

Fourier Transform Infrared (FTIR) Analysis of *Trapa bispinosa*: A Novel Adsorbent for the Removal of Cu (II) from Aqueous Solution in Chemically Treated Form

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Summary: Current study explored biosorption mechanism and kinetics of Cu (II) onto *Trapa bispinosa* peels (TBPs) biomass in surfactant (SDS, CTAB, and Triton X-100), organic acid (CA, TA, AA) and in Native (N) form during batch experiment. Equilibrium sorption capacity was determined at various solution parameters like pH, contact time and initial concentration. Increment in sorption capacity was observed with increase in pH until maximum is achieved at pH 5. Optimized time and concentration were 120 minutes and 100 ppm respectively. Best fitted pseudo-second order kinetic model on the data showed that sorption of Cu (II) is rate-controlling. Sorption capacity (mg g^{-1}) for Cu (II) ions increased while % removal decreased. SDS TBPs in comparison to all TBPs show highest sorption tendency as after SDS pretreatment TBPs surface is loaded with the negatively charged groups that provide more attachment sites for Cu (II) ions. Langmuir isotherm give best description of monolayer adsorption over the surface as it fitted better to data. FTIR analysis showed presence of functional groups like amine, carbonyl and hydroxyl groups. Ionization states of these functional groups are changed with pH.

Keywords: Biosorption, *Trapa bispinosa* peels (TBPs), Equilibrium sorption, SDS.

Introduction

Beginning of industrial sector is considered as one of the world most forceful commercial sector presenting huge opening for economic expansion. However, expansion in industrial sector is not only growing the world economically but also contaminating the world's atmosphere with the addition of toxic chemicals (heavy metals) into the environment [1]. Heavy metals are the main group of inorganic contaminants, have been reported to be carcinogenic [2]. Environmental contamination due to heavy metals is hazardous due to its accumulation and persistence in the ecosystem [3]. Occurrence of heavy metals in marine environment results in severe damage not only in aquatic life but also have rigorous consequences on humans brain, reproductive, nervous system failures and tumor formation [4]. Main industrial sources of heavy metal-bearing effluents in water resources include electroplating, chemical, metal-finishing and wood preservatives. Due to consequent interference of heavy metals with many beneficial uses of water has led to the development of laws to limit discharge of these metals from industrial effluents [2].

Cu (II) a major toxic heavy metal coming from electrical, electroplating, and metal finishing industries in the form of hydrolyzed ions or in the form of organic complexes [5]. At certain concentration of approximately 0.002 g.l^{-1} it becomes carcinogenic for living beings [6]. In human beings skin irritation, skin cancer, liver malfunctioning occurs due to excessive intake of Cu (II) [7, 8]. Permissible limit sets by The World Health Organization (WHO) for copper in drinking water is 2 mg L^{-1} [9].

In Pakistan major issue from last 20 years is the release of heavy metals into ground waters that is affecting regulatory status as well as economics of Pakistan. Thus making the elimination of heavy metals from polluted water essential [10]. Hence to sort the problem of ecological/ environmental pollution caused by Cu (II) different techniques like coagulation, exchange with ions, chelation are used but these are too expensive having insufficient efficiencies to remove metals at low concentration [11, 12]. However application of such techniques are restricted due to techno economical constrained, new separation techniques are mandatory for removing of

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metal from atmosphere or reduce them to tolerable levels inexpensively. Among aforementioned methods adsorption is an economical and efficient, especially when the source of the adsorption is economically feasible biomass.

The term biosorption is used to describe the binding of metal ions to dead or living biomass without involvement of metabolic process. It is a fast, economical, effective and eco-friendly technology, in contrast to expensive conventional techniques [2]. Biosorption mechanism involves physicochemical interaction between surface groups of biosorbent and metals that result either in formation of organo-metallic complexes, or simply exchange reaction between metals and functional groups [13]. Convention of using wastes produced from industries and agro waste is a cost effective option for producing low cost biosorbent helpful in the removal of metals from impure water. As a result orange wastes [14], papaya wood [15], grape stalk waste, broad bean, and peas [16], lemon peels, grape fruit peels, orange peels, apple kernel, and grape skins [17], coconut shell powder [18], coconut copra meal [19], and mango peel waste [20] have been evaluated for their sorption property.

