: *Adsorption, Cu^{2+} , Removal efficiency, Eucalyptus Bark, Isotherms*

1. Introduction

Ezana is the second largest gold mining company in Ethiopia with a capacity of producing 4.5kg of gold per day. The project area is located close to the rural northwestern lowlands where basic data on the physical and biological environment is lacking. The gold mining operations in Ezana (Meli) where the waste water was discharged as slurry through the pipelines into only one tailings pond, which is covered by geotextile membrane on the bottom and plastic geo membrane on the top. The wastewater is recycled using the overflow return water pump from tailing pond to prevent seepage, but that is not sustainable due to creation of a small perforation plastic geo membrane wastewater and is leaching into the ground water. Moreover, the dam due to smaller in size frequently overflows during summer and is discharged to the nearby river. There are a lot of merits of adsorption including low cost, locally abundant, require, less maintenance, simple alkali and acid treatment etc. The presence of different heavy metals in wastewater due to toxicity and non-biodegradability tends to accumulate in down streams [1]. In Ethiopia, the application of advanced technology is technically complex, expensive, and non-feasible. Having the above mentioned problems in mind, the factory need to develop on-site facilities to treat their own effluents using low-cost technologies based on locally available, cheap, environmental friendly sorption materials like eucalyptus bark in order to minimize the contaminant concentration. Adsorption is a natural process by which molecules of a dissolved compound i.e. adhere to the surface of an adsorbent solid [2,3]. The present study focused on adsorption of copper using eucalyptus bark. The purpose of treating the adsorbent with acid was to remove lignin part of the material prior to adsorption thereby increasing their percent removal [2]. Copper was selected as potential contaminant due to its maximum concentration than other element i.e. Cu (8360 to 59280 ppm) and Pb (6.4 to 1652 ppm) of Ezana (Meli) [4]. Sulfuric acid

was used to treat eucalyptus bark for removal of lignin which packs the cellulose and it increases the carboxyl active groups which are used for increasing the adsorption efficiency [5]. The bio adsorbents have The affinity for heavy metal ions to form metal complexes or chelates through their functional groups like carboxyl, hydroxyl, phosphate, sulfate, thioether, phenol and carbonyl amide have the behavior of the bio adsorbent [4]. The effect of physical parameters such as pH, adsorbent dosage and contacting time was investigated to examine the efficiency of eucalyptus bark. The efficiency of eucalyptus bark was examined by using the effect of physical parameters such as pH, adsorbent dosage and contacting time. Batch study was conducted using heavy metal containing real wastewater sample laboratory from five selected sites of tailing storage dam. The heavy metal were analyzed by digesting with acid to prevent precipitation due to high acidity of the sample then diluted with deionized water.

1.1. Eucalyptus bark (EB) as adsorbent

Eucalyptus trees are evergreen in all season, fast growing, locally available, cheap and huge available in almost everywhere. Due to cost consideration, it is used as an adsorbent which is an important parameter for selection and design of for this adsorption process. R. Saliba et al., (2001) studied the benefits of eucalyptus barks for the adsorption of heavy metal ions and dyes. Copper adsorption by activated carbon from EB have the optimum pH 5 and reached equilibrium within 45 min for whole range of concentration (0.1-10 mM) [6]. Further, Akmal et al., (2014) the biosorption system of Cu(II) ions from aqueous solution using eucalyptus bark powder at pH values (pH>5), and dramatically decreased the biosorption yield. The deviation of pH can be explained by considering the surface charge on the biosorbent. The highest biosorption efficiency for Cu(II) ions on *Eucalyptus* bark powder was observed at pH 5.0 [7].

At higher pH values (>6) due to promote higher adsorption capacity, it decreases the electrostatic repulsion between cations and the positively charged surface. Therefore, highest adsorption often occurs at high pH level. However, at this pH range, the formation of insoluble hydrolyzed species $(\text{CuOH})^+$, $(\text{PbOH})^+$, $\text{Cu}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$, this condition is often not clear as the metal precipitation could lead to a misunderstanding for the adsorption capacity [1].

2. Materials and Methods

2.1. Chemicals

Most of the chemicals were analytical grade and the chemicals would be collected from Ezana gold mining development Plc laboratory and chemical shops in Addis Ababa and most of them were analytically grade. NaOH and H_2SO_4 were used to adjust the solution pH and pretreatment of Eucalyptus Bark by H_2SO_4 . Throughout the experimental studies distilled water main benefits to perform [1]. $\text{Al}_2(\text{SO}_3)_3$, FeCl_3 , Potassium dichromate were used for COD and KI, AgNO_3 for determination of cyanide using titrimetric in the outlet waste water; and HNO_3 , HClO_4 and HF were also used for digestion of the wastewater sample.

2.2 Equipment

The major equipment's like batch reactor was used for removal of heavy metal using adsorbent, shaker, FAAS (gases: acetylene + air) obtained from Ezana (Mekelle, Meli) model NovAA400P, Germany for estimation of metal ion concentration. The equipment like air tight container, oven drier, heating bath, micropipette, mechanical stirrers, common laboratory glassware (flasks, beaker), COD (digester, sucker), analytical instrument used for the preparation sorbent. Analytical instruments like digital balance for weight measurement and pH-meter for reading pH were also used. The titrimetric by using standard solution to titrate cyanide, turbidity meter used to determine turbidity of the sample and digester for COD.

2.3 Method

2.3.1 Preparation and Characterization of Eucalyptus Bark

The proximate analysis was characterized by the following:

$$\text{Moisture content (\%)} = 100 * \frac{W_1 + W_2 - W_3}{W_2}, \quad (2.1)$$

Where W_1 = weight of the dish, W_2 = weight of the sample, W_3 = weight of residue after drying.

$$\text{Ash content} = 100 * \frac{W_3 - W_1}{W_2}, \quad (2.2)$$

Where W_1 = weight of the dish, W_2 = weight of the sample, W_3 = weight of residue after igniting

$$\% \text{ volatile mater (VM)} = \% \text{ loss in weight} - \% \text{ moisture}, \quad (2.3)$$

$$\text{Bulk density (g/cm}^3\text{)} = 100 * \frac{\text{Weight of dry sample (g)}}{\text{Volume of packed sample (cm}^3\text{)}}, \quad (2.4)$$

$$\% \text{ Fixed Carbon} = 100 - (\% \text{ moisture} + \% \text{ Volatile Matter} + \% \text{ Ash}). \quad (2.5)$$

To determine the specific surface area of the adsorbent by Sear's method and the titrations were carried out with standard 0.1M NaOH in a thermostatic bath at 25°C from pH 4.0 to pH 9.0 [8]:

$$S \left(\frac{m^2}{g} \right) = 32V - 25. \quad (2.6)$$

Where V is the volume of 0.1M NaOH solution in ml required to achieve pH of 9 from pH 4 with 0.5g of sorbent and 10g of NaCl in 50mL of distilled water.

The X-ray diffraction analysis was determined by crystalline index (CI) and calculated by Segal's formula using intensity measurement at 22.5° and 18.5° (amorphous background) 2θ [9]:

$$CI = 100 * \frac{(I_2 - I_{am})}{I_2}, \quad (2.7)$$

Where, I_2 denotes the maximum intensity of the 2 peak at about 2θ reading and I_{am} is the lowest intensity of the amorphous corresponding to 2θ value near to the peak 1.

The preparation of Bark of Eucalyptus tree species which were collected from the local area Addis Ababa and washed dried using oven and ground into small particles size [4], in these studies the sample was crushed manually into a small pieces and dried in sun light for 3days. It was then washed by distilled water to remove some foreign materials (dusts). Finally, the bark powder would dried in oven at 105°C for 24hrs [10]. The laboratory procedure was briefly described in **Figure 1**.

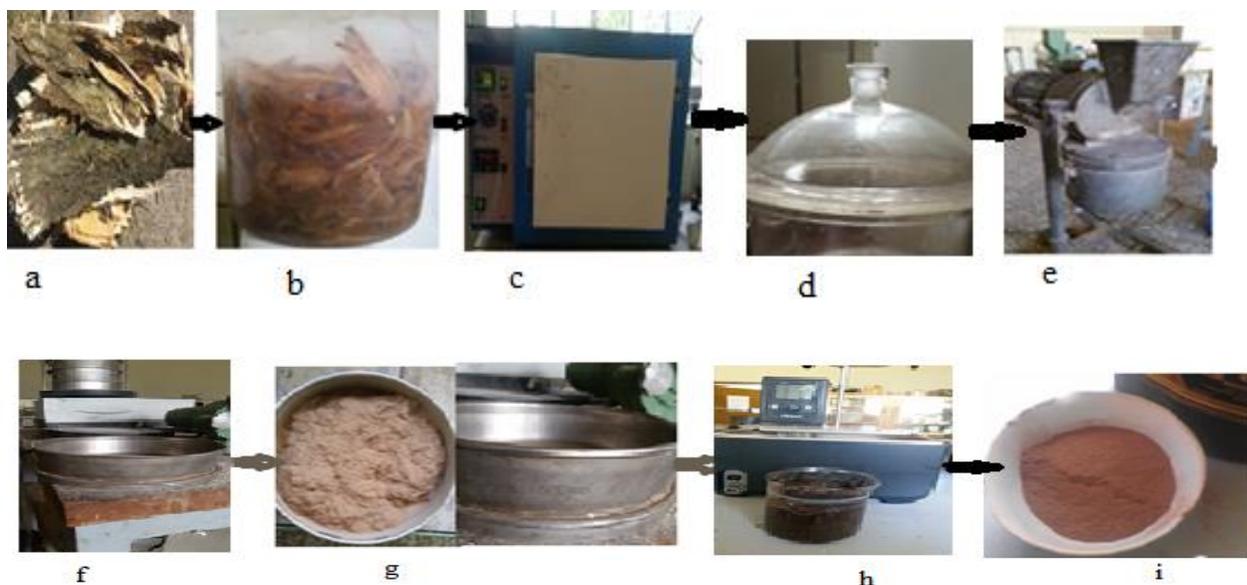


Figure 1. (a) Collected sample bark (b) bark washed by distilled water (c) dried in oven (d) dissector (e) centrifugal mill (f) Mesh 0.5-1mm (g) grinded bark and sieve 500µm (h) bark in hot water bath with H₂SO₄ (i) Powder treated bark

2.3.2 Preparation of sample wastewater

The wastewater sample was collected from Ezana gold mining factory discharged in to the dam by selecting from four sites (south, west, north, east inlet into the dam). For transporting and taking sample, plastic bottles were used and the bottles were cleaned using HNO₃ acid and distilled water. The concentration of waste water from four sites and maximum value obtained

for Cu (71ppm) at east outlet slurry in to the dam. The analysis was undergone using flame atmospheric spectroscopy (FAAS).

