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Removal of Zn (II) and Cu (II) Ions from Aqueous Solution by Dried Prosopis *JULIFLORA*

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Abstract: The use of cheap and ecofriendly adsorbents was been studied to find an alternative substitution of activated carbon for the removal heavy metals from wastewater. Prosopis juliflora is an invasive weed which posing a great environmental threat to other flora all over the world. In this study, the influence of physico-chemical key parameters such as the solution pH, the contact time, adsorbent dose, etc. The obtained experimental results have been fitted according to the two known adsorption models of Langmuir and Freundlich. The adsorption best fits the Langumir adsorption isotherm, which shows homogenous nature of adsorption. Prosopis juliflora can be a novel adsorbent according to results obtained in this study on the adsorbent dried prosofis juliflora. It is recommendable to use this weed as an adsorbent as it is obvious of solving two problems with one cure in the environment.

Keywords: Adsorption, Prosofis, Cu, Zn, Heavy Metals

1. Introduction

Heavy metals are any element in the *d*-block of the periodic table or transition metals that have specific gravities at least five times the specific gravity of water. Examples include iron (Fe), cobalt (Co), chromium (Cr), copper (Cu), zinc (Zn), silver (Ag) and cadmium (Cd) [1]. Many are known to be toxic to both humans and other living forms at lower concentration. It is well perceived that there is a permissible limit of each metal, above which It is generally toxic [2]and some are even hazardous, their accumulation over time causing headache dizziness, respiratory difficulty, hemolytic anemia, massive gastrointestinal bleeding, liver and kidney failure and death [3].

Most of these metals were present in our environment only in minute amounts until recent centuries, when the orientation toward industrialization and production brought about our many technological advances. At present, these toxic metals have polluted our atmosphere, waters, soil, and food chain [4]. Heavy metal pollution derives from a number of industries such as electroplating, pharmaceutical, metal purification, preparation of nuclear fuels, electroplating, mining, tanneries, painting, car radiator manufacturing as well as agricultural sources where fertilizers and fungicidal spray intensively used [5].

Unlike organic contaminants, heavy metals do not normally undergo biological decay and are thus considered a challenge for remediation. Many governments have enacted laws to hinder discharging heavy metals into water bodies and using toxic substances such as lead [6]. However, heavy metals still find their way to water supplies. Accordingly, many studies have been done for removal of heavy metals including chemical precipitation, ion exchange, reverse osmosis and ultra filtration are among the commonly used in industries. However, these technologies are becoming uneconomical and unfavorable (some of them produce large toxic sludge like precipitation) to remove heavy metals from industrial wastewaters [7]. As a result the effluent treatment in developing countries is expensive. The indigenous production of treatment techniques that use locally available

non-conventional materials to treat pollutants seems to be the solution to the increasing problem of treatment of effluents so that searching for a low cost and easily available adsorbent has led to the selection of materials from agricultural and biological origin as adsorbents. That is biosorption.

Biosorption can be defined as removal of metallic ion by means of passive adsorption and complexation by living biomass or organic waste [8]. Biosorption is a process in which solids of natural origin are employed for binding of heavy metals. It is the physico - chemical binding of metal species in biomass [9]. More specially, the metal binding in biosorption may be due to a combination of several sequestering mechanisms such as complexing, co-ordination, chelation, adsorption, ion exchange [10].

The main advantage of using biosorption technology is the cost effectiveness of using the biosorbent, since it may be derived from various cheap raw materials [8]. Besides this, biosorption offers advantages of low operating cost, minimizes the volume of chemical, no toxic sludge produced at the end of the process (because it can be recycled), no additonal nutrient requirement, regeneration of the biosorbent, possibility of metal recovery and is highly efficient in matal ion removal from dilute solution [11]. These advantages served as potential incentives for promoting biosorption as a viable clean-up technology for heavy metals pollution.

Various waste biomaterials such as grape stalk waste [12], green coconut shell powder [13], chaff [14], crab shell particles [15] and rice husk, walnut hull, mango seed husks, sawdust, sugarcane bagasse, sugar beet pulp, coffee husk [16] have been studied for the removal of heavy metal ions from the effluents. In addition to biomaterials, microorganisms have also been used as metal sorbents. *Eichhornia crassipes* has been reported to remove heavy metals from aqueous solutions [17].

Prosopis species is one of the highly invasive plants in the world. Among the 45 recognized *Prosopis* species [18], *Prosopis glandulosa, P. velutina, P. juliflora and P. pallida* are reported to be generally problematic [19]. *Prosopis* has invaded millions of hectares of land in the arid and semi-arid continents of Asia, Africa, Australia and Americas. In Africa alone, *Prosopis* is believed to have invaded over 4 million hectares, threatening crop and rangeland production, desiccating water resources and displacing native flora and fauna [20].

However, no previous study have been reported on the application of Prosopis juliflora for wastewater treatment purposes for Zn (II) and Cu (II) ions removal So that the aim of this research is to investigate the use of powdered Prosopis juliflo rain the removal of Zn (II) and Cu (II) ions from aqueous solutions. Using these alien weed as biosorbent can be an alternative way to monitor the spreading in the environment to some extent.

