RESEARCH ARTICLE
KINETIC AND ISOTHERMAL STUDIES ON THE REMOVAL OF COPPER (II) FROM AQUEOUS SOLUTION BY ARAUCARIA COOKII: RESPONSE SURFACE METHODOLOGY FOR THE OPTIMIZATION OF PARAMETERS

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ABSTRACT

The biosorption of Copper by Araucaria cookii was investigated using batch process. The parameters influencing the biosorption are pH, initial metal ion concentration, adsorbent mass, contact time and particle size. Kinetic studies were performed using Pseudo first order and Pseudo second order equations. The adsorption parameters were determined using Langmuir and Freundlich Isotherm Models which showed good fitting of experimental data. The Response Surface Methodology is used to optimize the biosorption of copper using Central Composite Design (CCD) model. The CCD model was designed using polynomial equation for parameters using Design Expert Software (Version 8.0.7.1). Using this methodology the removal of copper achieved by Araucaria cookii was 90.42% under optimum conditions of pH 5.5, initial metal ion concentration 187.50 mg L⁻¹, contact time 47.5 min, adsorbent mass 1.5 mg L⁻¹ and particle size 250 µm. Due to its efficient adsorption of Copper, Araucaria cookii is an excellent biomaterial for recovering copper from industrial effluents.

INTRODUCTION

Pollution by heavy metals from Industrial waste water is a common environmental hazard, since the toxic metal ions dissolved can ultimately reach the food chain and become a risk factor for human health. The electroplating industry and surface finishing of metals are important sectors producing enormous amounts of waste water containing mainly Copper, Lead, Nickel, Zinc and Chromium ions. Copper is present in the waste water of several industries such as metal cleaning, refineries, paper and pulp, fertilizer and wood preservation and it is highly toxic (Periasamy and Namasiyam, 1996). Copper and its compounds are ubiquitous in the environment and thus copper is found frequently in surface water. The World Health Organization (WHO) recommended a maximum acceptable concentration of copper in drinking water as 1.5 mg/L¹(Rao 1992).

Heavy metals can be extremely toxic as they damage nerves, liver, kidneys and bones, and also block functional groups of vital enzymes (Carson et al., 1986). The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage followed by depression and gastrointestinal irritation (Gotoh et al., 2004).

Several chemical methods have been devised for the treatment and removal of heavy metals. The commonly used procedures for removing metal ions from aqueous streams include Phytoremediation, Chemical Precipitation, Lime Coagulation, Ion Exchange, Reverse Osmosis, and Solvent Extraction (Rich and Cherry, 1987). But disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal have made these methods comparatively cost effective for removal of metals from effluents (Ahalya et al., 2003).

The search for new technologies for reducing toxic metals from waste waters has directed attention to biosorption techniques based on metal binding capacities of various biological materials. Biosorption is considered to be a fast physico-chemical process. It involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of biosorbent to the sorbate species, it gets attracted and bound by different mechanisms (Kratochil and Volesky 1998). Different parameters may affect the biosorption process to varying extent (Gadd 2009). pH is the most important parameter that affects the metals, the activity of the functional groups in the biomass as well as the competition of metallic ions (Galun et al., 1983).

The Central Composite Design (CCD) model commonly used for optimization of the different parameters using Response Surface Methodology (RSM). The optimization process involves performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the response and checking the adequacy of the model (Farshid and Habibollah, 2008; Kumar and Singh, 2009; Preetha and Viruthagiri, 2007).

This methodology is more practical compared to theoretical models as it arises from experimental methodology which includes interactive effects of the variables and, eventually, it
depressing the overall effects of the parameters on the process (Bas and Boyaci, 2007).

The aim of this work was to find out the effectiveness of Araucaria cookii plant leaves as a biosorbent for the removal of Cu (II) from waste water and also to optimize the different parameters including Initial concentration, pH, contact time, adsorption dose and particle size of the copper ions. The objective of this study includes Kinetic Adsorption and Isotherm Reaction. RSM model is also studied to investigate the response order of the entire factor face and also to locate the region of interest where the response reaches its optimum value using Central Composite Design by Design Expert Software (Version 8.0.7.1). Optimal reaction parameters for maximum biosorption are going to be generated using the software’s numerical optimization function.

