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Adsorptive Removal of Copper from Aqueous Solution by Using *Syzygium Cumini L*

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Abstract- Excess of copper in drinking water is significantly toxic to human being and ecological environments. Various treatment technologies for copper removal from industrial and municipal waste water effluents has been investigated in past. In the present study batch adsorption studies were carried out for adsorption of Cu by using natural cheap agro waste such as Syzygium Cumini L for removal of copper from aqueous solution. The effects of initial metal concentration, Dose, pH, contact time on the removal on Cu have been studied. Results indicate that contact time of 360 min is sufficient to achieve equilibrium at different concentrations. Determination of Cu was done using Atomic absorption spectrophotometer. The peak percentage adsorption of Cu was attained at pH 7.0.Adsorption parameters were determined using both Langmuir, Freundlich and Temkin isotherms, but the experimental data were better fitted to Langmuir equation than to Freundlich and Temkin equation.

Index Terms- — Adsorption, Adsorption Isotherms, AAS Batch study , Copper removal, Syzygium Cumini L .

I. Introduction

Water supports all forms of life on earth. The availability of clean water to the human population is of paramount importance. As the world population increases, water consumption also increases. Water pollution is a major problem in the global context and has even been suggested to be the leading cause of death and disease worldwide. The major contributor for this rise in the concentration level is in the extensive development of heavy & manufacturing industries that use metals & related compounds. Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied. Copper is a toxic metal. It causes a disease named Wilson's disease. It causes harmful biochemical effects, toxicity and hazards in flora, fauna and human beings. Intake of copper through air, water, and food beyond its permissible limits causes disease. Copper toxicity leads to serve mucosal irritation, corrosion, widespread capillary damage hepatic and renal damage, central nervous system irritation followed by depression. Over the last few decades, several methods have been devised for the treatment and removal of heavy metals. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, Chemical reduction, Xanthate process, Cementation, Solvent Extraction, Electro deposition, Reverse osmosis, Electro dialysis, Ion exchange, Donna dialysis may require working with corrosive chemicals, increase the volume of waste sludge, used a trial and error approach, high cost of electrodes has inspired researchers to investigate effective treatment process called Adsorption and to find suitable low cost adsorbents.. The objective of this study to evaluate the feasibility of using the Syzygium Cumini L seed powder for the removal of copper, optimize of the different operating parameters such as pH, adsorbent dose, contact time and initial copper concentration were studied, to find the equilibrium values, in order to get maximum efficiency study the comparison of Adsorption capacity of locally available adsorbent. Validate the results obtained, in terms of copper removal efficiency (percentage), using adsorption isotherms, viz. Langmuir, Freundlich, Temkin isotherm models.

II. Materials and Methodology

A. Preparation of adsorbent

Syzygium Cumini L is an evergreen tropical tree in the flowering plant family Myrtacae, native to India and Indonesia. Seeds were locally collected from Syzygium Cumini L tree located in Nasik. Flesh of the fruit was removed .The seeds were separated from the Syzygium Cumini L fruits by eating and seed was washed with the distilled water. The seeds were dried in shade and stored at 25^0C. The dried seed was ground and screened to uniform powder by using 150 microns sieve. Thus Syzygium Cumini L seed powder is stored in an air tight container for further usage.

B. Reagents and equipment's

Prepare a series of standard metal solutions in the optimum concentration range by appropriate dilution of the following stock metal solutions with water containing 1.5ml conc. (HNO_3)/l. Thoroughly, dry reagents before use. In general use reagents of the highest purity.

Copper

Dissolve 1.00g copper metal in 15ml of 1+1 HNO_3 and dilute to 1000ml with water;

1.00ml = 1.000mg Cu

Air, cleaned and dried through a suitable filter to remove oil, water and other foreign substances ,use metal free water for preparing all reagents and calibration standards and as dilution water. Acetylene standard commercial grade acetone.

C. Batch Adsorption study

Batch experiments were carried out in 250mL glass jar with 250 mL test solution at room temperature (29±2°C). The jar, along with known volume of test solution of fixed concentration at neutral pH, was shaken in Jar test apparatus at 100 rpm to study the equilibration time for maximum adsorption of copper. The effect of pH on copper was studied by adjusting the pH of test solution using 1N Hcl or 1N NaOH on fixed quantity of adsorbent. At the end of the desired contact time, the samples were filtered using Whattman no. 42 filter paper and the filtrate was analyzed for residual copper concentration by Atomic Absorption spectrophotometer: Model No. AA-200, PERKIN described in the standard methods of examination of water and wastewater. The batch study was performed to determine the optimum condition and to study the effect of pH, adsorbent dose, contact time and initial copper concentration on the test solution.