General Objective

1) The general objective of this study was to investigate the adsorption efficiency of untreated dried Prosopis juliflora for the removal of Zn (II) and Cu (II) ions from aqueous solution.

Specific Objectives

1) To investigate the removal efficiency of dried Prosopis juliflora for Zn (II) and Cu (II) ions from aqueous solution.
2) Determination of the effects of contact time, adsorbent dosage, pH and initial metal ion concentrations on Zn (II) and Cu (II) ions removal efficiency of untreated dried Prosopis juliflora.
3) To plot the Langmuir and Freundlich isotherms and explain the nature of adsorption.

2. Materials and Methods

2.1. Apparatus and Materials

2.1.1. Apparatus

The Apparatus used in this study were: FAAS(MP 220) to measure metal ion concentration, Rotary shaker (Orbital shaker SO1, UK) to agitate the sample, pH meter(MP 220) to measure pH of the solution, Electronic balance (OHAUS, Swizerland) for weighting, Erlenmeyer flasks, Magnetic stirrer for stirring solution, Desiccator (Nikko Japan super dry SD-504) to keep a sample less humid, Electrical mill (IKA WERKE) to grind sample, Whatman No-1 (125mm) filter paper, Sieve to get 1mm particle size, Hot Air Oven (Contherm 260M) to dry sample and fridge.

2.1.2. Chemicals and Reagents

Analytical grade reagents; $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ (Blulux Laboratories Pvt. Ltd-op) were used to prepare standard solutions of the metals studied. Concentrated HNO_3, NaOH, HCl (Blulux Laboratories (p) Ltd- 121001) and buffer solutions (E. Merck) solution were also used.

2.2. Experimental Methods and Procedures

2.2.1. Cleaning Sampling Equipment

All plastic bags, polyethylene bottles, plastic bottles, plastic scoops and glasswares were thoroughly washed with detergent, rinsed with water and then with distilled water before soaking in to HNO_3 for about 24 hours. Containers were finally rinsed with deionized water before being used for sampling.

2.2.2. Experimental Site

This study was be carried out by collecting Prosopis juliflora Arba Minch city, Ethiopia which is located 500 KM away from Addis Ababa the capital city of Ethiopia.

2.2.3. Preparation of Biosorbent (Dried Prosopis Juliflora)

The Prosopis juliflora was collected from experimental site using plastic bugs and was powdered and sieved to get uniform size (50-100) mesh particle size. Then it washed with distilled water to remove dirt and was boiled to remove color, and dried at 105°C for 5 h in a convection oven and stored in sealed plastic bags prior to study.

2.2.4. Preparation of Adsorbate Solutions (Synthetic Solution)

Stock standard solutions, having concentrations of 1000 mg/L, of Cu (II) and Zn (II) ions were prepared by dissolving 3.93g of copper sulfate ($CuSO_4.5H_2O$) and 4.4g of Zinc sulfate ($ZnSO_4.7H_2O$) respectively in 1L volumetric flask and diluted to the mark with double de-ionized water to avoid errors in the results. Finally, small drops of concentrated nitric acid solution was added to each stock solution to avoid precipitate formation and these solutions were used to prepare working solutions of various concentrations by appropriate dilution. Standard solutions of both metal ions were prepared by diluting secondary stock solution of 50 mg/L.

2.3. Batch Mode Adsorption Studies

Batch mode adsorption studies for individual metal ions were carried out using 250 mL Erlenmeyer flask. The effects of different parameters such as adsorbent dose, pH, contact time and adsorbate concentration were studied. The Erlenmeyer flasks were pretreated with the respective adsorbate for 24 hours to avoid adsorption of the adsorbate on the container walls. Standard solutions of the metal ions were mixed with the Prosopis juliflora powder and agitated at 120 rpm on a mechanical shaker. This was carried out by varying the metal ion concentrations, contact time, pH and the mass of Prosopis juliflora powder used for adsorption. Finally, the resulting suspension of each of the metal ions was filtered using a Whatman No.1 filter paper and the filtrate was analyzed for the corresponding metal ion concentration. Removal efficiency was finally calculated by using the relationship in equation 1.

$$Adsorption \ (\%) = ((Co - C_e)/Co) \times 100 \qquad (1)$$

Where Co = the initial concentration (mg/L) and C_e= final concentration (mg/L) of the metal ions being studied. Adsorption capacity of the Prosopis juliflora powder is the concentration of the metal ion on the adsorbent mass and was calculated based on the mass balance principle [21].

$$q_e=(Co-C_e)\times V/M \qquad (2)$$

Where q_e = adsorption capacity of Prosopis juliflora(mg/g)
V = the volume of reaction mixture (L)
M = the mass of adsorbent used (g)
Co = the initial concentration (mg/L) of the metal ions and
C_e = final concentration (mg/L) of the metal ions

2.3.1. Effect of Contact Time

Contact time is one of the most important parameters for the assessment of practical application of sorption process (Shan *et al* 2007). For the determination of the rate of Cu (II) and Zn (II) ions biosorption by the Prosopis juliflorapowder from 100 mL of standard solutions, the quantity of metal ions adsorbed was determined by varying the contact time: (30, 60, 90, 120 and 150 min). Other parameters were kept constant.