2.3.3 Determination of heavy metals (Cu, Fe, Mn, Pb, Cd, Cr, Ni, Co and Zn)

The blank sample was determined by transferring 100ml of distilled water in to beaker so as to allow a blank correction. First, the water sample was digested with 100cm³ then, put in to beaker and finally five ml concentrated HNO₃ was added. After that, the beaker placed on a hot plate and evaporated to about 20min then beakers were cooled, successively another five ml of concentrated HNO₃ was added. The beakers were closed by watch glass and also put to the hot plate. The heating was continued, and until the solutions appear light colored and clear add small content of HNO₃. The distilled water was used for washing of beaker wall and watch glass, and finally to remove some insoluble materials that could clog the atomizer the samples were filtered [9]. The elements that were accredited in the Ezana laboratory institution was Au, Ag, Cu, Zn, Ni, Pb and Co. However, the others non-accredited (Mn, Fe, Cr and Cd) were possible to read by changing the flame. Cu (II) and Pb (II) samples (40ml) were added into conical flasks of 250ml and 10ml HNO₃, respectively with time 6hr, temperature 90-100°C in the digester then dilution with 100ml flask and filled into test tubes then read using atomic adsorption spectroscopy (AAS).

2.3.4 Batch adsorption experiments

Adsorption efficiency in percent and milligram of copper adsorbed per gram of adsorbent was calculated:

$$\% R = 100 * \frac{C_0 - C_f}{C_0}, \quad (2.8)$$

Where % R is percent removal, C_o is initial concentration and C_f concentration after adsorption.

$$q = 100V * \frac{C_0 - C_f}{M}, \quad (2.9)$$

Where q is metal ion removal in mg/g, C_o is initial concentration, C_f is concentration after adsorption, M is adsorbent mass in gram and V is volume of wastewater used during the experiment [11].

2.3.5 pH

To determine the effect of pH on the adsorption process, to find the optimum pH and the experiments were carried out at three levels (2, 5, 8). The pH of the solution was adjusted by addition of 0.1M NaOH and H₂SO₄ as needed. These experiments conducted at different contact times while keeping the adsorbent dose constant and different adsorbent doses while keeping the contact time constant, the shaker at 175 rpm and at room temperature. The experiments were carried out three trial and the optimum results.

2.3.6 Contact time

The adsorption efficiency affected by contacting time and the optimum selected value for the process studied by conducting the experiment under 30, 90 and 150 min contact of the adsorbent. The wastewater sample for various pH by keeping the amount of adsorbent dosage constant and for various adsorbent doses while keeping constant pH. Nevertheless, agitation speed in rpm, room temperature, particle size and initial concentration constant throughout the experiments. These durations were selected because many studies in the literature show that too much contact time will not have a significant change on the adsorption [9], [6] and [12].

2.3.7 Adsorbent dose

The selected doses for the removal of Cu are 0.6, 1.8 and 3g, and the effect of adsorbent dosage on percentage removal efficiency of bark powder was studied [12] and [13]. The experiments were conducted under different pH, while keeping contact time constant and under different contact time while keeping constant pH.

2.3.8 Adsorption isotherm

This isotherm describes the equilibrium interaction between adsorbate concentration in the liquid phase and adsorbent surface at a given condition. The description how pollutants relate with the adsorbent materials, expression of the surface properties, abilities (capacity) of adsorbents, effective design of the adsorption systems. Thus, are critical for optimization of the adsorption mechanism pathways [4]. In this study, the experimental result was analyzed against two isotherm equations (Langmuir and Freundlich). The adsorption data for the removal of copper was correlated with Langmuir (C_e/q_e) vs. (C_e) and Freundlich models of $\log C_e$ vs. $\log q_e$ adsorption isotherm. Its applicability was estimated with the correlation coefficient (R^2) which was found from the graph.

3. Results and Discussion

3.1 Characterization of adsorbent

This section describes physio- chemical and surface characteristics of eucalyptus bark produced at previously predicted optimum production parameters using equation 2.1 to 2.6.

Table 1 Laboratory result of Eucalyptus bark

Parameters	Current result	References
Moisture content (%)	2.273	5.1 [14]
Ash content (%)	7.763	19.0 [14], 4.88 [15]
Bulk density- q_b (g/cm ³)	0.8676	0.25 [15], 1.55 [16]
Volatile matter (%)	64.5	65.7 [14]
Fixed carbon (%)	29.8	21 [16]
Specific surface area (m ² /g)	55.1 m ² /g	66 [17]
Point of zero charge value (pHpzc)	4	<4 pH, the surface charge

		<p>of the adsorbent material acquires positively charged due to protonation of functional groups [2] and [13].</p>
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The point of zero charge for eucalyptus bark (EB) was determined at the point of intersection of this curve yielded is presented in figure 2. The result of this study showed that pH_{pzc} of treated biomass eucalyptus bark as powder was 4. As a result of this value, the pH values should be maintained greater than 4 in order to ensuring a predominant negatively charged surface between adsorbate molecules and biomass of adsorbent resulting to an electrostatic attraction. Below four pH, the adsorbent biomass acquires positively charged surface due to protonation of functional groups which making H^+ ions compete effectively with the Cu^{2+} cation as a result, a decrease in the amount of adsorbate adsorbed is expected [2] and [13].

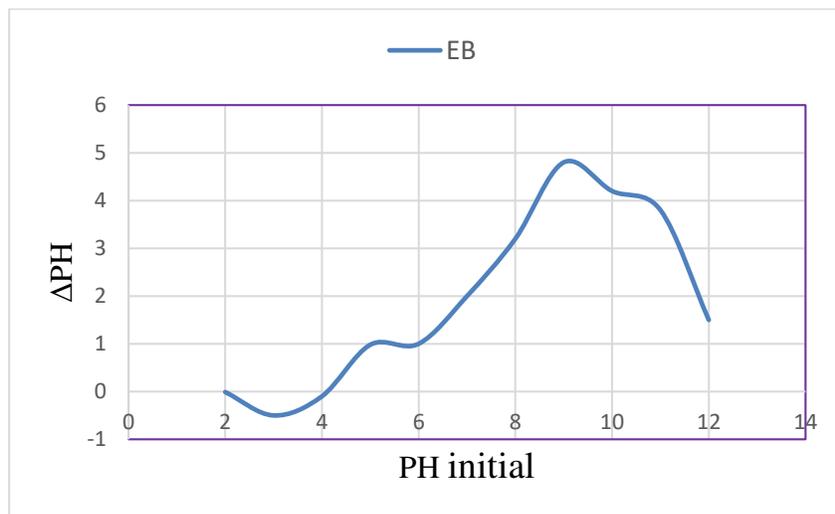


Figure 2 Point of zero charge (pH_{pzc}) of Eucalyptus bark

3.1.1 Fourier transform infrared spectroscopy (FTIR) analysis

Some important changes in some bands were observed as presented in Figure 3. According to Anon, (2018) [8] and M. Sulyman et al., (2017) [6] the region between 3800 cm^{-1} - 3000 cm^{-1} indicates the crystalline structure of cellulose. The range covers the sum of the vibration of valence bands of H₂ bond of O-H group with the bands of intra-molecular hydrogen bonds. The shift in band position supports that -OH and C=O groups interact with copper during bio sorption process. The possible bio sorption may be due to physical bio sorption, complexation with functional group, ionic exchange, and chemical reaction with bio sorbent sites. The IR spectrum of unloaded and loaded with Cu²⁺ bark powder is presented in Figure 3 and it shows the presence of different functional groups. The broad and strong absorption peak around 3425 cm^{-1} is an indicative of hydroxyl groups. The bands at 2924 cm^{-1} in IR spectra of the adsorbent may be due to the C-H stretching vibrations. The shift in the peak of OH stretching from 3424 to 3436 , the peak of C-O stretching become very weak after an adsorbent is loaded with Cu²⁺ [14]. The raw bark loaded with metal ion shows that the peaks are five as seen in Table 2 (before metal adsorption) and after binding with metals had shifted slightly from FTIR spectrum of table 2. This was due to the participation of these functional groups in the binding of metal ions. The shifting of wave number depends on the concentration of metal present in the given sample agreed with the literature [7] and [11].

Table 2 FTIR absorption frequencies (cm^{-1})

Adsorbent	Metal ion adsorption	O-H	C-H	C=O & -NH ₂	C=C	C-O-C
Eyuclapltus bark (EB)	Before treatment	3425	2927	1611	1392	1033
	After (loaded)	3425	2917	1621	1312,1412	1043

	treatment					
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The FTIR absorption frequencies (cm^{-1}) were almost similar with many papers reported [19] and [8].

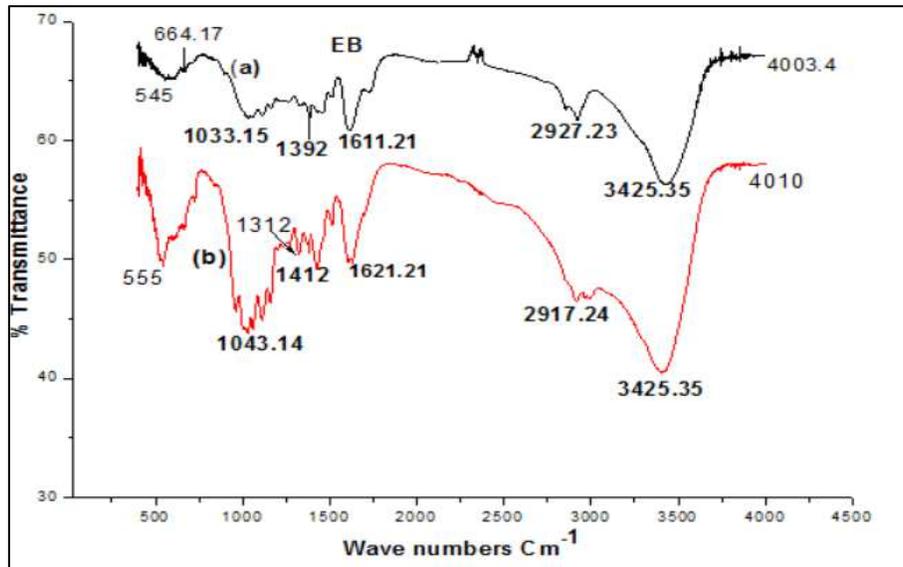


Figure 3 FTIR analysis of eucalyptus bark before and after metal ion adsorption

3.1.2 X-ray diffraction analysis

Eucalyptus bark showed two peaks (Figure 4) one in the region of 15.17° , which corresponds to the amorphous region and other at 22.44° , which corresponds to the crystalline region. The crystalline at peak 2 at the maximum intensity (I_2), peak1 is the lowest intensity of the amorphous (I_{am}) (2204, 1489), respectively, were obtained. Therefore, the result CI using the equation 2.7 was 32.44%.