In extension of the search for new and more efficient biosorbent for heavy metals removal from waste waters, *Trapa bispinosa* peels, a primary food processing industry waste and novel plant material, was studied as sorbent helpful in removing heavy metal like Cu (II) in form of ions from aqueous solution. *Trapa bispinosa* (Water chestnut) is a marline plant fruit (edible). 3750 kg is the yield per acre of this plant crop approximately [21]. *Trapa bispinosa* fruit is plump with firm, creamy colored, unblemished flesh and a brown outer peel. *Trapa bispinosa* is reported to be beneficial in cases of constipation, gas and intestinal putrefaction. It is a low-calorie food, containing ample protein, calcium, phosphorus, iron, and vitamins B and C. High carbohydrate content of it makes it a very good source of starch for both domestic and industrial uses [22]. An important ground about *Trapa bispinosa* peels (TBPs) adsorbent is that it is the waste by product which even constitutes disposal problem. Hence we are using a waste in treatment of another waste.

TBPs have a potential to sequester metals from the aqueous solution as being the plant origin biomaterial it contain hemicellulose, lignin, lipids, proteins and starch. These surface groups play an important role in sequestration of heavy metal via process of complexation [23]. The modification of biomass surface has emerged as a very important

field towards checking the specificity and binding capacity while retaining the bulk phase characteristics. Consequently, the plan of our study is to assess the biosorption potential of plant origin biomaterial TBPs for the removal of Cu (II) ions from aqueous solutions in Native, Surfactant and Organic acid modified form. The study includes an assessment of the effects of various parameters like initial metal ion concentration, pH and kinetics. The kinetic models and equilibrium isotherm models related with the process were fitted. FTIR analysis will reveal the functional groups of Native, Surfactant and Organic acid modified TBPs.

Results and discussion

Effect of Pretreatment:

Binding sites involved in the removal of metals are thought to be hydroxyl and carboxyl functional groups present in cellulose and pectin, when plant origin biomaterial is used for sorption study [24]. Evaluation of the results from Fig. 1 clearly indicated that the sorption capacities of the adsorbents towards Cu (II) are in the order SDS TBPs (91.05) > Triton X-100 TBPs (85) > CA TBPs (84) > AA TBPs (77) > CTAB TBPs (71) > TA TBPs (67.5) > N TBPs (59.3). SDS TBPs in comparison to Native and all other modified biomasses show highest sorption tendency mg g^{-1} because its pretreatment was performed for orientation of negative charged head of SDS on the sorbent surface hence greater sorption of Cu (II).

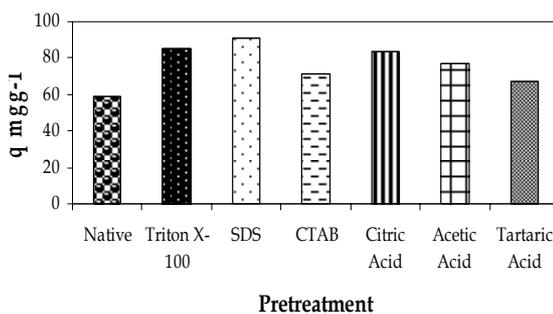


Fig. 1: Effect of Pretreatment.

Effect of pH

Initial pH of solution is the major parameter that not only affects the attachment sites in biosorbent but also the solution chemistry hence affecting the sorption mechanism [25, 26]. Fig. 2 depicts a sharp increase in the Cu (II) sorption as pH increases from 2 to 6 and precipitations was observed at pH 6, hence pH 5 was taken as suitable pH for Cu

(II) sorption. Cu (II) may most likely be bound on the surface of the TBPs via ion exchange mechanism [27].