2.3.2. Effect of Adsorbent Dosage

The effect of adsorbent dosage was studied by using 0.5, 1, 2, 3, 4 and 5g of Prosopis juliflora in 250 mL Erlenmeyer flasks with metal ion concentration of 50 mg/L and the adsorption efficiency for different doses was determined by keeping other parameters constant.

2.3.3. Effect of pH

The effect of pH on the biosorption of metal ions was studied within the range that will not be influenced by the metal precipitated [22]. To determine the effect of solution acidity on the efficiency of adsorption, pH of the solutions were adjusted between 1-8 and 2-9 for Cu (II) and Zn (II) ions respectively and adsorption experiments were carried out by keeping other parameters constant.

2.3.4. Effect of Initial Concentration

This step determines the effect of metal ions concentration on metal ions removal efficiency of adsorbent (Prosopis juliflora powder). The effect of metal ions concentration was determined using concentrations of 10 mg/L, 30 mg/L, 50 mg/L, 70 mg/L, 90 mg/L and 100 mg/L for each metal ions and keeping other parameters constant.

2.4. Data Analysis and Interpretation

The data generated were analyzed by using Microsoft Excel to compute the mean, standard deviation and linear regression values.

3. Results and Discussion

3.1. The Optimum Condition for Cu (II) and Zn (II) Ions Removal by Prosopis Juliflora

3.1.1. Effect of Adsorbent Dosage

The effect of the adsorbent dose was studied at room temperature using different adsorbent doses of 0.5g, 1g, 2g, 3g, 4g and 5g. For all these runs, initial concentration of both Cu (II) and Zn (II) ions, pH of solutions, agitation speed and contact time were kept constant. Figures 1 and 2 show the effect of adsorbent dosage on the adsorption of Cu (II) and Zn (II) ions respectively.
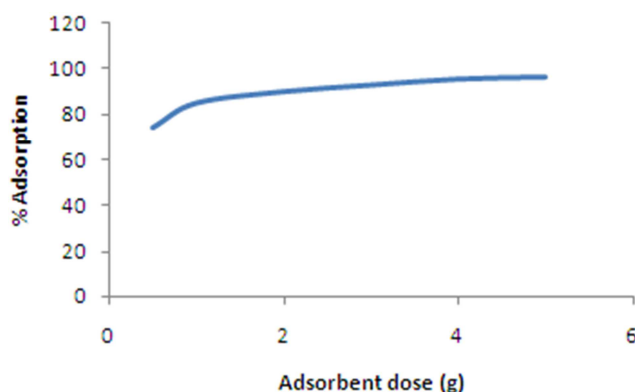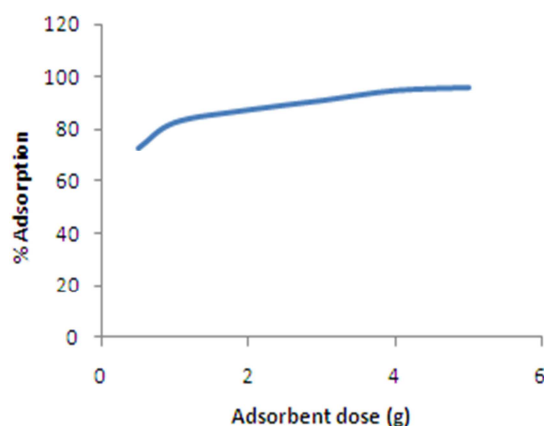

Figure 1. *Cu(II) ions removal efficiency (%) (Initial concentration = 50 mg/L, contact time = 90 min, solution pH = 5, agitation speed = 120 rpm).*
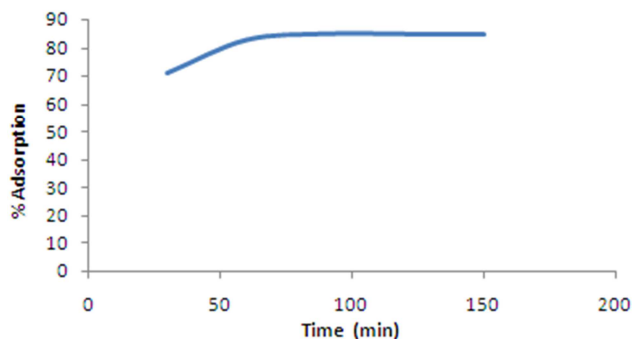
Figure 2. *Zn(II) ions removal efficiency (%) (Co =50 mg/L, contact time = 90 min, solution pH = 6, agitation speed = 120 rpm).*