MATERIALS AND METHODS

Biomass preparation

The plant Araucaria cookii belonging to the family Araucariaceae which is commonly called Christmas tree was used in this study. Leaves of plant were collected from Mysore City, Karnataka, India. They were washed with deionised water, cut into small pieces, sun dried for seven days followed by drying in an oven at 70°C for 24 h. Subsequently, the leaves were grounded and sieved to get four fractions (100 µm, 200 µm, 300 µm and 400 µm). The sieved biosorbent was washed several times with double distilled water to remove dust particles and dried then stored in a dry place until usage.

Preparation of the Adsorbate

Metal ion solution of Cu (II) was prepared from CuSO₄·5H₂O (Merck- A.R. grade). Stock standard solution of concentration 1000 mg L⁻¹ was prepared in double distilled water and further working solutions of lower concentrations were prepared as and when required. The pH of the solution was adjusted using 0.01 M HCl and 0.01 M NaOH. The final concentrations of metal ions were analysed by AAS.

Surface characterisation of copper onto A.cookii by SEM

The surface physical morphology of the adsorbent was observed under the Scanning Electron Microscope. The biosorbent was assessed by SEM image of unloaded and loaded copper ions by Leo 435 VP (Leo electron microscopy Ltd., Cambridge, UK 1997).

Experimental design and optimization

The adsorption of copper by Araucaria cookii under optimum conditions was determined by applying Response Surface Methodology (RSM). RSM is a collection of mathematical and statistical techniques useful for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response (Montgomery Douglas, 2005). The main objective of studying RSM is to determine the optimum operational conditions for the process or to determine a region that satisfies the operating specification (Myres, and Montgomery, 2001). This is widely used in chemical engineering, notably to optimize adsorption process (Ricou, 2001). It can be expressed as

\[ Y = f(x_1, x_2) + e \]  (1)

Where, \( x_1 \) and \( x_2 \) are independent variables and the response \( y \) depends on them. The dependent variable \( y \) is the function of \( x_1, x_2 \) and the experimental error term is denoted as \( e \).

If the response can be defined by a linear function as first independent variable, then the approximating function is a first order model. A first order model with two independent variables can be expressed as:

\[ Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + e \]  (2)

If there is a curvature in the response surface, then the degree polynomial should be used. The approximating function with two variables is called a second- order model and it is expressed as:

\[ Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + e \]  (3)

In the present study, the factors considered are pH, contact time, metal ion concentration, adsorbent dose and particle size variation. The pH value of 1-10, contact time of 5-90 min, metal ion concentration of 25-350 mg L⁻¹, adsorbent dose of 0.1- 3.5 g/L and particle size variation of 100 – 400 µm were used as input variables under Central Composite Design model as shown in (Table 1).

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Batch experiments

The effect of pH, contact time, metal ion concentration, particle size variation and biomass are the parameters used in the study for the removal of Cu (II) by Araucaria cookii. Batch adsorption experiments were conducted at room temperature for experimental run. A desired known pH was adjusted by taking 20 ml of 1000 mg L⁻¹ in a clean conical flask. A constant stirring speed of 180 rpm was used in a rotary shaker for a suitable adsorbent of 2 g/L. Samples were withdrawn at appropriate time intervals (5-90 min) and they were centrifuged at 5000 rpm for 15 min and filtered. The supernatant was analyzed for residual metal ion concentration.

The amount of Cu (II) uptake by the plant adsorbent was calculated as the difference between the initial and final concentration of Cu (II) after adsorption in the aqueous solution. The percent removed of Cu (II) was calculated using the following formula:

\[ q = V (C_0 - C_f) / m \]  (4)
Where, q is the (Cu (II)) uptake (mg/g), C₀ and Cᵣ are the initial and final Cu (II) levels mg L⁻¹ in the solution respectively. V is the solution volume (L) and m is the mass (g) of adsorbent.

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A= Contact time, B= Biomass, C= Concentration, D= Size variation, E= pH.