This might be, according to Anon, (2018) [8] and P.patnukoa et al., (2008) [15], due to absence of great part of poly cellulose and lignin due to an increase of the cellulose amorphous fraction made possible for the hydroxyl ions directly act on cellulose fibers promoting hydrolysis of the

cellulose chains. A crystalline index increasing directly related to rigidity of the cellulose structure and leads to higher tensile strength of the powder [19].

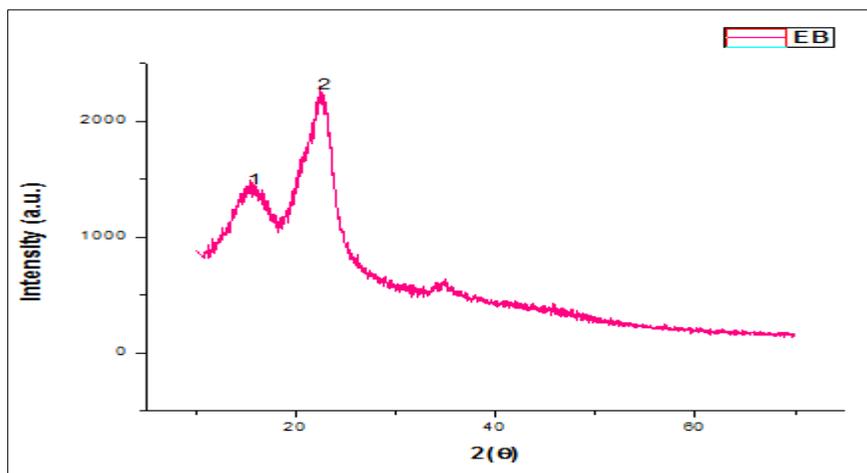


Figure 4 X-Ray diffractometer analyses for treated Eyuclaptus bark (EB)

3.2 Experimental results of wastewater from tailing dam effluent

The present studies of laboratory analysis of Ezana (Meli) wastewater samples are presented in Table 3. The results were carried out with digesting and without digesting with acid to prevent precipitations due to high acidity of the samples and then diluted with deionized water.

Table 3 The laboratory result and effluent standard to discharge in the comprehensive environmental response, compensation, and liability act (CERCLA) list of priority chemicals (2005) and for industrial waste water and water for drinking [20] and [3]

Heavy metal and others	USA Standard	Permission level	Current laboratory result	
			With digestion	Without digestion
Fe (mg/l)	0.2-0.05	2.0	313.11	6.0
Pb (mg/l)	0.015-0.0072	0.15-0.2	16.0	3.12
Cd (mg/l)	0.005-0.00025	0.06	0.02	0.01
Cr(VI) (mg/l)	0.01-0.0034	0.05-0.1	0.43	below detection limit
Zn (mg/l)	5.0-0.008	0.5	0.34	below detection limit

Mn (mg/l)	0.05-200	1.0	0.94	0.02
Cu (mg/l)	1.3-0.005	0.3	71.0	18.0
Co (mg/l)	-	-	0.1688	0.17
Cd (mg/l)	0.00025	0.05	0.021	0.013
Ni (mg/l)	5.0-0.02	0.5	0.14	0.079
Temp. (°C)	-	40	-	10-33
Cyanide@ To<11°C(mg/l)	-	0.1	below detection	0.025
Cyanide WAD (mg/l)	-	0.5	below detection	0.00
pH	≥6.5≤9.5	6-9	below detection	8-8.5
Electrical conductivity (µs/cm)	≤2500	750	below detection	2980
Turbidity (NTU)		75	below detection	7800
TDS (mg/l)		50	below detection	1214
TSS (mg/l)		1000	below detection	750
COD (mg/l)		250	below detection	120

The cyanide concentration in the process effluent measured during the night to get low temperature below 11°C in the site of out let effluent (discharging from the pipe) one-hour difference 0.025mg/l and in the afternoon were zero.

Table 4 General waste water characteristics

Parameters	Laboratory result of present study	References
High TDS (mg/l)	1213	500-2000 [21]
Low SS (mg/l)	750	10-100 [22]
Low COD (mg/l)	120	10-100 [23] [24]
Near neutral pH	8-8.5	7-9.5 [23] [24]
High conductivity (µs/cm)	2890	600-10,000 [21]

The pH of waste water in the dam gradually decreased over time and might be due to neutralization of the alkaline environment by rain water and possibly also as a result of CO₂ uptake and other compounds which may contribute to acidity.

3.3 Batch adsorption of Copper onto Eucalyptus bark

3.3.1 Effect of pH

As shown in figure 5 the effect of pH on adsorption showed the maximum removal of Cu occurred at pH 5 (90min, 1.8g) > pH 8 (90min, 3g) > pH 2 (150min, 1.8g). From pH 8 to pH 5 an increase in adsorption was observed and at low pH i.e. below pH 2 very less Cu was removed. At pH 2, the adsorption capacity was 58.9% at constant Cu (71ppm) which is not far from the result of almost 65% of Cu removal was observed at this pH at 100 mg/l Cu concentration [25]. The pH of sample wastewater decreased from 8 to 5 and the percentage removal rapidly increased (79.75% to 92%) and further decreasing pH to 2 leads the removal efficiency to rapidly decrease from 92% to 58.9%. At pH 5 with concentration of 50mg/l removal efficiency of copper by algae as adsorbent from mining waste water was 87% [25]. For adsorption this heavy metal the efficiency of the adsorbent at pH 8 was found to be 79.75%. This value agreed with the explanation to optimum pH values (3-6) and linked H⁺ was released from the active sites, and adsorbed amount of metal ions was increased [14,23].

The results in this factor variation of removal from pH 8 to 2 have varied almost simultaneously and this might be due to further increase of the pH leads to the precipitation rather than adsorption. Generally, after pH 5 there was a slight decrease in adsorption and at low pH i.e. below and above pH 5 very less copper was removed. The metal uptake capacity also increased due to the presence of negatively charged functional groups on the adsorbent surface, resulting in increased binding sites with increasing the pH [26].

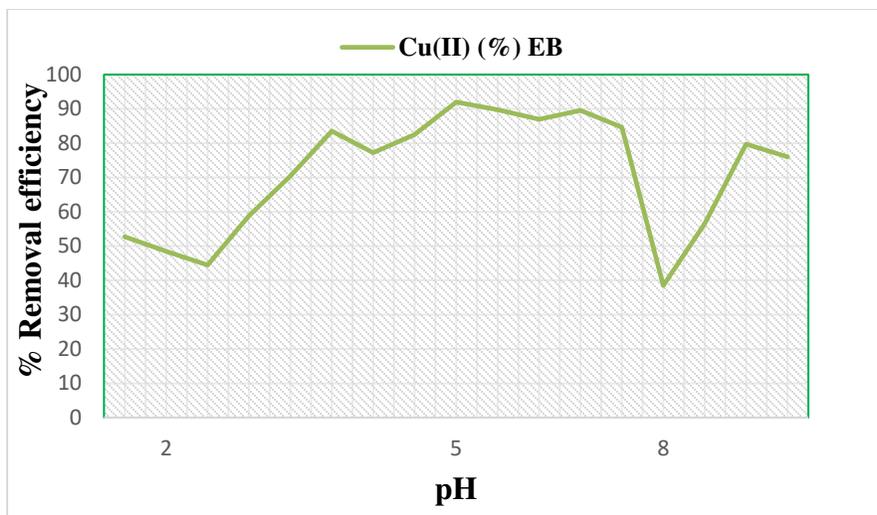


Figure 5 Effect of pH on copper ions removal efficiency on to Eucalyptus bark (EB)

3.3.2 Effect of adsorbent dosage

As seen from Figure 6, the removal capacity increased with increasing the amount of adsorbent dosage for most of the result with small variation. The removal efficiency of Cu (II) by EB based on the dose 0.6g, 150min, pH 5, 1.8g, 90min, pH 5 and 3g, 30min, pH 5 were 77.25%, 92% and 79.75%, respectively. Adsorption of metals often refuse the formation of link between metal ion and the active site due to excessive protonation at low pH <3 of the active site at the carbon surface . Usage of Eucalyptus bark (EB) as a dosage increased in percentage of removal increased may be due to the availability of more active sites in adsorbent surface [27].

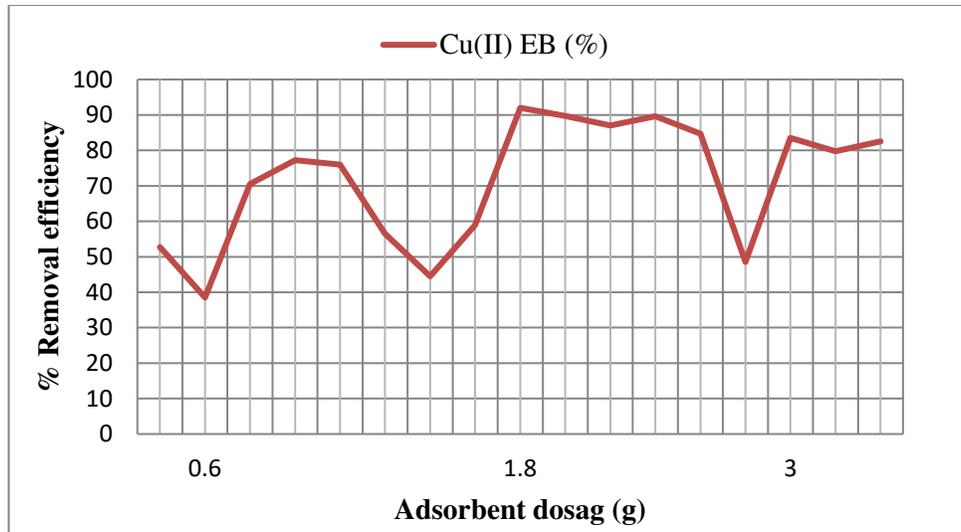


Figure 6 Effect of adsorbent dosage on copper ions removal efficiency on to Eyuclaptus bark

3.3.3 Effect of contact time

The adsorption efficiency of copper at three different contacting time (30 min, 90 min and 150 min) where at pH 5, 3g, pH 5, 1.8 g and pH 5, 3g were 83.5%, 92% and 82.5%, respectively. Hence, the present result shows that the low cost adsorbent, locally available and environmental friendly of treated Eyuclaptus bark (EB), and increase in the concentration of Cu in samples of sediments compared to sediment samples could be connected with their precipitation in accordance with the results presented by Bhattacharya (2017) [24]. The active surface sites had been exhausted/finished as a result of a lapse time was completed. Hence, it becomes difficult to be occupied by the remaining cations. This may be due to repulsive forces between the cations attached onto the solid surface and cations dispersed in the liquid phase remaining in the solution of Cu (II).