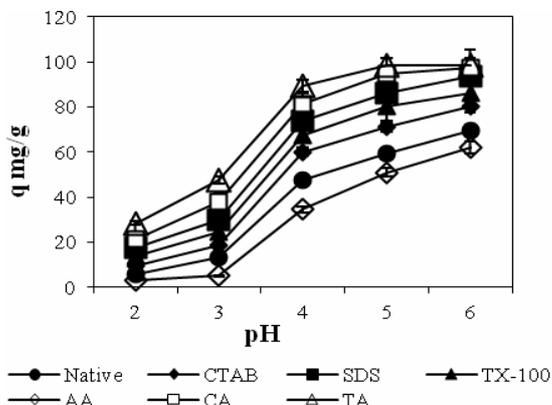


Fig. 2: Effect of pH.

The low sorption of Cu (II) at pH 2 is apparently due to the high acidity of solution, due to the higher availability of H⁺ ions net charge on the binding sites is positive due to protonation that reduces the number of negatively charged sites availability for the binding of metal ions hence results in lower sorption of Cu (II) [27]. In addition, with the increment in pH, deprotonation of adsorbent cell wall resulted in high availability of binding sites for the metal to bind. At optimum pH value surface of TBPs is favorable for attachment because of negative charge that is created due to the dissociation of the functional groups [28] and favorable to the sorption of Cu (II) that is major ion in the solution at pH 5 [29].

Effect of Initial Metal Concentration

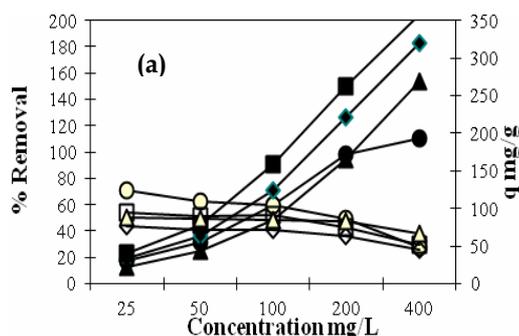
Fig. 3(a) and (b) show that the sorption capacity (q mgg⁻¹) of TBPs increases while % removal decreases with increase in initial Cu (II) concentration. The reaction of metal ions in solution with the sorbent may be described as:



M= Metals, n= charge and B = active sorption sites of the adsorbent [20].

Increase in metal sorption at low concentrations due to higher availability of metal ions and binding sites on the biomass for sorption [30, 31]. However, at higher concentrations, diffusion of metals is at slower rate because of higher ions and lower availability for binding [32]. Higher the concentration higher will be collision between the

metal ions and the sorbent hence all metal ions may interact with the adsorbent and be removed from the solution but as the concentration of metal ions increases these active sites reduces. Consequently, the sorption approached saturation stage as the fixed number of binding sites were exhausted and hence decrease in % removal observed [33, 31].



(□) % Removal SDS (●) q for SDS (◇) % Removal CTAB (◆) q for CTAB (○) % Removal Native (●) q for Native (Δ) % Removal TX-100 (▲) q for TX-100

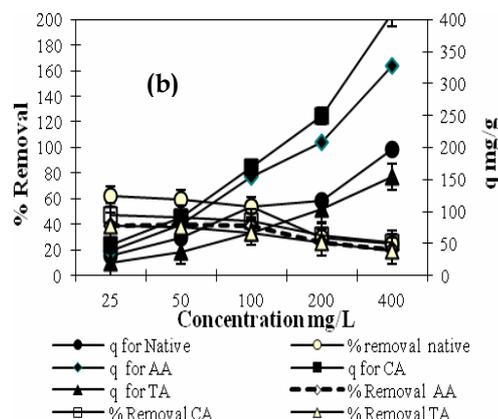


Fig. 3: Effect of Concentration.

Equilibrium Studies

Modeling of equilibrium data is essential for the industrialization of biosorption since it give information for the comparison among different biomaterials under different operational conditions, designing and optimizing operating procedures [2]. Equilibrium data was fitted on the Langmuir, Freundlich and Temkin isotherms models for the evaluation of relationship between the metal sorption capacity (q_{eq}) and concentration of metal ions (C_{eq}) at equilibrium. Isothermal models are classical in describing the equilibrium between initial and final

metal ion concentration at equilibrium at constant temperature [20].