In both cases adsorption efficiency increased with adsorbent dose in the range from 0.5- 1g and showed little variation with further increment. This trend was found to be similar for both metal ions and may be due to the saturation of sorption sites at higher biosorbent concentration. This indicates that removal efficiency is directly related to the number of available adsorption sites [23]. Biosorbent quantity is therefore, very essential because it determines the capacity of biosorbent for removal of a particular metal ion from solution. The results show that the adsorption capacity decreased from 7.45 to 0.97mg/g for Cu (II) and from 7.26 to 0.96 mg/g for Zn (II) ions however, percentage absorption increased from 74.54% to 96.76 for Cu(II) and from 72.64 to 96.26% for Zn (II) with increase in the dose of drired Prosopis juliflora from 0.5-5g. These results are in agreement with studies by [24]. In all subsequent studies, 1.0 g of the sorbent was taken as optimum dosage.

3.1.2. Effect of Contact Time

To determine the optimum contact time for Cu(II) and Zn(II) ions adsorption, 50 mg/L solution of both ions was added into 1.0 g of Prosopis juliflora adsorbent and agitated by varying the contact time from 30 to 150 minutes at 30 minutes interval. The results obtained are given in Figures 3 and 4.

Figure 3. *Cu(II) ions removal efficiency (%) at various contact time (Co = 50 mg/L, dose = 1.0 g, solution pH = 5, agitation speed = 120 rpm).*
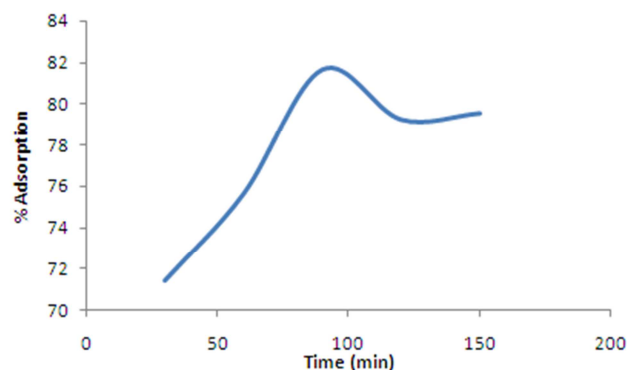
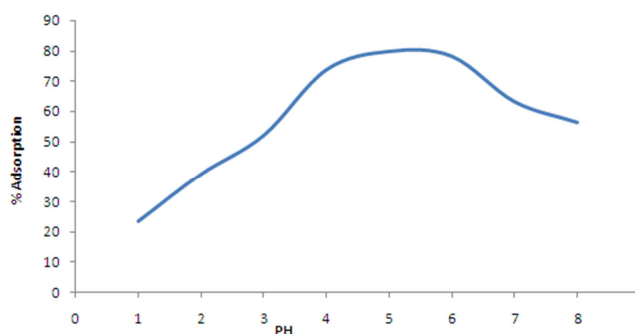
Figure 4. *Zn(II) ions removal efficiency (%) at various contact time (Co = 50 mg/L, dose = 1.0 g, solution pH = 6, agitation speed = 120 rpm).*

The results clearly revealed that adsorption process took place in two stages. Rate of adsorption was higher at the first stage, where about 85.12% and 81.66% of adsorption were completed for Cu (II) and Zn (II) ions respectively. This is due to availability of a large number of active sites on the adsorbent. As these sites are exhausted, the uptake rate was controlled in the second stage at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. This is in accordance with the observations of other similar studies [25]. The removal efficiency turned sharply at contact time of 90 minutes for both Cu (II) and Zn (II) ions. At these points, the amount of the respective metal ions adsorbed on the sorbent was in a state of dynamic equilibrium with the amount of metal ions desorbed from sorbent and the increment became stable. Due to this reason the optimum contact time for both metal ions were taken as 90 minutes for the subsequent investigations.
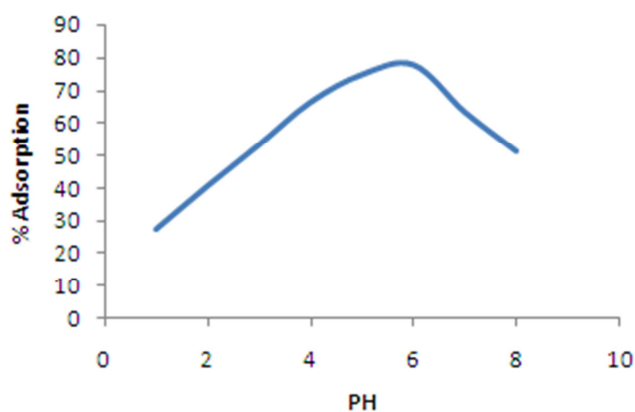
3.1.3. Effect of pH

The effect of pH on the extent of adsorption of Cu (II) and Zn (II) ions on the Prosopis juliflora powder was studied by varying the pH in the range of 1.0 – 8.0 and 2.0 – 9.0 for the two metal ions respectively. At metal ions concentration 50 mg/L and agitation speed of 120 rpm, the contact time for both Cu (II) and Zn (II) ions was set at 90 min. The results obtained are illustrated in Figures 5 and 6.