D. Data modeling

The efficiency and copper adsorption capacity from the residual copper concentration was calculated by the following equations.

The percent removal efficiency of the copper was calculated as follow,

$$\% \text{ Removal} = \frac{Ci - Ce}{Ci} x100 \qquad (1)$$

Where, Ci is the initial copper concentration (mg.L-1), Ce is the equilibrium concentration of copper solution (mg.L-1).

$$\text{Adsorption capacity (qe)} = \frac{(Ci - Ce) * V}{m} \qquad (2)$$

Where, Ci is the initial copper concentration (mg.L-1), Ce is the equilibrium concentration of copper solution (mg.L-1), V is the volume of solution used in the batch (lit.), m is mass of adsorbent (g), qe is adsorption capacity (mg of copper removed/ g of adsorbent).

III. RESULTS AND FINDINGS

A. Effect of Adsorbent dose on percentage copper removal

One of the parameters that strongly affect the adsorption process in an aqueous solution is the adsorbent dose. This is an important parameter, because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate .More specifically, the increase rate of this parameter was high for higher adsorbent doses, due to the greater availability of active sites on the surface of the materials, and low for lower adsorbent doses, due to the progressive saturation of these active sites. However, the amount of Cu (II) adsorbed per adsorbent mass unit decreased considerably as the adsorbent dose increased. This can be attributed to adsorption sites remaining unsaturated during the adsorption reaction. In addition, it could also be noticed that the majority of the tested materials, steady state was reached for an adsorbent dose value 0.1g/l Therefore, the optimum adsorbent dose of 0.1 g/L was selected in all the subsequent experiment.

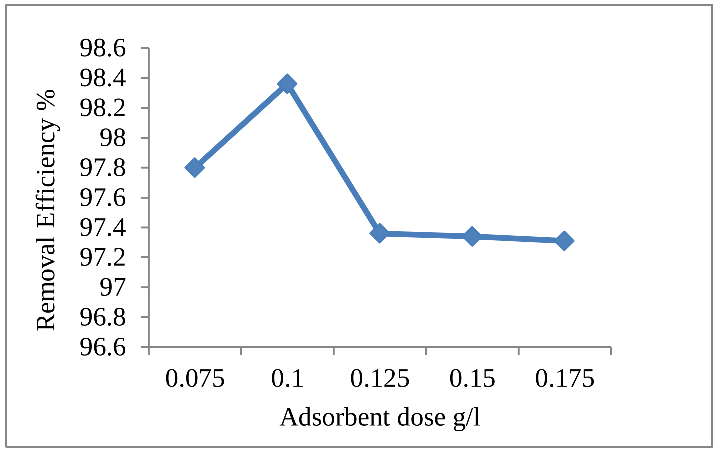

Figure 1: Graph for effect of Adsorbent dose on copper removal

B. Effect of Initial metal concentration on percentage copper removal

The mechanism of metal adsorption from an aqueous solution is particularly dependent on the initial metal concentration in the solution. According to the results increasing the initial Cu(II) concentration caused an increase in the amount of Cu(II) adsorbed per adsorbent mass unit. This was due to the increase in the driving force for mass transfer, which is the concentration gradient. In addition, a decrease in the Cu (II) removal could be noticed as the initial Cu(II) concentration in the solution increased, due to the saturation of the active sites in the solution (El-Ashtoukhy et al., 2008). These findings agree with previous studies (Aydin et al., 2008; El-Ashtoukhy et al., 2008; Zheng et al., 2008).

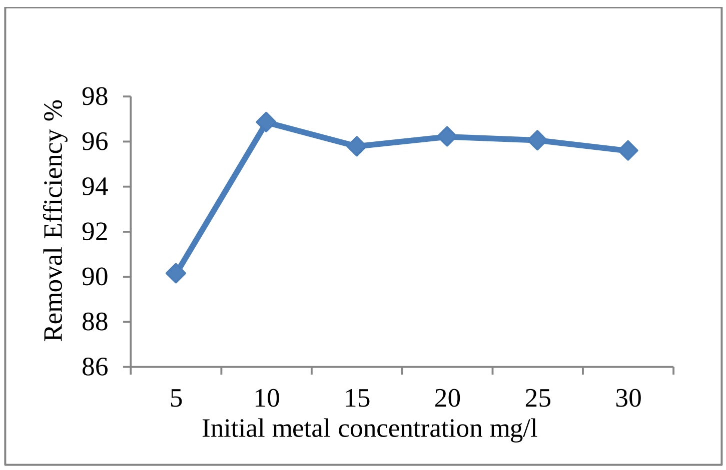

Figure 2: Graph for effect of Initial metal Concentration on copper removal

C. Effect of pH on percentage copper removal

The pH of an aqueous solution is one of the most important controlling parameters in the heavy metal adsorption process. It affects the surface charge of the adsorbent and the degree of ionization and speciation of the heavy metal in the solution. This study was carried out in a pH range 2-11 since copper starts to precipitate above pH 7. The optimum Cu (II) uptake of 97.16%, by Syzygium Cumini L respectively, was observed at pH 7.