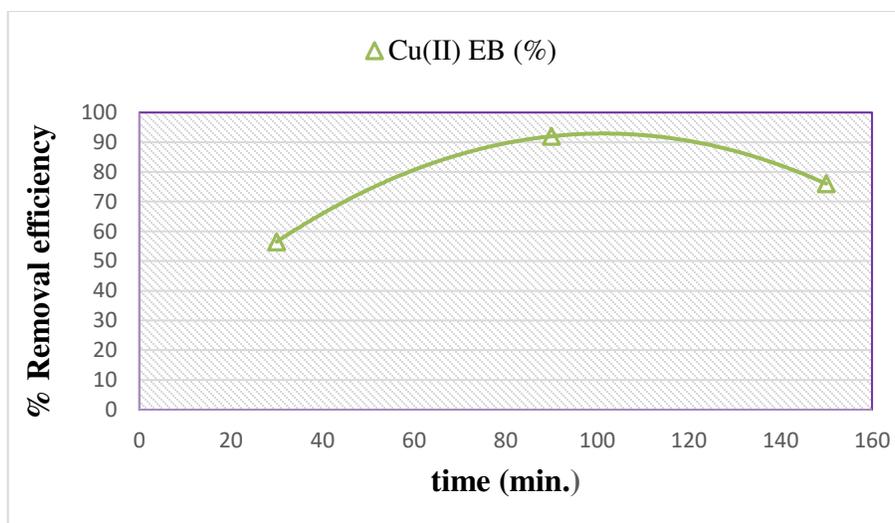


Figure 7 Effect of contacting time on copper ions removal efficiency on to Eyuclaptus bark

Moreover, adsorbate solutions with higher initial concentration take as constant due to the presence of a higher amount of adsorbate species and might take relatively longer contact time to attain equilibrium [7,14,29].

3.4 Adsorption isotherm

The isotherms i.e. Langmuir and Freundlich are the most commonly used models to describe the experimental result of adsorption. In the current study, Langmuir and Freundlich were applied to examine the adsorption process of Cu (II) at different conditions of factors. From these two the best model is Langmuir adsorption. As result, it is successfully applied in many adsorption processes of other reported.

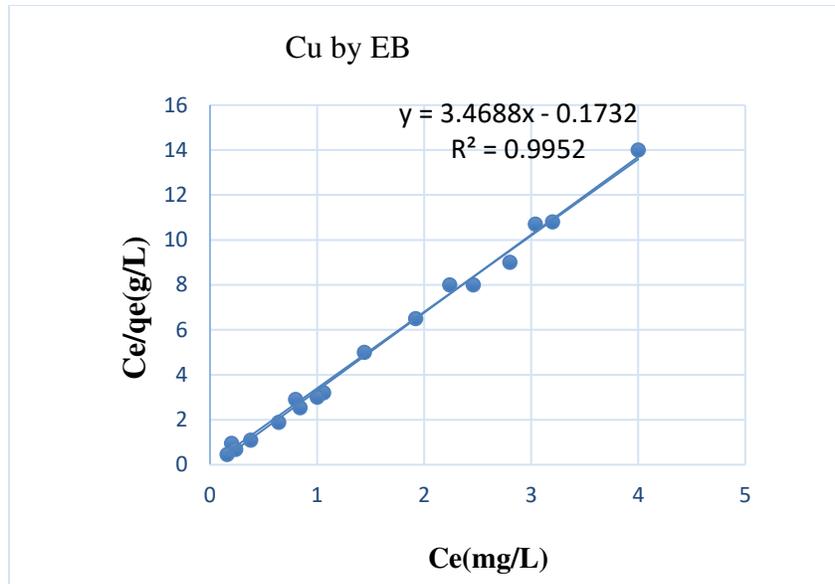


Figure 8 Equilibrium study using Langmuir model

The adsorption of solutes from a liquid to a solid surface is reflected by Langmuir adsorption isotherm model. Based on this the Langmuir model provides a satisfactory description of the adsorption equilibrium. Therefore, Langmuir model is selected to be the best model for describing the adsorption.

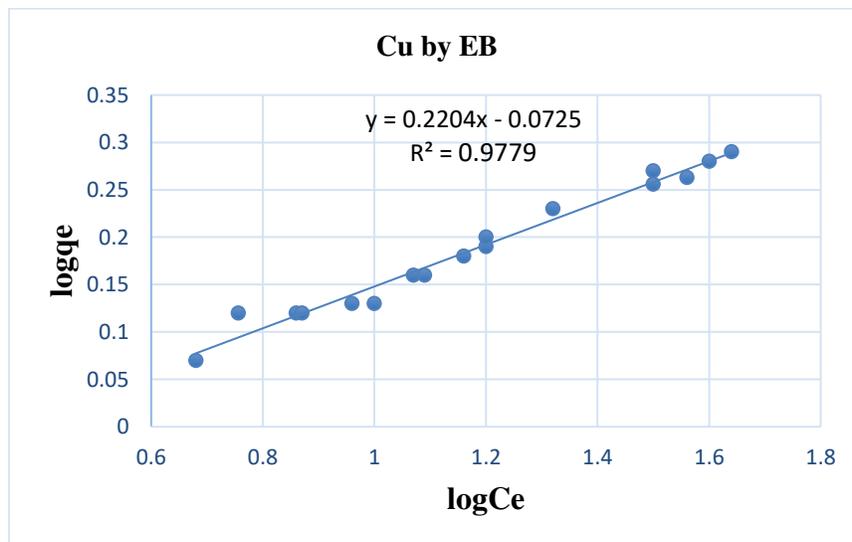


Figure 9 Equilibrium study using Freundlich model

The coefficient of determinations identified that Langmuir isotherm model better fit with the experimental data with $R^2 > 0.99$. The Isotherm models in table 5 below shown; value of respective parameters at different contacting time and correlations coefficient.

Table 5 Langmuir and Freundlich isotherm constants

Adsorbent (EB)	Langmuir constant			Freundlich constant		
	$q_{max}(mg/g)$	$b(L/mg)$	R^2	n	$K_f(mg/g)$	R^2
	0.8789	0.512	0.9952	4.539	0.848	0.9779

3.5 Desorption experiments

Even if, the desorption efficiency increased with an increase in the concentration from 0.1M of the agent (HCL, H₂SO₄ and HNO₃) after some time the bio sorbent deteriorating at higher concentration of the same and it was noticed that HCl gave maximum desorption (99%) as compared to H₂SO₄ (83%), HNO₃ (74%) and H₂O₂ [4].

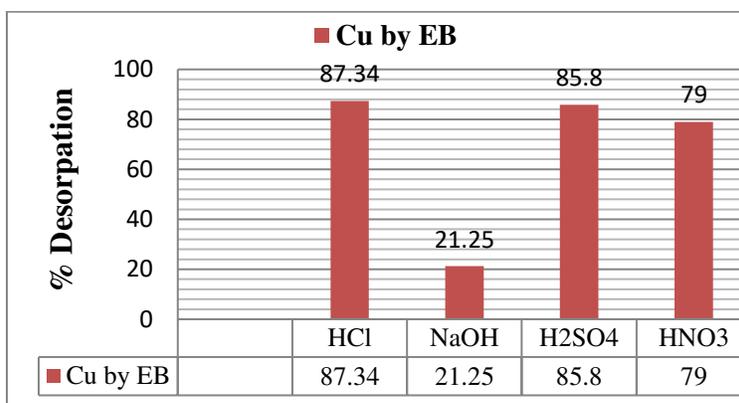


Figure 10 Desorption efficiency using various solvents

This desorption experiments were carried out by batch mode and efficiencies have been compared with each other of the solvent. It was performed to explore the potential reusability of the Eyuclaptus bark for other adsorption process and recovery of metal ions (copper).

4. Conclusion

Eucalyptus bark is environmental friendly, locally available almost everywhere and low cost offers a lot of advantage. This as bark powder showed high percentage adsorption efficiency for divalent cation copper from mining waste water. Eucalyptus bark was characterized using selected proximate analysis such as low % moisture content, low % volatile matter and relatively low ash content, indicating that bulk density (g/cm^3) relatively small, high content fixed carbon that biomaterials should be excellent raw material for adsorbents. Wastewater compositions analyzed were pH 8-8.5, EC ($\mu\text{s}/\text{cm}$) 2980, turbidity in (NTU) 7800, temperature ($10\text{-}33^\circ\text{C}$), TDS (1213ppm), TSS (750ppm), COD (120 ppm) and WAD CN^- with $\text{Temp} < 11^\circ\text{C}$ (0.025ppm). There are high positive loading values/greater than permissible limit for electrical conductivity (EC), total dissolved solid (TDS), TSS and turbidity which is an indication of mixed sources of pollution. The heavy metals determined from effluent in ppm were Fe^{2+} (313.11), Cu (71), Pb (16), Mn^{2+} (0.94), Cr^{3+} (0.43), Zn (0.34), Co (0.17), Ni (0.1) and Cd (0.02); except Cd and Zn all these elements were beyond permissible level.