Figure 5. *Effect of pH on Cu(II) ions removal efficiency (%) (Co = 50 mg/L, dose = 1g, time = 90min, agitation speed = 120 rpm).*

Figure 5 shows that the maximum percent removal of Cu(II) ions on the adsorbents was observed at pH 4-5 and

significantly decreased by reducing the pH values and slightly decreased at higher pH values. The removal efficiency increased from 23.5% to 79.82% as pH increased from 1 to 5; therefore, optimal metal ions removal efficiency occurs at pH 5. The maximum percent removal of zinc ions was observed at pH 4–6 as shown in Figure 6, and significantly decreased at lower pH value. The removal efficiency increased from 27.66% to 78.04% as pH increased from 2 to 6; hence pH 6 was fixed as optimal pH value for further investigations. According to [26], little sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for sorption sites. This means that at higher H^+ concentration, the biosorbent surface becomes more positively charged, thus, reducing the attraction between adsorbent and metal ions. In contrast, as the pH increases, more negatively charged surface become available, thus facilitating greater metal ions uptake [21, 26]. At a higher pH, the Cu(II) and Zn(II) ions precipitated as their hydroxides which decreased the rate of adsorption and subsequently the percent removal of metal ions.
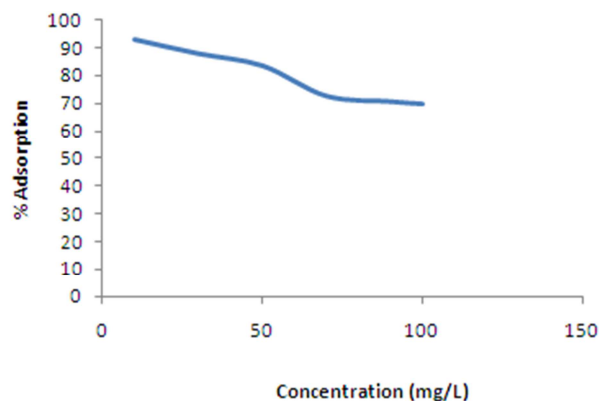

Figure 6. *Effect of pH on Zn(II) ions removal efficiency (%) (Co = 50 mg/L, dose = 1g, time = 90min, agitation speed = 120 rpm).*

The decrease in the adsorption rate in the pH range from 5 to 8 for Cu(II) and 6 to 9 for Zn(II) ions might be attributed to the formation of $Cu(OH)_3^-$ and $Zn(OH)_3^-$ ions taking place as a result of dissolution of $Cu(OH)_2$ and $Zn(OH)_2$ respectively. This is attributed to the adsorbent surface being negative at the above pH range, which cannot absorb the negatively charged ions $Cu(OH)_3^-$ and $Zn(OH)_3^-$ respectively, rather than repel each other.

3.1.4. Effect of Initial Concentration of Metal Ion

The effect of initial concentration of metal ions on the extent of adsorption of Cu (II) and Zn (II) ions on the Prosopis juliflora powder was studied using the initial concentration of metal ions of 10mg/L, 30 mg/L, 50 mg/L, 70 mg/L, 90 mg/L and 100mg/L with contact time of 90 min, agitation speed of 120 rpm and pH of 5 for Cu (II) and 6 for Zn (II) ions. The results obtained are illustrated in Figures 7 and 8.

Figure 7. *Effect of initial concentration on Cu(II) ions removal efficiency (%) (PH = 5, dose =1g, time = 90 min, agitation speed = 120 rpm).*
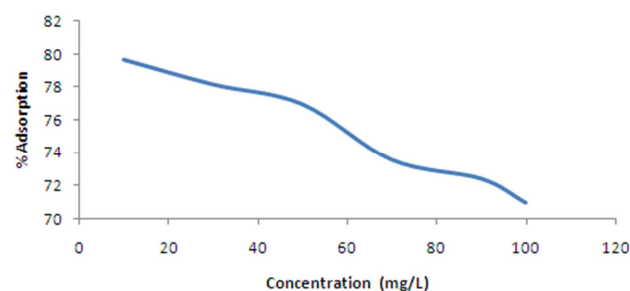
Figure 8. *Effect of initial concentration on Zn(II) ions removal efficiency (%) (PH = 6, dose = 2g, time = 90 min, agitation speed = 120 rpm)*

At lower concentration (10 to 30mg/L), ratio of the initial moles of metal ions to the available adsorption sites was low and subsequently the fractional sorption became independent of initial metal ions concentration. However, at higher concentration of Cu (II) and Zn (II) ions, the available sites for sorption became fewer compared to the moles of metal ions present and hence the percentage adsorption of the metal ions would be dependent upon the initial metal ions concentration. The result indicates that percentage Cu (II) and Zn (II) ions removal decreases as the initial concentration of both metal ions was increased. Cu (II) removal ranged from 83.82% to 69.67% and Zn (II) removal from 79.70% to 70.98% for the initial concentration of 10–100 mg/L for both metal ions. This can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration (Yu *et al.*, 2003). Since% R = (C^o - C^e)/$C^{o,}$ another reason for decrease in percent removal is larger increase in the denominator (C^o) value in comparison with that of the numerator (C^o - C^e) value. In addition, the adsorption capacity (qe) of Cu (II) and Zn (II) ions removed (mg per gram) of the adsorbent is lager for higher concentration. For this reason, 50mg/L was chosen as optimum initial concentration for both metal ions.