Langmuir Isotherm

Theoretically Langmuir isotherm relies on the physical and chemical interaction (or both) postulated to occur between the solute and the available vacant sites on the sorbent surface described below:

$$\frac{C_e}{q_e} = \frac{1}{X_m K_L} + \frac{C_e}{X_m} \quad (2)$$

C_e = equilibrium metals concentration (mgL^{-1})
 X_m = complete monolayer (mg g^{-1})
 K_L = Langmuir constant
 q_e = Sorption capacity (mg g^{-1})

Langmuir isotherm describes the sort of attachment over the adsorbent surface. It describes the homogeneity of adsorbent surface. According to this model after saturation of surface no further attachment of metal ions occurs, and this attachment is at particular surface [32].

Freundlich Isotherms

The Freundlich isotherm describes heterogeneity of sorbent surface with the help of following experimental equation given below:

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

K_F, n = Freundlich constants

Temkin Model

It can be described as follow

$$Q_e = B \ln K_T + B \ln C_e \quad (4)$$

This model was obtained with consideration of adsorption interaction and adsorption substances which was attained by designing diagram $\ln C_e$ based on Q_e .

B = equilibrium binding constant (L g^{-1}),
 \ln = Temkin constant (kJ mol^{-1}),
 T = absolute temperature (K) [34].

Table-1 and Fig. 4 and 5 elucidate the comparison of Freundlich, Langmuir, Temkin isotherm constant and their correlations coefficients (R^2) with the experimental q_{exp} . Langmuir isotherm

model fitted better on data than Freundlich isotherm model as proved by R^2 values that was higher for Langmuir isotherm model than for Freundlich model which is an indication of the applicability of the Langmuir isotherm for the Cu (II) sorption by native and all other pretreated biomasses under observation.

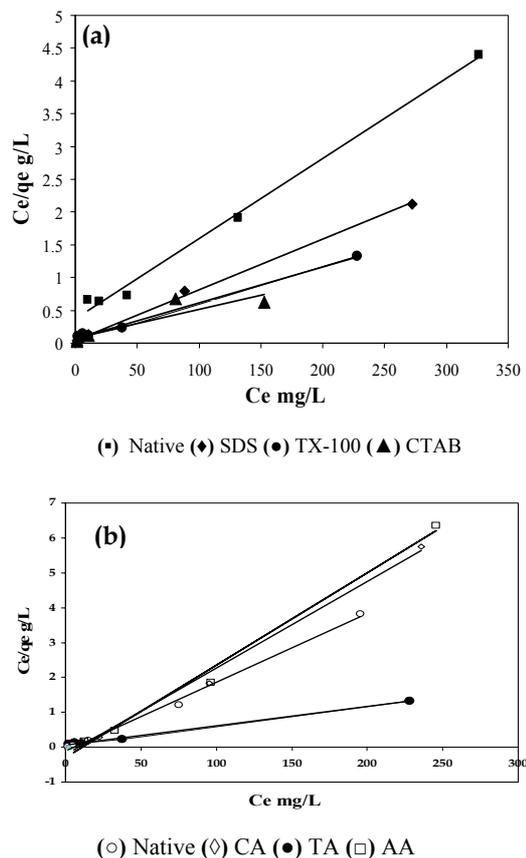


Fig. 4: Equilibrium sorption Langmuir isotherms for Cu (II)

Effect of Contact Time

Fig. 6 shows Cu (II) sorption, as a function of contact time. Fig. 6 depicts that sorption of Cu (II) occur in two phases. It was observed that rate of sorption was rapid during initial 120 min and after that sorption process proceed slowly until reaches up to the saturation. Higher initial sorption was likely due to higher availability of extra cellular binding sites initially resulting in high metal ions interaction with the sites, hence a higher rate of adsorption [35]. Whereas slow sorption phase likely resulted from intracellular binding and also due to slower diffusion of solute into the interior of the adsorbent [36].