To evaluate the effects of parameters like pH, contacting time and adsorbent dose the batch adsorption studies were carried out. The result found from the experiment was the percentage of adsorption increased directly with an increase in pH (2 - 5), contact time (60 min – 90 min) and adsorbent dose (0.6 – 1.8)g. In this work, the maximum adsorption of Cu (II) (i.e. 92%) was obtained at pH 5, 90 min and 1.8g of adsorbent dose. There was also decreasing trend with an increase of three variables in the solution even if by taking one variable as fixed value beyond

optimum value $pH > 5$, contacting time > 90 min and similar result in the dosage value. Langmuir model was best fitted to the sorption data with a highest correlation factor R^2 describing the adsorption of Cu (II) as 0.99. The adsorbent was more efficient due to low cost, locally abundant and in all case without using other treatment beyond acid treatment.

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Competing of Interest

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials:

Data supporting our findings is contained within the manuscript; any additional data will be shared upon request to the corresponding author.

Authors' contributions

Mebrahtom Hagos is first author and organized the data; Kibrom Alebel Gebru is co-corresponding authors of this work. Abubeker Yimam reviewed, edited and commented the data presented in this work. All authors read and approved the final manuscript.

REFERENCES

- [1] P. Patnukao, A. Kongsuwan, P. Pavasant, Batch studies of adsorption of copper and lead on activated carbon from *Eucalyptus camaldulensis* Dehn. bark, *J. Environ. Sci.* 20 (2008) 1028–1034. [https://doi.org/10.1016/S1001-0742\(08\)62145-2](https://doi.org/10.1016/S1001-0742(08)62145-2).
- [2] K.A. Gebru, C. Das, Removal of Pb (II) and Cu (II) ions from wastewater using composite electrospun cellulose acetate/titanium oxide (TiO₂) adsorbent, *J. Water Process Eng.* 16 (2017) 1–13. <https://doi.org/10.1016/j.jwpe.2016.11.008>.
- [3] S. As, D. Intervention, I. Committee, C. Land, CHAPTER 4 Geochemical Assessment, (n.d.) 60–74.
- [4] A. Dixit, S. Dixit, G. Cs, Bior emediation & Biodegradation Eco-friendly Alternatives for the Removal of Heavy Metal Using Dry Biomass of Weeds and Study the Mechanism Involved, 6 (2015). <https://doi.org/10.4172/2155-6199.1000290>.
- [5] R. Saliba, H. Gauthier, R. Gauthier, The Use of Eucalyptus Barks for the Adsorption of Heavy Metal Ions and, 2 (2001) 119–129. <https://doi.org/10.1260/026361702320360540>.
- [6] M. Sulyman, J. Namiesnik, A. Gierak, Low-cost Adsorbents Derived from Agricultural By-products / Wastes for Enhancing Contaminant Uptakes from Wastewater : A Review, 26 (2017) 479–510. <https://doi.org/10.15244/pjoes/66769>.
- [7] S.K. Akmal, J. Malathi, Y. Vijaya, M.V. Subbaiah, Available online at Indian Journal of Advances in Chemical Science Equilibrium and Kinetic Studies for The Biosorption System of Cu (II) Ions From Aqueous Solution Using Eucalyptus Bark Powder, (2014) 151–157.
- [8] Anon, MSc Thesis Nienke.pdf, 2018.
- [9] M.J. Islam, REMOVAL OF TOXIC METAL IONS FROM BIO-ADSORBENT, (2011)

1–167.

- [10] D. Banks, P.L. Younger, R.A. Egil, R.I. Sheila, Mine-water chemistry : the good , the bad and the ugly, 32 (1997).
- [11] T. Chen, G. Huang, C. Chen, Y. Huang, Reducing industrial wastewater and recovery of gold by direct contact membrane distillation with electrolytic system, 23 (2013) 209–214.
- [12] H.A. El-araby, A. Moneim, M. Ahmed, A.H. Mangood, A.A. Abdel-rahman, Sesame Husk as Adsorbent for Copper (II) Ions Removal from Aqueous Solution, (2017) 109–152. <https://doi.org/10.4236/gep.2017.57011>.
- [13] 2008 Oliveira, Franca et al., Heavy metal removal from wastewater using various adsorbents : a review Renu , Madhu Agarwal and K . Singh, (2017) 387–419. <https://doi.org/10.2166/wrd.2016.104>.
- [14] V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, 97 (2006) 15–20. <https://doi.org/10.1016/j.biortech.2005.02.010>.
- [15] P. Patnukao, P. Pavasant, Activated carbon from Eucalyptus camaldulensis Dehn bark using phosphoric acid activation, Bioresour. Technol. 99 (2008) 8540–8543. <https://doi.org/10.1016/j.biortech.2006.10.049>.
- [16] Anon, Chromium Removal from Chromium Rich Tannery Wastewater using Eucalyptus camaldulensis Dehnh . Bark Powder as an Adsorbent , the Case of Modjo Tannery , Ethiopia ., 2015.
- [17] R. Asadi-Kesheh, S.A. Mohtashami, T. Kaghazchi, N. Asasian, M. Soleimani, Bagasse-Based Adsorbents for Gold Recovery from Aqueous Solutions, Sep. Sci. Technol. 50 (2015) 223–232. <https://doi.org/10.1080/01496395.2014.949771>.
- [18] L.W. Lun, A.A.N. Gunny, F.H. Kasim, D. Arbain, Fourier transform infrared

- spectroscopy (FTIR) analysis of paddy straw pulp treated using deep eutectic solvent, 020049 (2017) 020049. <https://doi.org/10.1063/1.4981871>.
- [19] Z. Ezzeddine, E. Al Sayed, H. Rammal, A. Hijazi, H. Hamad, H. Akhdar, Bioadsorption of Pb ²⁺ and Cu ²⁺ on Eucalyptus Camaldulensis Leaves, *Int. J. Environ. Agric. Biotechnol.* 238 (2017) 2456–1878. <https://doi.org/10.22161/ijeab/2.5.38>.
- [20] U.S. Epa, Consolidated List of Chemicals Subject to the Emergency Planning and Community Right- To-Know Act (EPCRA), Comprehensive Environmental Response , Compensation and Liability Act (CERCLA) and Section 112 (r) of the Clean Air Act, 112 (2020).
- [21] H.B. Dharmappa, M. Sivakumar, R.N. Singh, Wastewater Minimization and Reuse in Mining Industry in Illawarra Region, (1995) 11–22.
- [22] U.N.E.P.D. of T.I. and E. UNEP, Mining and sustainable development II: Challenges and perspectives. United Nations Environment Programme Division of Technology Industry and Economics., *Ind. Environ.* 23 (2000) 1–96.
- [23] G. Sivakumar, V. Hariharan, M. Shanmugam, K. Mohanraj, Fabrication and Properties of Bagasse Ash Blended Ceramic Tiles, 6 (2014) 4991–4994.
- [24] R.S. Singh, S. Bera, IMPACT OF MINING ON HERBACEOUS GROUND COVER AND WILD FAUNA IN BIRSHA- DAMOH FOREST RANGE OF MALANJKHAND COPPER MINES OF INDIA, 5 (2017) 1–7.
- [25] J.P.E. Cont, *Journal of Pollution Effects & Control* Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials : A Review, 5 (2017) 1–13. <https://doi.org/10.4172/2375-4397.1000180>.
- [26] M.B. Lavanaya, B. Nagaraju, M. Pradeep, Removal of Lead from Waste Water using

Lantana Camara as Adsorbent, (2019) 1531–1533.
<https://doi.org/10.35940/ijeat.F8150.088619>.

- [27] A.I. Esmael, M.E. Matta, H.A. Halim, F.M.A. Azziz, Adsorption of Heavy Metals from Industrial Wastewater using Palm Date Pits as Low Cost Adsorbent, (2014) 71–76.
- [28] S.S.A. Bhattacharya, Drinking water contamination and treatment techniques, *Appl. Water Sci.* 7 (2017) 1043–1067. <https://doi.org/10.1007/s13201-016-0455-7>.
- [29] G.V. V, R.K. Singh, V. Sahu, A comparative study on the removal of heavy metals by adsorption using fly ash and sludge : A review, 2 (2013) 45–56.

Figures



Figure 1

(a) Collected sample bark (b) bark washed by distilled water (c) dried in oven (d) dissector (e) centrifugal mill (f) Mesh 0.5-1mm (g) grinded bark and sieve 500 μ m (h) bark in hot water bath with H₂SO₄ (i) Powder treated bark