The effect of pH on adsorption of copper was studied. The pH was in the range of pH 1-10. The experiments were carried out by adding 2 g of biosorbent with 20 ml of 1000 mg L⁻¹ of Cu (II) solution in a clean conical flask. The pH was adjusted using 0.01M HCl and 0.01 M NaOH. The samples were centrifuged, decanted and Cu (II) was measured by AAS.

In order to study the effect of size of adsorbent on biosorption, 20 ml of 1000 mg L⁻¹ of copper with particle size of adsorbent varying from 100-400 μm at pH 6, contact time of 90 min and shaking for 30 min, then the resulting mixture was filtered.

To find out the adsorption capacity of Cu (II) ion different dosages varying from 0.1 – 3.5 g were taken in clean conical flask containing 20 ml of 1000 mg L⁻¹ of copper solution and pH was adjusted to pH 6. The resultant solution was agitated for 30 min in a rotary shaker.

The effect of contact time on adsorption of copper on to A. cookii was studied by taking 20 ml of 1000 mg L⁻¹ copper solution in a clean conical flask containing 2 g of biosorbent and adjusting pH to 6, with the contact time intervals of 5-90 min and shaken in a rotary shaker for 30 min.

The effect of metal ion concentration on adsorption by A. cookii was studied by taking copper solution ranging from 25 to 350 mg L⁻¹ in clean conical flasks and maintaining the pH at 6. The mixture was shaken for 30 min in a rotary shaker and the resulting mixture was filtered.

**RESULTS AND DISCUSSION**

**SEM Studies**

The SEM image and morphology of A. cookii used in the experiments are shown in (Fig.1). SEM images of unloaded and loaded Cu (II) ions were analyzed (Fig. 1a and 1b) with the pore size of the adsorbent being 100 μm. In Fig. 1a the surface of the internal structure is not very rough and has large surface area before the adsorption. Fig. 1b show white small blocks on the surface and are closely packed; this is because of the sorption of copper ions in the aqueous solution. Hence based on the morphology, A. cookii is suitable and can be used as biosorbent for the removal of copper in the aqueous solution.

**Effect of initial pH on the biosorption**

The pH of the aqueous solution is an important controlling parameter in the adsorption process (Asmal et al., 1998). At lower pH, H⁺ ions compete with metal cations for the exchange sites in the system. The heavy metal cations are
completely released under circumstances of extreme acidic conditions (Forstner and Wittmann 1981). To understand the adsorption mechanism, the biosorption of Cu (II) as a function of pH was measured from pH 1-10 and the results are shown in (Fig.2). Maximum percent removal of copper (98.7%) was recorded at pH 6. The surface of the biomass shows with the increase in the characteristics which controls the biosorption process.

The pH dependence of metal biosorption is due to the solubility of metals and the ionization state of various functional groups like carboxylate, phosphate and amino groups (Yin et al., 1999). At lower acidic pH the overall surface charge on the active sites becomes positive and metal cations and protons compete for binding sites on the cell wall, which results in lower uptake of metal (Dursun, 2006). With increasing pH the negative charge density on the cell surface increases due to protonation of the metal binding sites. The available binding sites then compete with metal ions which

**Effect of biomass dosage**

The effect of various dosages of *A.cookii* leaves powder was studied using 200 mg L\(^{-1}\) of initial Cu (II) concentration at pH 6.0. Fig. 3 shows increase in percent removal of copper from 58% to 98.7% with increase in dose of adsorbent and beyond that it remains constant. Increase in the adsorption with increasing dose of adsorbent is due to the increase in surface area and more adsorption sites available (Mall et al., 2006; Ola Abdel Wahab, 2007).

**Effect of Particle size**

In order to understand how particle size affects the adsorption, a series of experiments were conducted using *A. cookii* leaves powder. The average particle size was changed from 100 to 400 µm keeping the other variables constant. The experiment has revealed that the saturation capacity of metal ions adsorption of *A. cookii* decreased by increasing the particle size (Fig. 4). This can be attributed to the relationship between the effective specific area of the adsorbent particles and their sizes. At 100 µm size the maximum adsorption was 97 % and when the particle size increased from 100 to 400 µm the rate of adsorption decreases from 99 % to 75 %. This implies that smaller particles have large surface area and hence the percentage of adsorption is more.