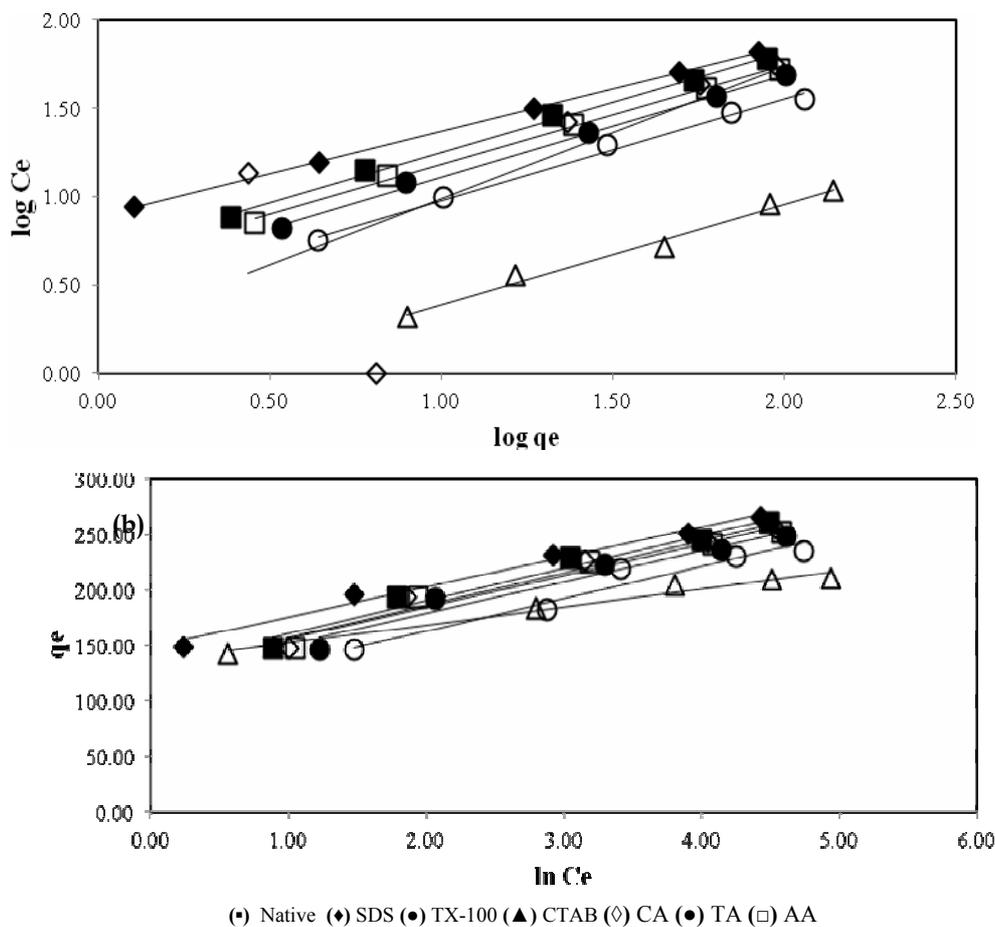


Fig. 5: Equilibrium sorption Freundlich isotherms (a) Temkin model (b) for Cu (II).

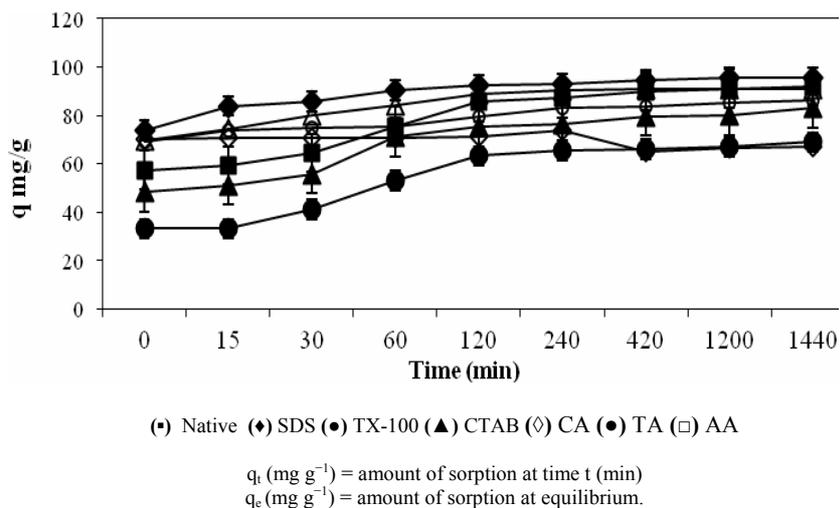


Fig. 6: Effect of contact time onto Cu (II) sorption by TBPs.