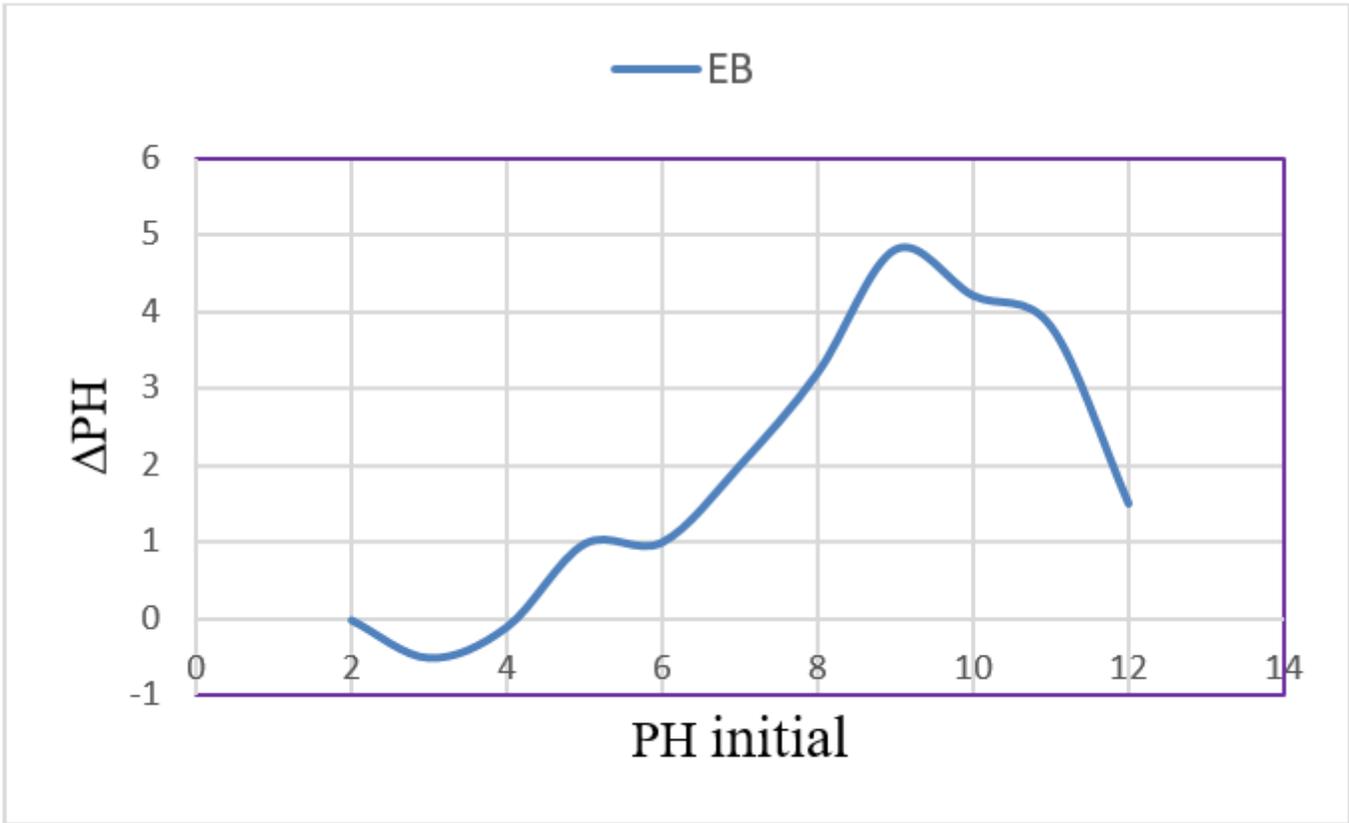


Figure 2

Point of zero charge (PH_{pzc}) of Eucalyptus bark

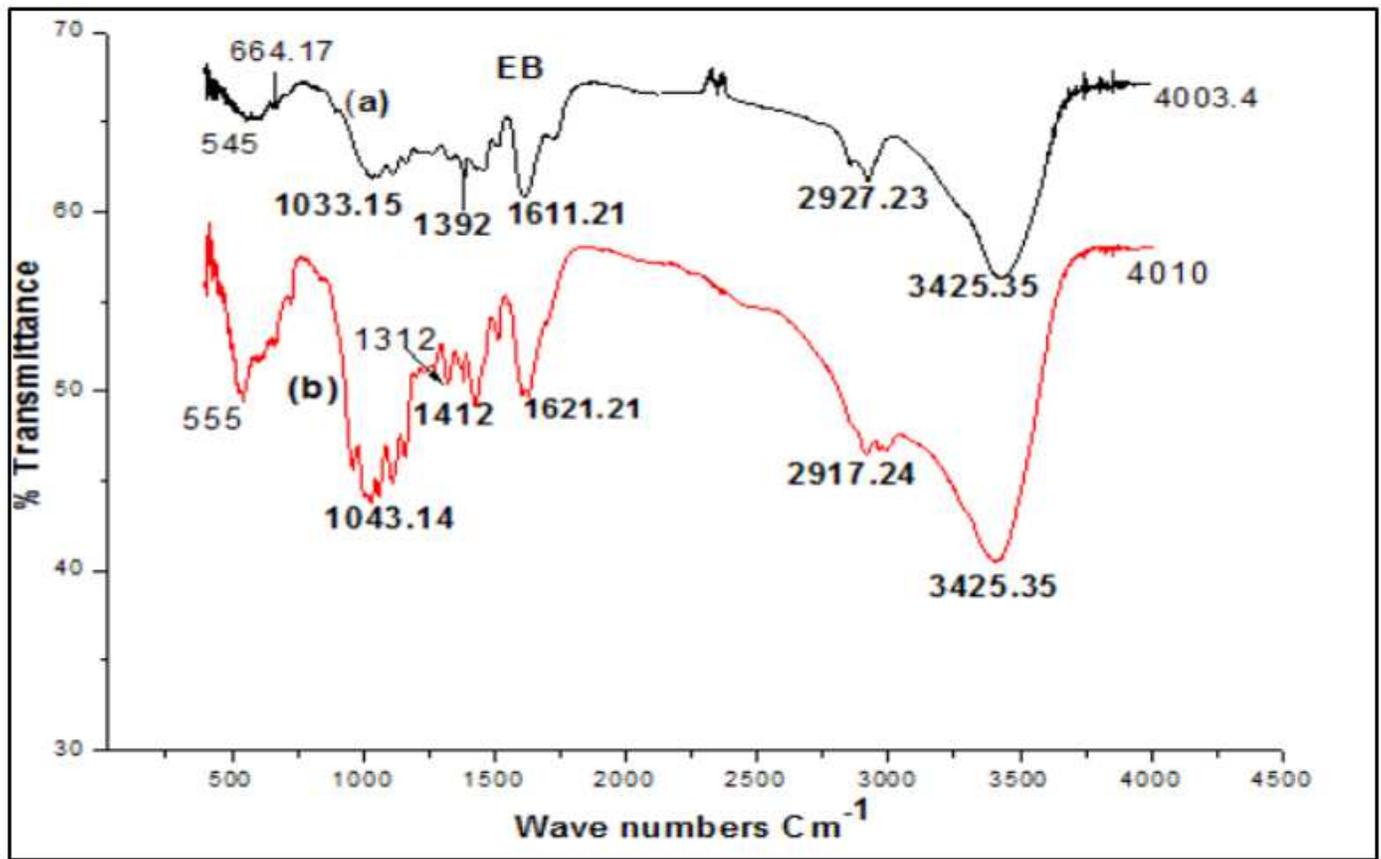


Figure 3

FTIR analysis of eucalyptus bark before and after metal ion adsorption

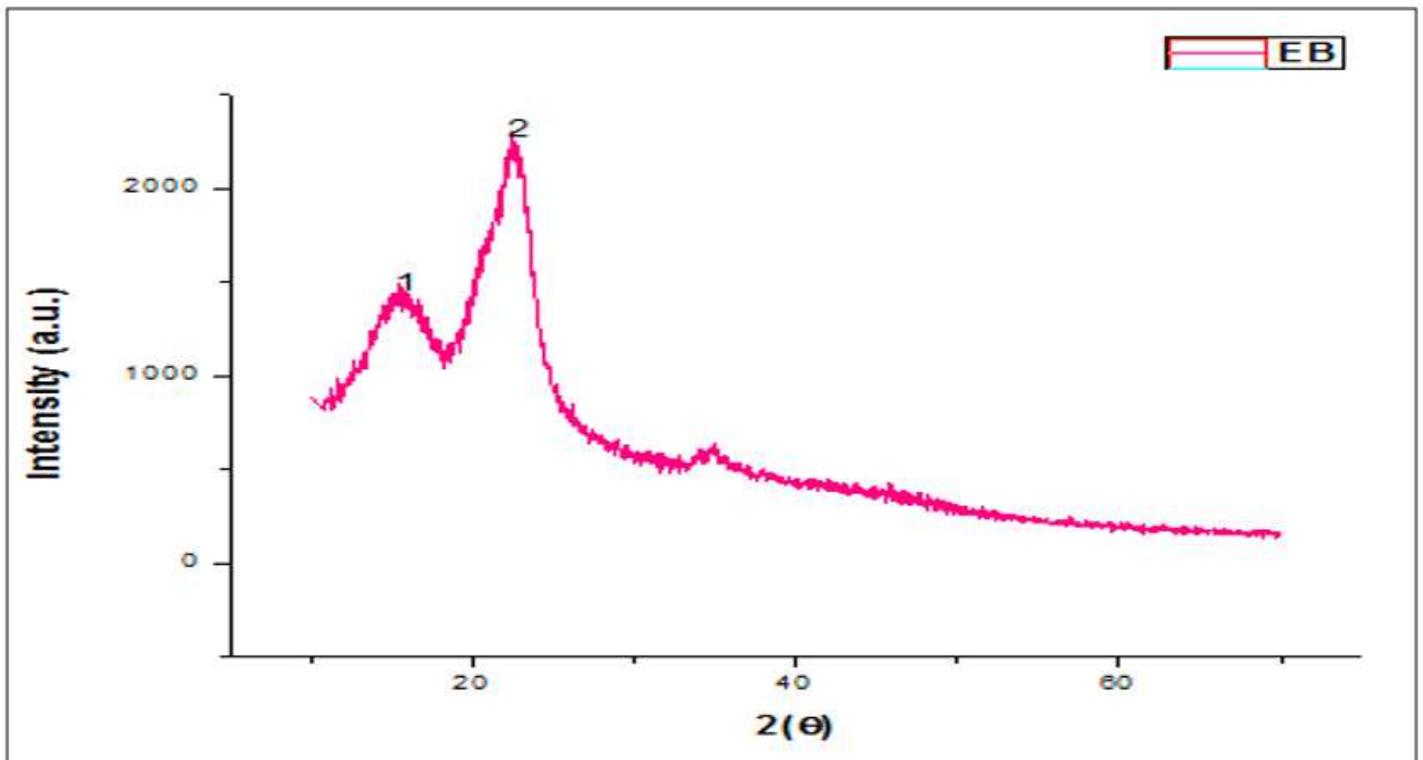


Figure 4

X-Ray diffractometer analyses for treated Eyuclapltus bark (EB)