**Effect of Contact Time on biosorption**

The effect of contact time on biosorption of copper by *A. cookii* is shown in (Fig. 5). It can be observed that rapid sorption (85 %) takes place within the first 20 min and equilibrium is reached at 30 min with maximum sorption of 98.7%. This is because of the availability of maximum sorption sites. After 30 min the rate of sorption becomes constant due to decrease in the number of available sites which in turn remains constant.

**Effect of Metal Ion Concentration and Adsorption Kinetics**

The effect of metal ion concentration on sorption of copper by *A. cookii* is depicted in (Fig. 6). The pH was kept constant along with all other parameters. As the percent adsorption was higher at lower concentration of Cu (II) in solution (25-350 mg L\(^{-1}\)) the maximum percentage removal of copper was achieved at 98.7%. The increase in copper concentration with biosorption capacity is due to interaction between higher metal ions and the sorbent. In addition, the increased concentrations of metal ions compete with the metal binding sites of the biomass resulting in low sorption of metal ions (Akar and Tunali, 2006).

![Fig. 2 Effect of pH on adsorption of Cu (II) by *A.cookii*](image)

![Fig. 3 Effect of adsorbent dose on adsorption of Cu (II) by *A.cookii*](image)

![Fig. 4 Effect of adsorbent size on adsorption of Cu (II) by *A.cookii*](image)

![Fig. 5 Effect of time on adsorption of Cu (II) by *A.cookii*](image)

![Fig. 6 Effect of metal ion concentration on adsorption of Cu (II) by *A.cookii*](image)
**Pseudo- First Order Model**

The pseudo-first order model expression describes the adsorption based on solid capacity and is generally expressed as (Lagergren, 1898; Ho, 1996).

\[
\frac{dq}{dt} = k_1 (q_e - q_t)
\]  

Where \( q_t \) is the amount of metal adsorbed (mg g\(^{-1}\)), \( q_e \) is the amount of metal adsorbed at time \( t \) (mg g\(^{-1}\)), \( K_1 \) is the rate constant of pseudo first order adsorption (l/min).

\[
\log (q_t - q_e) = \log q_e - k_1 / 2.303 t \ (\text{linear form})
\]  

In the values of Pseudo first order reaction, the metal adsorption rate constant \( (K_1) \) onto Araucaria cookii were applicable from the straight line plot of \( \log (q_t - q_e) \) against \( t \) (Fig. 7). The data is fitted with a poor correlation co-efficient (Table. 2), indicating that rate of removal of copper by Araucaria cookii does not follow the pseudo first order equation. The calculated slopes and intercepts from the plots were used to determine the rate constant \( k_1 \) and equilibrium capacity \( (q_e) \) (Dinesh Mohan et al., 2006).

**Pseudo Second Order Model**

The pseudo second order equation is greatly influenced by the amount of metal on the adsorbent’s surface and the amount of metal adsorbed at equilibrium. It predicts the behavior over the whole range of data. This can be written in terms of amount adsorbed by the equation (Hamadi et al., 2001; Cheung et al., 2000).

The kinetic rate equation can then be written as

\[
\frac{dq}{dt} = K_2 (q_e - q_t)^2
\]  

Where \( q_t \) and \( q_e \) are the amount of metal adsorbed at time \( t \) and at equilibrium (mg g\(^{-1}\)) and \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo second order adsorption rate constant. For the same boundary conditions the integrated form of equation (5) becomes

\[
\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t
\]

The initial adsorption rate (\( h \)) is defined as the product of \( K_2 \) \( q_e^2 \) and expressed as

\[
\text{Rate} (h) = K_2 q_e^2
\]

Where \( K_2 \) and \( h \) values were determined from the slope and intercept of the plots \( t/q \) against \( t \) (Fig 8). The straight line in the plot of linear pseudo-second order equation shows good agreement of experimental data with the pseudo second order kinetic model for different initial metal ion concentrations. The values of the experiments and correlation co-efficient are also presented (Table. 2). The correlation co-efficient of all examined data were found as \( R^2 = 0.999 \). This shows that the equation model is based on the assumption of chemical sorption between adsorbent and adsorbate and provides the best correlation of the data (Dinesh Mohan et al., 2006) of metal on Araucaria cookii. The sorption rate (\( h \)) has been widely used for evaluation of sorption rates (Ko et al., 2004). In the present study of copper the value of \( h \) is 15.61 and \( K_2 \) is 0.9473. Similar observations have been made in the biosorption of Copper and cadmium on Kraft lignin (Dinesh Mohan et al., 2006).