Table-1: Linearized Langmuir, Temkin and Freundlich isotherm model for Cu (II) sorption by TBPs.

Biosorbent	Langmuir isotherm model			Experimental	Freundlich isotherm model			Temkin model
	X_m mgg ⁻¹	K_L mgg ⁻¹	R^2		q_{eq} mgg ⁻¹	K_f mgg ⁻¹	R^2	
n TBP	129.87	0.0212	0.9937	110	21.19	7.22	0.9411	0.875
SDS TBP	250	0.052	0.997	183	23.17	2.36	0.9729	0.974
CTAB TBP	243.90	1	0.9966	204	12.51	2.28	0.9247	0.973
Triton X-100 TBP	360.49	0.0217	0.9975	269	10.51	2.98	0.9726	0.987
Acetic acid TBP	250	0.0143	0.9263	271.4	204.5	8.851	0.8378	0.960
Citric acid TBP	172.41	0.0619	0.9944	328.7	164	23.54	0.9595	0.934
Tartaric acid TBP	185.18	0.0182	0.9864	294.3	154.5	9.078	0.9738	0.974

Kinetic Modeling

Kinetics of metal sorption determines the time during which adsorbent show higher affinity for metal. Kinetics equations describe the attachment of metals onto adsorbent surface. Experimental data was fitted to the kinetic models like pseudo-first order and pseudo-second order to study the mechanism of Cu (II) sorption.

Pseudo-first-order equation [35] is generally expressed as follows:

$$\text{Log}(q_e - q_t) = \frac{\log q_e - k_1}{2.303} \times t \quad (5)$$

k_1 (min⁻¹) = Rate constant for pseudo-first-order adsorption

The pseudo-second-order equation, can be expressed by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \times t \quad (6)$$

k_2 (gmg⁻¹ min⁻¹) = adsorption rate constant of pseudo second- order.

Table 2 showed that R^2 values for pseudo-first order kinetics are lower than R^2 values of pseudo-second-order kinetic model that suggest the applicability of pseudo-second-order expression as the best fit kinetic expression over data. It is clear from Table 2 that q_e values predicted using the pseudo-first order kinetics equation fails to be in agreement with the q_{exp} (experimental adsorption capacity). This conforms that it is not wise to use this model in predicting the sorption kinetics of Cu (II) sorption by TBP. Conversely, the q_e estimated from

the pseudo-second-order kinetic model was found to be in agreement with the q_{exp} . Applicability of pseudo-second-order kinetic model proved that sorption of Cu (II) is rate controlled [37, 20]. Fig 7 is well supporting the above data.

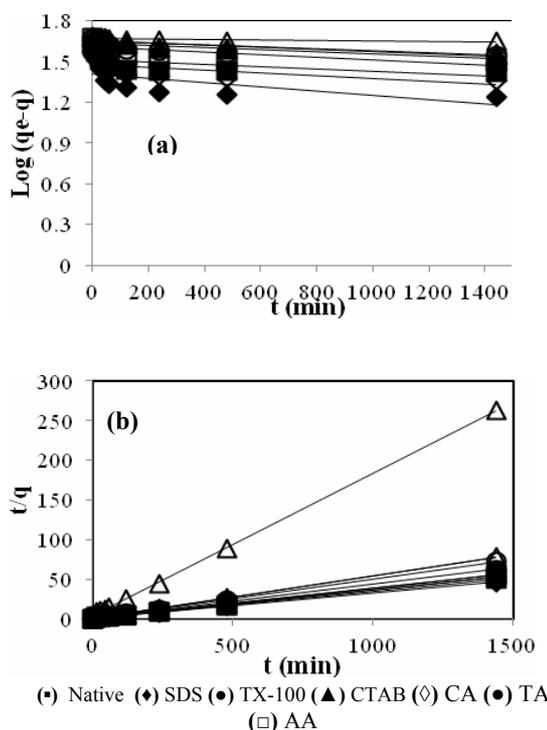


Fig. 7: (a) and (b) Pseudo-First order model and Pseudo second order Model for Cu (II) sorption