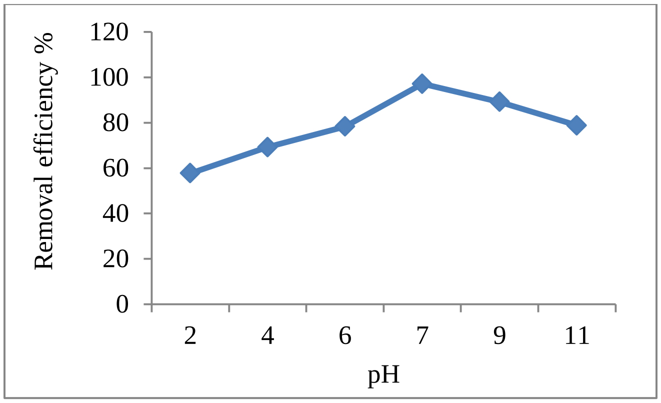

Figure 3: Graph for effect of pH on copper removal

D. Effect of Contact Time on percentage copper removal

By increasing contact time, an increase in both the amount of Cu(II)adsorbed per adsorbent mass unit and the Cu(II) removal was obtained. In most cases, the quick initial rate of adsorption during the first few minutes of contact was followed by a slower one, until equilibrium state was reached. This was due to the existence of abundant vacant active Syzygium Cumini L sites, whereas as adsorption continued a progressive saturation of these active sites with time occurred. In addition, the required time to reach equilibrium was about 6 h, since an increase of contact time to 24h did not have any significant effects.

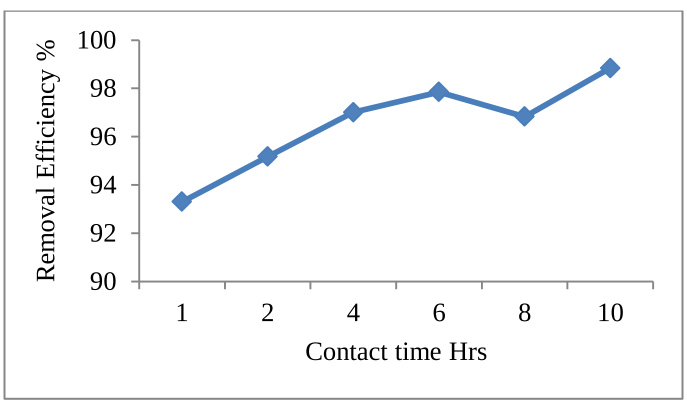

Figure 4: Graph for effect of Contact time on copper removal

E. Validation of results using adsorption isotherms

1) Freundlich model

Freundlich equation is derived to model, the multilayer adsorption for the sorption on heterogeneous surfaces.

The Freundlich model is formulated as :

qe = Kf (Ce)1/n (3)

Where, qe is the amount of ion adsorbed (mg/g), Ce is the equilibrium concentration (mg/L), Kf and 1/n are empirical constants, indicating the adsorption capacity and adsorption intensity, respectively. The above may be converted to a linear form by taking logarithms:

log qe = log Kf + 1/n logCe (4)

The values of Freundlich constants (slope) and adsorption capacity (intercept) were obtained from the linear correlation plots between log qe with log Ce

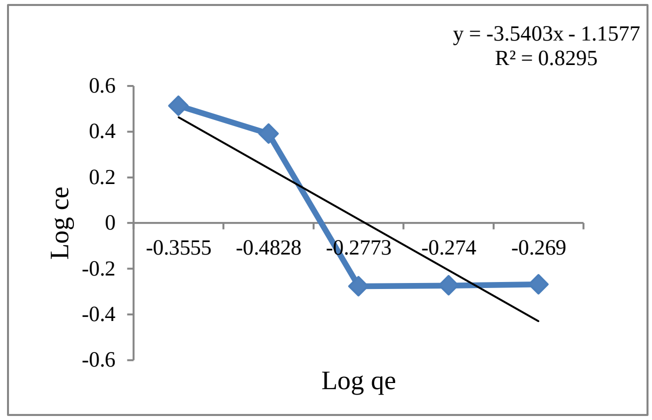

Figure 5: Freundlich model for removal of copper using S.Cumini L

2*) Langmuir model*

. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. Based upon these assumptions, Langmuir represented the following equation:

qe = QobCe/(1+bCe) (5)

The linear form of the Langmuir isotherm is expressed as follows.