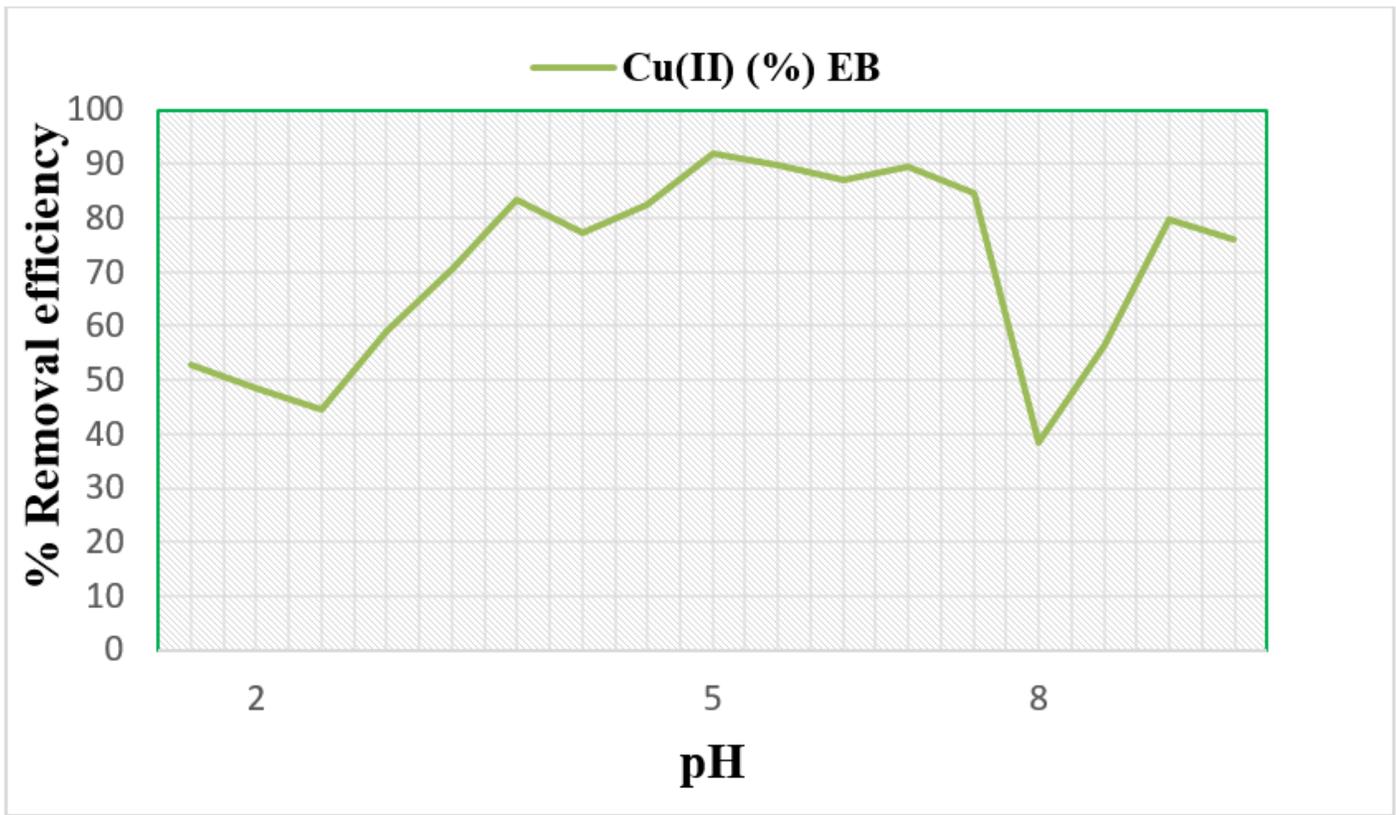


Figure 5

Effect of pH on copper ions removal efficiency on to Eyuclapltus bark (EB)

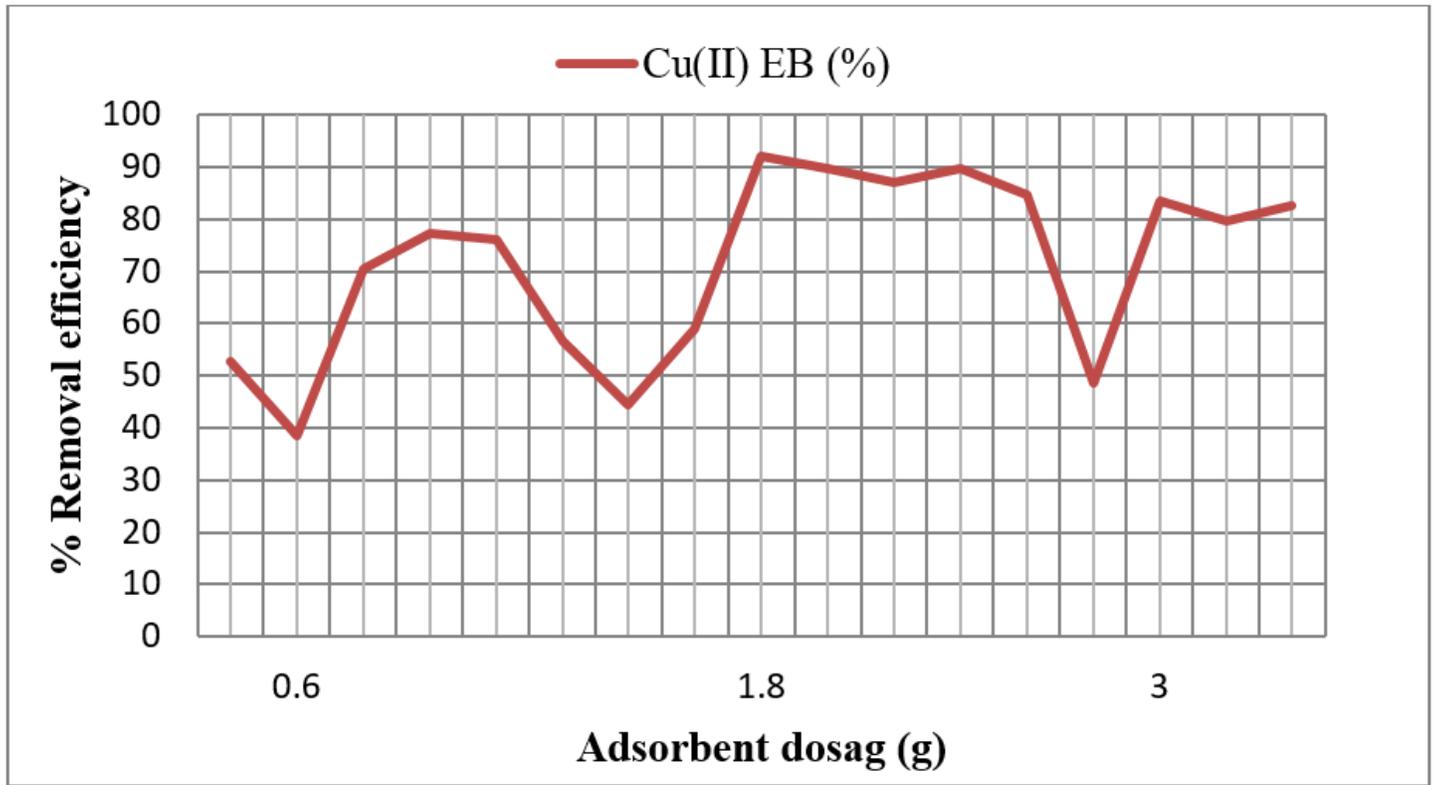


Figure 6

Effect of adsorbent dosage on copper ions removal efficiency on to Eucalyptus bark

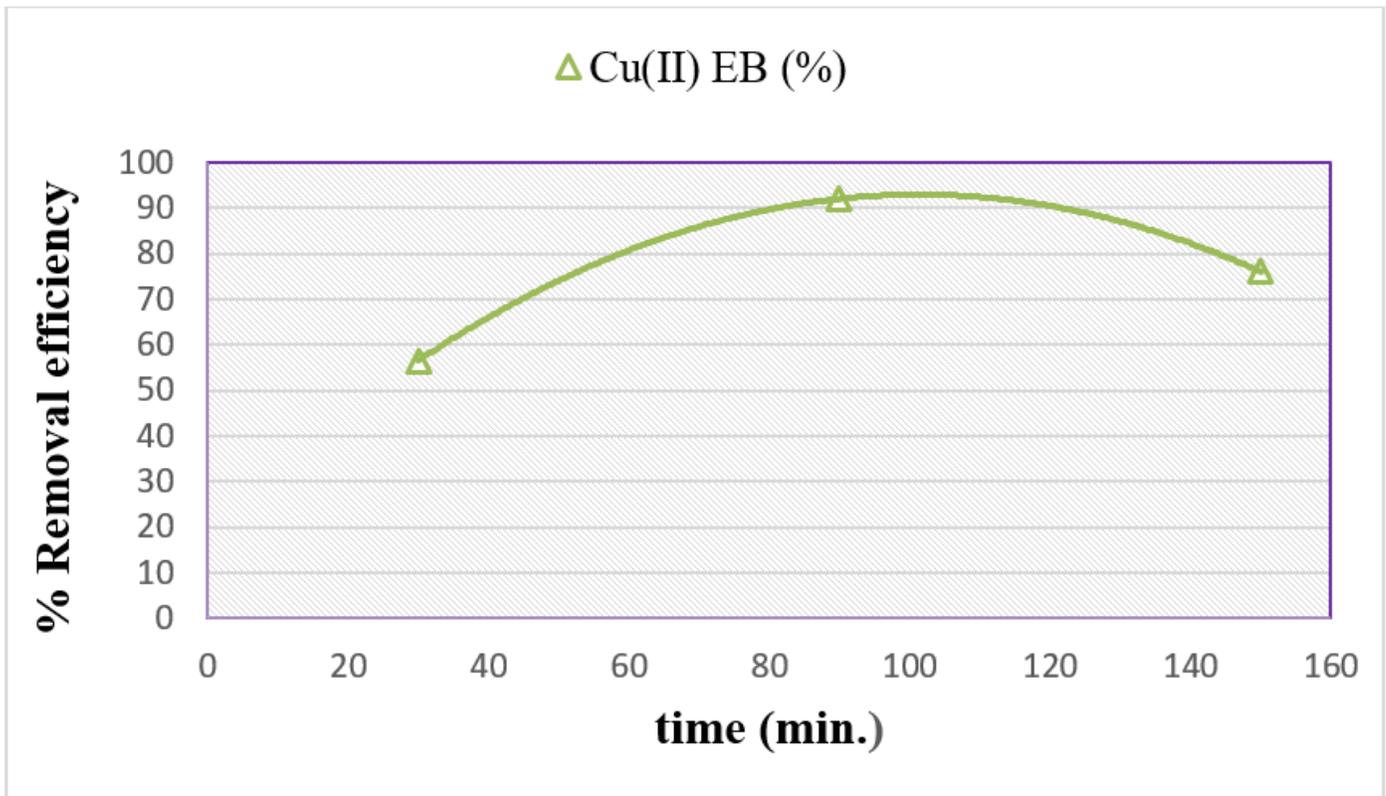


Figure 7

Effect of contacting time on copper ions removal efficiency on to Eyuclapltus bark Moreover, adsorbate solutions with higher initial concentration take as constant due to the presence of a higher amount of adsorbate species and might take relatively longer contact time to attain equilibrium [7,14,29].