3.2. Adsorption Isotherm

Adsorption isotherm is needed to explain the adsorption process and to determine the adsorption efficiency of an adsorbent. Out of the different adsorption isotherm models,

Langmuir's and Freundlich's model have been preferred by most of the studies concerning about adsorption. The present experiment also used Langmuir's and Freundlich's equations to explain the adsorption mechanism of the biosrbent considered.

3.2.1. Cu(II) Ions Adsorption Isotherms

Adsorption isotherm studies were carried out to determine an approximate value of adsorption capacity of an adsorbent using adsorbent doses of: 0.5, 1, 2, 3, 4 and 5 g. Using Langmuir's equation to analyze copper adsorption isotherm, the graph shows the relation between $1/Ce$ in the x axis and $1/qe$ in the y axis. On the other hand, the graph of Fruendlich's equation shows the relationship between log Ce in the X axis and log qe in the y axis.

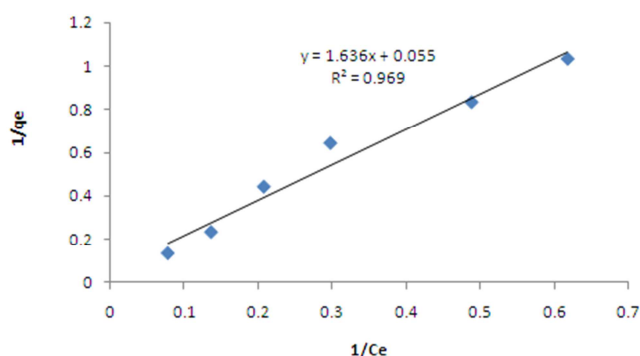*Figure 9. Langmuir adsorption isotherms for Cu(II) ions.*

Langmuir adsorption isotherm model for Copper (II) ions

The Langmuir model assumes monolayer coverage of adsorbent surface and no interaction of adsorbate in the plane of the adsorbent surface. The empirical Langmuir equation is written as shown in equation 3.

$$qe = q_m bCe/(1+bCe) \qquad (3)$$

The linear form Langmuir isotherm is given by the following equation (Langmuir, 1918)

$$Ce/q_e = 1/bq_m + Ce/q_m \qquad (4)$$

Another linear form can be obtained by dividing the above equation by C_e. Plotting $1/q_m$ against $1/Ce$, astraight line is obtained having a slope $1/bq_m$ and intercept $1/q_m$.

$$1/e = 1/q_m + 1/Ce (1/bq_m) \qquad (5)$$

According to Figure 9. Intercept Y ($1/q_m$) = 0.055, q_m = 18.18, Slope ($1/bq_m$) = 1.636, bq_m = 0.6113 and qe = 0.6113Ce/ (1+0.0336Ce)

From the Langmiur's equation, the maximum adsorption capacity (q_m) by Prosopis juliflora was 18.18 mg/g. That is one gram of the Prosopis juliflora can adsorb 18.18 mg copper. The essential characteristics of Langmuir isotherms can be expressed in terms of dimensionless equilibrium parameter R_L (Juang, 1997).

$$R_L = 1/ (1+bCo) \qquad (6)$$

Where Co = initial metal ion concentration in solution (mg/l)

b = characteristic constants related to adsorption energy

The parameter R_L is also called the "separation factor" and provides a quantitative description of the equilibrium regions: R_L = 0 for irreversible, R_L < 1 for favourable, R_L = 1 for linear, and R_L > 1 for unfavourable adsorption. In our experiment, the value of R_L = 1/2.68 = 0.373, which indicates a favorable adsorption. This means that Prosopis juliflora is a favourable adsorbent for the removal of Cu (II).
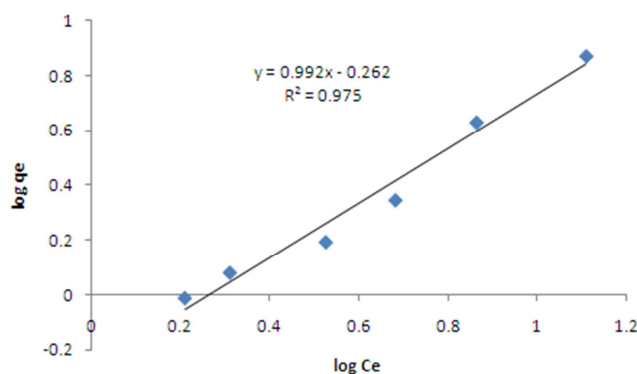

Figure 10. Freundlich adsorption isotherm for Cu(II) ions.