1/qe= (1/Qo) + (1/ QobCe) (6)

Where, qe is the amount of copper adsorbed per gram of the adsorbent at equilibrium (mg/g), Ce is the equilibrium concentration of adsorbate (mg/L), Qo is the adsorption capacity of adsorbent and b is a constant related to the energy adsorption.

The values of Langmuir constants (slope) and adsorption capacity (intercept) were obtained from the linear correlation plots between 1/qe and 1/ Ce.

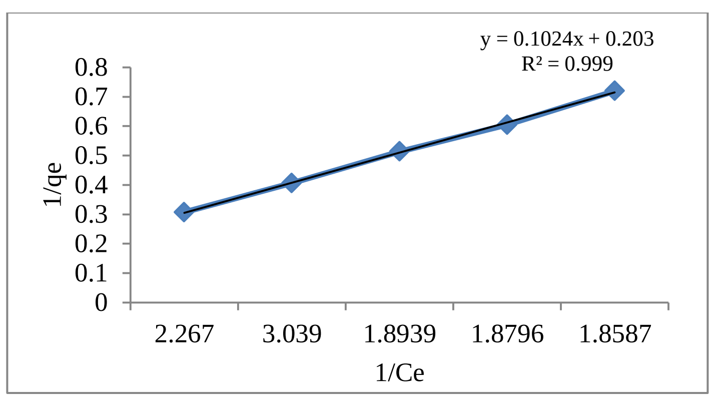

Figure 6: Langmuir model for removal of copper using S.Cumini L

3) Temkin model

The Temkin isotherm is represented by the following equation:

$$qe= RT/b \ln(KTCe) \quad (7)$$

The linear form of the Temkin isotherm is expressed as follows.

$$qe = B1\ln KT+B1\ln Ce \quad (8)$$

Where, B1 = RT/b

Where, qe and Ce have the same meaning as noted previously and the other parameters are called the Temkin constants, R universal gas constant (8.314 J mol−1 K−1), T is temperature in (K). The plot of qe versus log Ce will generate a straight line. The Temkin constants B1and KT can be calculated from the slope and intercept of the linear plot.

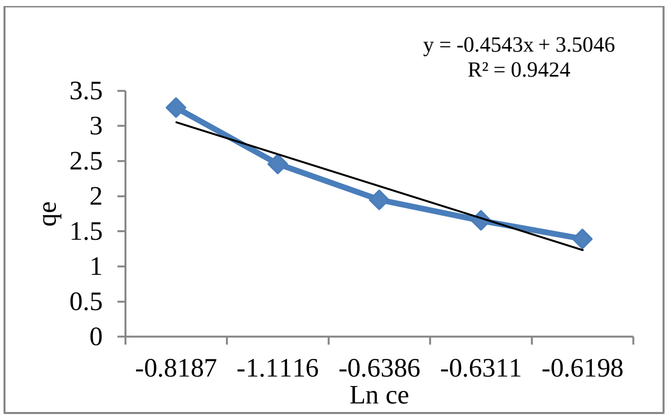

Figure 7: Temkin model for removal of copper using S.Cumini L

IV. CONCLUSION

The operational parameters such as pH, adsorbent dose, contact time and initial copper concentration were found to have predominant effect on the adsorption efficiency of Syzygium Cumini L seed powder.

The uptake of copper ions is possible between pH of 2.0 and 10; however pH of 7.0 gives maximum copper removal for Syzygium Cumini L seed powder.

The removal efficiency at pH=7 is about 97.16% whereas at pH=6 it is 78.36%. Which are also encouraging and might be improved by optimizing the operating parameters at the pH=7.

The percentage of copper removal was found to be a function of adsorbent dose and contact time at a given initial solute concentration In case of effect of adsorbent dose, equilibrium dosage of 0.1g was found for Syzygium Cumini L seed powder after that there is no any significant change on copper removal efficiency with increase in dose. While the maximum efficiency was found to be 99.84%.

The increase in copper concentration from 5 to 30mg/L the percentage of copper removal was decreased from 99.54-90.14% and curve gradually attains equilibrium after 720 min for Syzygium Cumini L seed powder. As there was no significant increase in percentage of copper removal after 360 min so equilibrium time of 360 min was chosen for Syzygium Cumini L seed powder.

The isotherm study for Syzygium Cumini L seed powder represent that the equilibrium data fits better to Langmuir model (i.e.R^2 value = 0.999 for S.Cumini L respectively) than Freundlich, Temkin model. According to Langmuir model the maximum adsorption capacity was found in case of Syzygium Cumini L seed powder were 49.9 mg/g respectively.

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