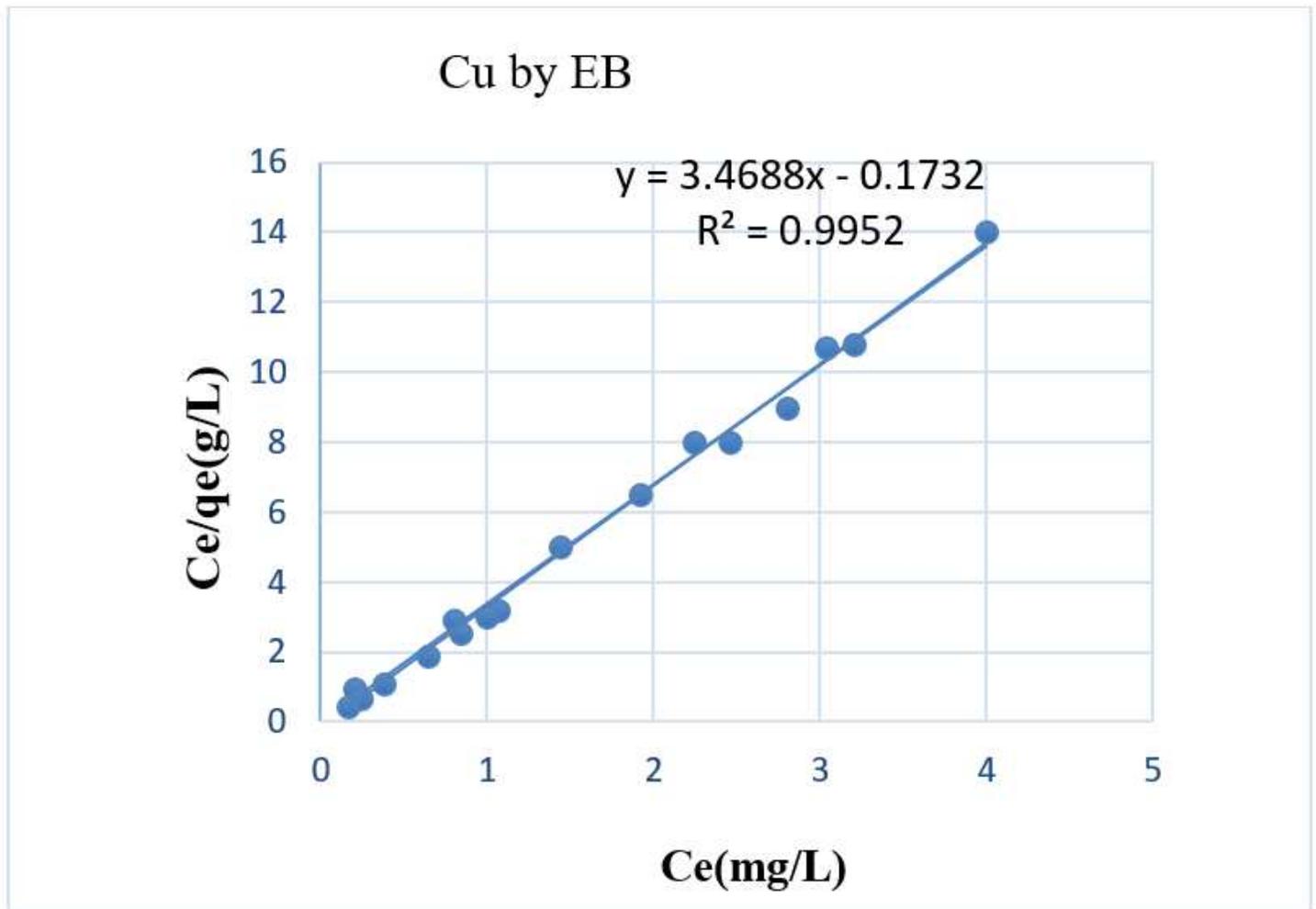


Figure 8

Equilibrium study using Langmuir model

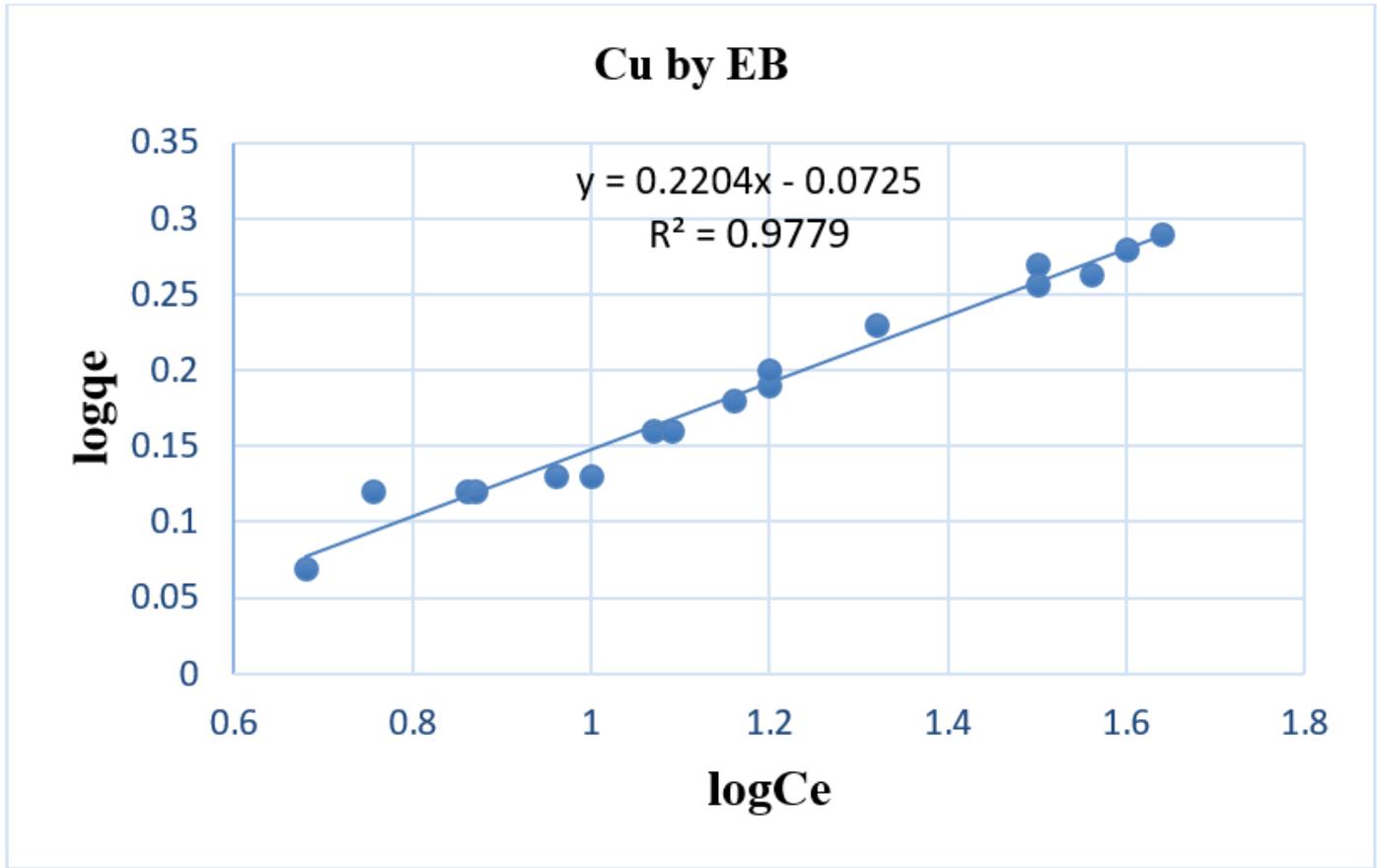


Figure 9

Equilibrium study using Freundlich model

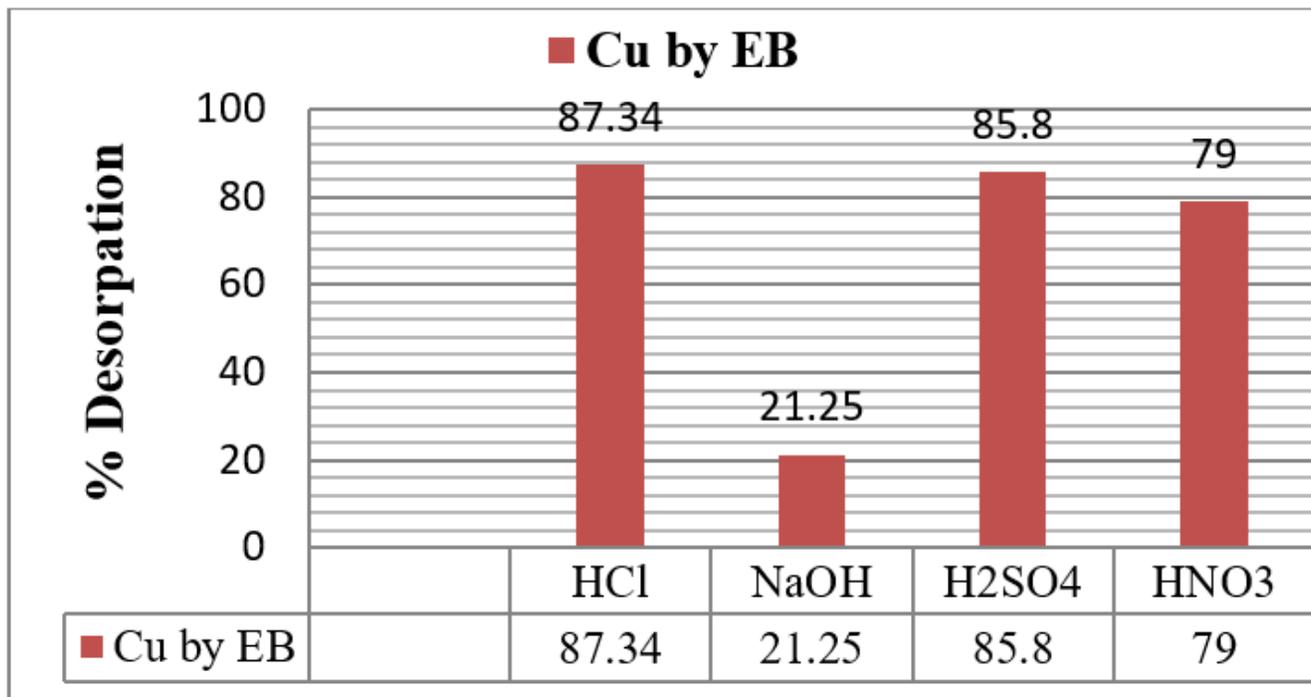


Figure 10

Desorption efficiency using various solvents