Freundlich adsorption isotherm for copper (II) ions

The Freundlich adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous system. The Freundlich equation is expressed in equation 7:

$$X/M = K_f Ce^{1/n} \qquad (7)$$

Where X = the amount of solute adsorbed

M = the weight of adsorbent

Ce = the solute equilibrium concentration

K_f = Freundlich adsorption capacity

n = Freundlich constant related to adsorption intensity

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. For linearization of the equation, it can be written in logarithmic form [27].

$$Log\ x/m = logK_f + 1/n\ log\ Ce \qquad (8)$$

Plotting log x/m versus log Ce, a straight line is obtained with a slope of 1/n and intercept of log Kf.

$$Log\ x/m = logK_f + 1/n\ log\ Ce \qquad (9)$$

According to Figure 10:

Slope 1/n = 0.992

Intercept $logK_f$ = - 0.262

Constant K_f = 0.547

Freundlich's equation

$$qe = K_f Ce^{1/n} = 0.547 Ce^{0.992} \qquad (10)$$

Another constant that was considered here was the value of 1/n. This value shows the concentration of solute adsorption. If the value of 1/n is close to 1, it shows that

just a little concentration change can relatively affect the adsorption. Besides, n value can indicate the capacity of adsorption and the adsorbent dose. If n is more than 1 (n>1), it means the adsorbent can effectively adsorb the solute. From freundlich equation the values of 1/n and n were obtained as 0.84 and 1.19, respectively. Since the values of 1/n lies between 0 and 1 and n>1, it indicates that the Prosopis juliflora can adsorb copper effectively.

The correlation coefficients (R^2) of Prosopis juliflora in Freundlich's equation exhibits higher value than Langmuir's (i.e. 0.975 and 0.969, respectively). However, in the broader perspective, both values appeared relatively higher than 0.9. Therefore, copper adsorption on Prosopis juliflora was fitted with both adsorption isotherms i.e. each site of a Prosopis juliflora can accommodate one molecule of copper ion or it is characterized by supporting surfaces of different affinity (heterogeneity of surfaces of Prosopis juliflora).

3.2.2. Zn(II) Ions Adsorption Isotherms

The study was carried out by using 0.5g, 1g, 2g, 3g, 4g and 5g dose of Prosopis juliflora. Figure 11 shows the relationship between the quantity of Zn (II) adsorbed per gram of adsorbent and the equilibrium liquid phase concentration at room temperature. Adsorption equilibrium isotherm models were used describe the adsorption process and the results obtained were analyzed using different isothermal equations. The graph obtained by Langmuir equation shows the relation between 1/Ce in the x axis and 1/qe in the y axis. On the other hand, the graph of Fruendlich's equation shows the relationship between log Ce in the X axis and log qe in the y axis.
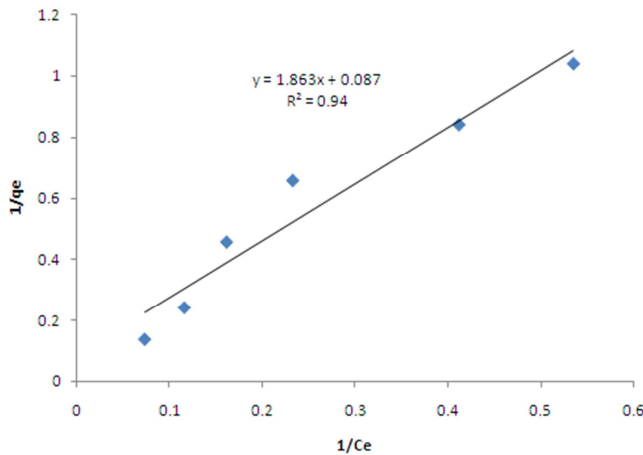

Figure 1. *Langmuir adsorption isotherm of Zn(II) ions.*

According to figure 11: Intercept Y ($1/q_m$) = 0.087, q_m = 11.5
Slope ($1/bq_m$) = 1.863, bq_m = 0.5368,
Langmiur's equation,

$$q_e = 0.5368Ce/ (1+0.04668Ce) \qquad (11)$$

Using Langmiur's equation, the maximum adsorption capacity by Prosopis juliflora was obtained as 11.5 mg/g.