**Isotherm Studies**

Biosorption of metal ions can be classified into two types: the Langmuir Model in which the amount of metal uptake by the biomass reaches equilibrium and the Freundlich Model in which the amount of metal uptake by the biomass increases with time (Chang and Hong, 1994). The equilibrium between an adsorbate on the active sites of an adsorbent and the adsorbent remaining in aqueous phase is usually presented in the form of Adsorption Isotherm. The effect of contact time on the biosorption of Cu (II) by A. cookii was studied and the results are shown in (Fig. 9).

Adsortion experiments were carried out at different initial Cu (II) concentrations ranging from 25 to 350 mg L\(^{-1}\). The adsorption efficiency decreased with increasing initial concentration of the metal ions (Deepa et al., 2013). Langmuir Isotherm is true with the homogeneous layer of metal adsorption and the linearized formula determined by slope and intercept is (Langmuir, 1918).

\[
\frac{C_e}{q_e} = \frac{1}{b Q_{max}} + \frac{C_e}{Q_{max}}
\]

Where \( b \) and \( Q_{max} \) are Langmuir constants expressing the equilibrium constant of adsorbent and adsorbate, respectively A plot between \( C_e/q_e \) and \( C_e \) is shown in (Fig. 9) and the values of \( Q_{max} \) and \( b \) are 19.96 and 0.05 respectively as shown in (Table 3). Langmuir model easily fits with copper ion adsorption on A. cookii with correlation coefficient of 0.9824.

As Langmuir model describes a monolayer, Freundlich isotherm model describes a multi layer adsorption with the assumption of heterogeneous surface in which the energy, a
term in the Langmuir equation varies as a function of the surface area. The model can be represented as (Freundlich and Helle, 1939)

$$q = K_f C_e / 1/n$$

(11)

And the linearized form can be represented as

$$\log (q) = \log (K_f) + 1/n \log (C_e)$$

(12)

Where $q$ is the amount of metal adsorbed per unit weight of the adsorbent at equilibrium (mg $q^{-1}$), $C_e$ is the equilibrium of metal concentration (mg L$^{-1}$), $K_f$ is the measurement of adsorption capacity (mg/g) based on Freundlich isotherm, $n$ is the adsorption equilibrium constant.

A linearized plot of $\log C_e / q_e$ and $\log C_e$ is shown in (Fig. 10).

When compared to the Langmuir, Freundlich model shows higher correlation coefficient and better fit as calculated from the slope and intercept. The values of $K_f$ and $n$ were 18.20 and 1.027 as shown in (Table 3). According to this model, value of $n$ between 1 and 10 corresponds to favorable adsorption (Febrianto et al., 2009).

**RSM approach for adsorption optimization**

The CCD model was used to evaluate the parameters for optimization of Copper adsorption onto $A. cookii$. The significance of the variables and their interactions were studied using analysis of variance which was fitted to second polynomial equation.

The parameter fitted to second polynomial equation is

$$\% \text{ Biosorption of Cu (II)} = +80.35 + 0.0208 * AB + 0.0136 * AC - 0.176 * AD + 0.0196 * AE - 0.00905 * BC + 0.118 * BD - 0.0131 * BE + 0.0769 * CD - 0.00855 * CE + 0.111 * DE$$

The analysis of variance (ANOVA) for the sorption of copper ions onto $A. cookii$ is given in (Table 5). The adequacy (statistical significance) of quadratic model was tested through F- and P values. A large F-value indicates that most of the variations can be explained by a regression equation whereas low values of “Prob > F” less than 0.05 indicate model terms are statistically significant (Myers and Montgomery, 2002). The Fisher’s F-value of 30.19 implies the model is significant. In this case A, B, C, D and E, are significant model terms (Table 4). The high coefficient of determination (R-Square value - 0.9042) showed that the quadratic polynomial was highly significant and sufficient to represent the actual relationship between the biosorption (%) and the significant variables. Low P value indicates the higher significance of the variables and hence it can be used for further analysis.