Table-2: Pseudo-First order and Pseudo-second order models for Cu (II) sorption by TBP.

Biosorbent	Pseudo-First order model			Experimental	Pseudo-second order model		
	q_e mgg ⁻¹	K_1 min ⁻¹	R^2		q_e mgg ⁻¹	K_2 min ⁻¹	R^2
n TBP	32.18	1.38×10^{-3}	0.655	89.46	89.28	8.52×10^{-4}	0.9996
SDS TBP	3.58	1.84×10^{-3}	0.605	94	60.24	4.49×10^{-3}	1
CTAB TBP	6.01	4.6×10^{-4}	0.466	58	58.13	9.08×10^{-4}	0.9992
Triton X-100 TBP	2.76	3.25×10^{-3}	0.707	99.2	99	0.19	0.9999
Acetic acid TBP	42.16	9.21×10^{-4}	0.6339	78.125	77.5	9.61×10^{-3}	0.9998
Citric acid TBP	34.09	9.2×10^{-4}	0.6575	84.74	85.1	8.30×10^{-4}	0.9999
Tartaric acid TBP	48.95	6.9×10^{-4}	0.4628	68.02	65.1	1.35×10^{-3}	0.9998

Fourier Transform Infrared (FTIR) Analysis

All materials contain some sort of functional group on their surface same is the case with TBPs. These functional groups are involved in sorption of metal, and can be identified by FTIR spectrophotometer. These functional groups absorb IR radiation at particular wave length and hence can be identified [38]. So FTIR analysis of TBPs in Native and organic acid pretreated form were taken in 400-4000 cm^{-1} range. The main functional groups are Amine, Carbonyl Hydroxyl group, and Carboxylic groups. Spectra of N TBPs displayed a number of absorption peaks, indicating the complex nature of the biomass examined. The broad absorption peak around 2342 and 2364 cm^{-1} is indicative of the existence of presence of Ethylene group. The peak observed at 3748.09 and 3681.58 cm^{-1} can be assigned to the stretching vibration of (N-H) Amine group. While the peaks observed in the region of 1700-1500 cm^{-1} indicate the presence of carbonyl group. Spectra of Cu (II) loaded biosorbent show absence of peaks in range of 3748.09 and 3681.58 cm^{-1} which indicate involvement of Amine group in sorption of metal. Peaks observed at 604.28 cm^{-1} indicate presence of C-Br group. Changes in the FTIR spectra were observed after copper biosorption. Similar type of difference was observed in the spectra of AA, CA and TA pretreated biosorbent and Cu loaded AA, CA and TA TBPs spectra. In the spectra of AA, CA and TA pretreated biosorbent peaks were observed in the wave number range of 644.18-1522.15 cm^{-1} , 608.71-834.85 cm^{-1} , 626-3850.08 cm^{-1} respectively. While for the Cu loaded AA, CA and TA spectra these peaks were shifted to 701.83 - 1548.75 cm^{-1} , 630.88-2360.20 cm^{-1} and 670.79-812.68 cm^{-1} respectively. This type of shift is indicative of involvement of these functional groups in process of sorption. Peaks in the range of 800-855 cm^{-1} are due to C-N bond vibration while at 2300 cm^{-1} are due to C=N bond vibration [39].