That is one gram of the Prosopis juliflora can adsorb 11.5 mg copper. The value of RL obtained is 1/3.334 = 0.3. The shape of isotherm by Langmuir's equation was therefore, favorable isotherm. This means that at equilibrium high concentration of copper was adsorbed on Prosopis juliflora surface compared to its amount remained in aqueous solution.
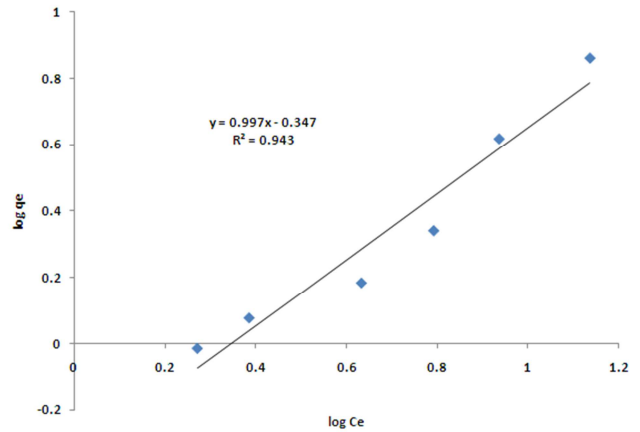

Figure 22. *Freundlich adsorption isotherm for Zn(II) ions.*

For linearization of the data, the Freundlich equation is written in logarithmic form.

$$Log\ x/m = logK + 1/n\ log\ Ce \qquad (12)$$

According to Figure 12:
Slope 1/n = 0.997
Intercept Y (logk) $logK_f$ = - 0.347
Constant K_f = 0.45
Freundlich's equation $q_e = {}_fCe^{1/n} = 0.45Ce^{0.997}$

The values of 1/n and n obtained from Freundlich's equation were 0.997 and 1.003 respectively. Since the values of 1/n lies between 0 and 1 and n>1, it indicates that the Prosopis juliflora can adsorb zinc effectively. From Figures 11 and 12 it can be seen that the Freundlich isotherm represented the experimental data better than Langmuir for zinc (II) ion adsorption with regression coefficient of 0.943 and 0.940 respectively.

Table 1. *Langmuir and Freundlich constants for the adsorption of Cu (II) and Zn (II) ions.*

Metal ion	Langmuir			
q_{max}	b	R^2		
Cu(II)	18.18	0.0336	0.969	
Zn(II)	11.5	0.047	0.94	
Freundlich				
R_L	K_f	1/ n	R^2	
Cu(II)	0.373	0.547	0.992	0.975
Zn(II)	0.30	0.45	0.997	0.943

q_{max} = maximum adsorption capacity (mg/g), b = constant related to binding energy, R^2= correlation coefficient, R_L = separation factor, K_f = Freundlich adsorption capacity, n = Freundlich constant related to intensity of adsorption.

Table 2. Comparison of the Adsorption capacities (qmax) of Cu (II) ions using different adsorbents.

Adsorbent	Adsorption capacity (mg/g)	References
Dried sunflower leaves	89.37	[28]
Sour orange residue	21.70	[29]
Papaya wood	19.88	[30]
Pomegranate peel	1.32	[5]
Coconut Shell Powder	7.413	[31]
Mango biomass	18.93	[32]
Potato peel	0.3877	[33]
Dicliptera bupleuroides Leaves	1.06	[34]
Urtica dioica Leaves	1.49	[35]
Prosopis juliflora powder	18.18	Present study

Table 3. Comparison of the Adsorption capacities (qmax) of Zn (II) ions using different adsorbents.

Adsorbent	Adsorption capacity (mg/g)	References
Dicliptera bupleuroides Leaves	2.55	[34]
Mango biomass	18.93	[33]
Bentonite and	79.2	[36]
kaolinite	6.35	
Urtica dioica Leaves	1.039	[35]
Coconut Shell Powder	7.413	[31]
Prosopis juliflora powder	11.50	Present study

The comparison of adsorbent capacity of Prosopis juliflora with other materials reported in literature is given in Table 2 and 3. Accordingly, the adsorption capacity of Prosopis juliflora powder obtained is good in comparison with the various low cost adsorbents.

4. Conclusion

The Results obtained strongly demonstrated from batch adsorption studies that pH, biomass dose, initial metal concentration and contact time affect the metal ions uptake capacity of biosorbents. The effect of adsorbent dosage on the adsorption of metals showed that the percentage of metal removed increased with increase in adsorbent dosage due to increased adsorption surface area. For all the adsorbents studied adsorbent dosage of 10g/L was used as optimum dosage for adsorption of about 80% of the initial metal concentration. The optimum pH for the removal of copper Cu (II) was 5 and 6 for zinc (II). The amount of the metal removed at optimum pH increased with increase in initial metal concentration but the percentage adsorbed decreased with increase in initial metal concentration due to limited number of active sites.

The maximum uptake capacity for Cu (II) was 18.18 mg/ g at pH 5 and for Zn (II) 11.5mg/g at PH 6, with 1 g of adsorbent in 100 mL of 50 mg/L initial metal ion concentration for 90 min. The adsorption equilibrium data obtained for removal of Cu (II) and Zn (II) on Prosopis juliflora powder at a fixed initial concentration and varying adsorbent dose well fitted into the Langmuir and Freundlich adsorption isotherms, but with higher correlation coefficient for Freundlich model, which shows the adsorption is homogenous. Prosopis juliflora can be a novel adsorbent according to results obtained in this study. It is recommendable to use this weed as an adsorbent as it is obvious of solving two problems with one cure.

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