The variables and their levels selected for the study of Biosorption were: Contact time (5-90 min), Biomass (0.1-3.5 g), ion concentration (25-350 mg L$^{-1}$), Particle Size (100-400 µm) and pH(1-10). These are based on the preliminary experiments using conventional optimization method as shown in Table 1. The variables and their respective levels are presented in Table 4, which represent the actual experiments carried out for developing the model. The data obtained were fitted to a second-order polynomial equation. Subsequent regression analyses, analyses of variance (ANOVA) and response surfaces were performed using the Design Expert Software (Version 8.0.7.1).

**CCD optimization of the selected parameters**

The quadratic optimization of the selected parameters was performed using the Response Surface Methodology (RSM). Two parameters were plotted at any one time on the $x_1$ and $x_2$ axes, respectively, with other remaining parameters set at their centre points.

**pH v/s Biomass**

RSM (Fig 11) shows the interaction between the effect of pH and adsorbent dose. The maximum optimum adsorption set at the centre points was at pH 5.5. The maximum removal of copper was 90.42%, which was obtained at biomass of 2 mg L$^{-1}$.

**pH v/s size**

The effects of pH and size are shown in (Fig 12). A response surface plot for interaction between pH and size was generated and pH was kept constant. The optimum size for the removal of copper was 250 µm.
**pH v/s contact time**

Fig. 13 shows the interactive effect of pH and contact time using copper solution onto A. cookii. The solution was kept constant for pH, metal ion concentration, particle size and adsorbent mass. The agitation time kept for the aqueous solution was from 5 to 90 min. In the initial stage the adsorption went on increasing from 5 min and at the maximum adsorption it was stagnant and no considerable change throughout the experiment was observed. The optimum adsorption at the centre point of copper was in 47.5 min.

**pH v/s concentration**

The adsorptions of Cu (II) with effects of pH and metal ion concentration have been shown in (Fig. 14). A response surface plot with the interaction of these parameters was generated with pore size and biomass. The maximum removal of copper was 90.42% at the centre point of 187.50 mg L\(^{-1}\) concentration.

The response surface plots for the biosorption of copper with effects of pH, particle size, metal ion concentration, contact time and adsorbent mass have been shown in (Fig.11-16). Second order polynomial models with two tests of parameters were represented in the number of combinations which is maintained at zero levels. Response surfaces were performed using the Design Expert Software (Version 8.0.7.1). The maximum adsorption for optimal set of copper onto A. cookii is pH 5.5, metal ion concentration 187.50 ppm, particle size 250 \(\mu\)m, contact time 47.5 min and adsorbent dose 1.5 mg L\(^{-1}\). By using the optimum conditions for the biosorption of copper the maximum removal of copper achieved was 90.42%.

**CONCLUSIONS**

The main aim of this study was to determine the optimum conditions to remove Cu (II) by Araucaria cookii in aqueous solution. The fit model was checked by correlation coefficient (\(R^2 = 0.9042\)) for the obtained quadratic model indicates the high correlation between observed or the experimental value of response as response value predicted by the statistical model. Kinetics was described by pseudo first order and pseudo second order reaction and isotherms by Langmuir and Freundlich equation with correlation coefficient. The maximum adsorption of copper using RSM was 90.42% and the parameters were optimally set as follows: pH- 5.5, ion concentration-187.50 mg L\(^{-1}\), contact time-47.5 min, Biomass-1.5 g, and particle size-250 \(\mu\)m. Hence Kinetics and Isotherm data provided would be useful for the fabrication and design of experimental set up. Araucaria cookii which is easily available in nature is best suited as a biosorbent for the removal of copper from industrial effluent.

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**References**


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