Experimental

Preparation Trapa bispinosa peels (TBPs) biosorbent

Trapa bispinosa peels (TBPs) used in the present experiments was obtained from the waste of starch producing industry with reference to National Institute of Food Science and Technology, University of Agriculture, Faisalabad, Pakistan. The used sample was ground, screened, selecting particles of 0.255 mm in size. The modified TBPs sample was prepared by surfactant and organic acid treatment, that was carried out by placing the TBPs sample in contact with 0.1M Sodium dodecyl sulphate (SDS), Triton X-100 (TX-100), Cetyl trimethyl ammonium bromide (CTAB), Tartaric acid (TA), Citric acid

(CA), and Acetic acid (AA) for 24 h at 120 rpm., with constant shaking for 24 h. The solid/liquid ratio was 10g /100 mL. The slurry was allowed to settle for 48 h. It was then filtered, washed with DD H_2O , dried at 60 $^{\circ}\text{C}$ for 6 h until constant weight is achieved. It was ground and screened. Then the TBPs particles of 0.255mm were selected and sealed at room temperature in bottle along with untreated (Native) sample for further use.

Cu (II) Stock Solution

Cu (II) stock solution 1000 ppm was prepared by dissolving weighed amount of copper sulphate ($\text{CuSO}_4\cdot\text{H}_2\text{O}$) powder in distilled water. Dilutions made from Cu (II) stock solution when required. pH was adjusted to 5 before sorption experiments with 0.1 N NaOH and HCl.

Sorption Experiments

Sorption capacity of TBPs was evaluated in subsequent way:

The prepared solutions i.e. 100mL of 100 ppm Cu (II) solution with pH values ranging from 2 to 6 were relocated in a 250 mL conical flask along with 0.1 g of N TBPs, SDS TBPs, CTAB TBPs, AA TBPs, CA TBPs, TA TBPs, Triton x-100 TBPs, sealed and shake in a temperature (26 $^{\circ}\text{C}$) controlled shaker at 120rpm for 24 hours, remaining concentration of metal was analyzed using Atomic Absorption spectrophotometer.

Concentration of Cu (II) ions was varied from 25-400 mgL^{-1} in order to determine the optimum biosorption concentration. It was assessed by contacting 0.1 g of N TBPs, SDS TBPs, CTAB TBPs, AA TBPs, CA TBPs, TA TBPs, and Triton x-100 TBPs with Cu (II) metal solution of different initial concentration ranging from 25-400 mgL^{-1} . Collected sample was analyzed after proper dilution using Atomic Absorption Spectrophotometer (AAAnalyst Perkin Elmer).

Kinetics experiments were performed by contacting 0.1g of of N TBPs, SDS TBPs, CTAB TBPs, AA TBPs, CA TBPs, TA TBPs, Triton x-100 TBPs with 100mg/100 mL of Cu(II) metal solution in 250 mL conical flask, shaken on an orbital shaker at the 120rpm, 1 ml of sample was pipette out using 10 ml syringe at time interval of 0,15, 30, 60,120, 240, 480 and 1440 min. Collected sample was analyzed after proper dilution using Atomic Absorption Spectrophotometer (AAAnalyst Perkin Elmer).

The percent sorption of metal ions onto N TBPs, SDS TBPs, CTAB TBPs, AA TBPs, CA TBPs, TA TBPs, and Triton X-100 TBPs was calculated for each sample using:

$$\% \text{ Sorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (7)$$

C_i = initial metal ion concentration (mg dm⁻³)

C_e = equilibrium metal ion concentration in (mg dm⁻³)

FTIR Analysis

FTIR analysis was carried out for the evaluation of functional groups involved in sorption, N TBPs, SDS TBPs, CTAB TBPs, AA TBPs, CA TBPs, TA TBPs, Triton X-100 TBPs were analyzed using FTIR spectrophotometer.

Conclusion

Biosorption is a cost effective method for the removal of heavy metals and other pollutants from aqueous solution as it utilizes the agro waste or any other industrial waste as a biosorbent, further its sorption tendency can be enhanced by the chemical treatments. FTIR study reveals the functional groups thought to be involved in sorption process. Best results were obtained by SDS treated TBPs. From present research it was concluded that sorption process is pH, Time dependant and also metal concentration.

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