Bioremediation of Cu (II) from aqueous solutions onto *Acacia nilotica* tannin gel by batch mode study

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Abstract-The biosorption of Cu (II) from aqueous solutions by Acacia nilotica tannin gel (TGAN) was investigated as a function of initial pH, contact time, initial metal ion concentration and tannin extract concentration. The aim of this study was to understand the mechanisms that govern copper removal and find a suitable equilibrium isotherm and kinetic model on TGAN using a batch reactor. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin equations. The equilibrium data fit well in the Langmuir isotherm. The experimental data were analyzed using four sorption kinetic models, the pseudo-first-order, pseudo-second-order, Elovich and the Intraparticle diffusion equation to determine the best fit equation for the biosorption of copper ions onto Acacia nilotica tannin resin. Results show that the pseudo-second-order equation provides the best correlation for the biosorption process than pseudo first order, whereas the Elovich equation also fits the experimental data well. Total phenolic content was found to be 490 g/mg for tannin. The FTIR results of tannin and tannin resin of acacia nilotica are also reported. The Taguchi method was used to find the optimum conditions for tannin resin preparation.

Index terms - *Acacia nilotica*, Tannin gel, Kinetics, Isotherm, Taguchi method, SEM studies, Binary and tertiary studies.

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1. INTRODUCTION

The remediation of several pollution problems is a target of many researchers nowadays. Technical ways of solving environmental concerns and menaces such as the dumping of surfactants, dyes, pharmaceuticals and other hazards are available long time ago, but making them cheaper and sustainable is still a challenge [1]. Heavy metal ions such as Pb, Cd, Hg, Cr, Ni, Zn and Cu are non-biodegradable, can be toxic and carcinogenic even at very low concentrations, and, hence, usually pose a serious threat to the environmental and public health [2].

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. The production of copper has lifted over the last decades and due to this copper quantities in the environment have expanded. Copper is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives and it is highly toxic [3].

Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants have a chance of survival. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [4]. The main techniques that have been used on copper content reduction from industrial waste are chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis and solvent extraction [5, 6]. However, these methods require high capital investment as well as creating sludge disposal problem [7] and also a limitation in the pH range, they do not appear to be highly effective.

Among these various treatment techniques, activated carbon adsorption is one of the most commonly used due to its high efficiency and easy operation [8, 9]. Many researchers suggest a cost effective process, such as biosorption, for removing heavy metals from wastewaters [10]. Biosorption, a biological method of environmental control can be an alternative to conventional waste-treatment facilities [6].

To remove some heavy metals there are other studies in which various waste biomaterial sources in different part of the world are used as adsorbent. For instance; tea waste adsorbent for Cu and Pb [11], pectin compounds for Pb [12],lichen (Cladonia furcata) biomass for Pb and Ni [13], diethylenetriamine functionalized polymeric adsorbent for Cu and Pb [2], crab and area shell biomass for Cuand Pb [14], olive stone waste for Cu, Pb, Cd and Ni [15], tamarind wood activated carbon for Pb [16], treated sawdust (Acacia arabica) for Cr(VI), Cu and Pb [17], anaerobic granular biomass for Cu, Pb, Cd and Ni [10], formaldehyde polymerized banana stem for Pb[18], Cassia grandis seed gum-graft-poly(methylmethacrylate) for Pb [19].

Tannins, natural biomass containing multiple adjacent hydroxyl groups and exhibiting specific affinity to metal ions, can probably be used as alternative, effective and efficient adsorbents for the recovery of metal ions. Several studies have been proposed in the literature about the use of modified tannin resins, in relation with heavy metal biosorption from water, researchers synthesized adsorbents from commercial tannins and applied them to remove heavy metals from wastewater, such as uranium [20],americium [21], chromium [22], copper [23], lead [24], thorium[25], gold [26] and palladium [27]. These studies illustrate that it is possible to remove heavy metals from wastewater with tannin adsorbents.

Tannins are an important class of secondary plant metabolites, water-soluble polyphenolic compounds of molecular weight ranged between 500 and some thousands Daltons. There are three kinds: hydrolysable, condensed and complex tannins [28]. However, tannins are water-soluble compounds, thus when they are used directly as an adsorbent for recovery of metals from aqueous systems, they have the disadvantage of being leached by water. To overcome this disadvantage, attempts have been made to immobilize tannins onto various water-insoluble matrices [29].

The Taguchi method involves reducing the variation in a process through robust design of experiments. The overall objective of the method is to produce high quality product at low cost to the manufacturer. The Taguchi method was developed by Dr. Genichi Taguchi of Japan who maintained that variation. Taguchi developed a method for designing experiments to investigate how different parameters affect the mean and variance of a process performance characteristic that defines how well the process is functioning.

The objective of this study is to systematically examine adsorption mechanisms, adsorption isotherms, adsorption kinetics and properties of a tannin gel adsorbent extracted from *Acacia nilotica* tannin (TGAN) for removal of Cu^{2+} from aqueous solution, and also find biosorption of binary and tertianary metal solution onto the surface of *Acacia nilotica* tannin gel (TGAN).

2. EXPERIMENTAL METHODS

2.1 TANNIN EXTRACTS

100g of *Acacia nilotica* leaves powder were cleaned and they were put in 600 mL of distilled water. Then 5g of NaOH were added and the mixture was stirred in magnetic stirrer at 90°C for 1 hour. Solids were separated by filtration and liquid fraction was dried in oven (65°C) for overnight. The resultant was considered as tannin extract. Total phenolic content of tannin content was calculated.

2.2 TANNIN GEL PREPARATION (TGAN)

Tannin gels were prepared according to the basis of Nakano et al., [30]. Five grams of tannin extract were dissolved in 32 mL of 0.125 mol L^{-1} NaOH and 30mL of distilled water at 80°C. When mixture was homogeneous, certain amount of aldehyde was added and reaction was kept at the same temperature for 8h until polymerization was considered completed. Then, the apparent gummy product was lead to complete evaporation of water remain and dried in oven (65°C) overnight. After drying, tannin rigid gels were crushed and sieved to produce tiny diameters. They were washed successively with distilled water and 0.01 mol/L HNO_3 to remove unreacted sodium hydroxide. Finally, the adsorbent was dried again in oven at 80°C [31].

2.3 GENERAL ADSORPTION TEST

In order to test the ability of each tannin gel in the removal of heavy metals, dyes or surfactants, a standard protocol of adsorption was developed. Samples of aqueous solutions with the corresponding pollutants (Cu^{2+}) were put into 100 mL-flask under strict thermal control. A fixed amount of tannin gel was added to each flask (0.1 mg) with 50 mL volume of contaminated aqueous solutions. Shaker was applied for an hour and the absorbance of model compound before and after trial was determined. Triplicate also be done and the percentage of that adsorption is 43.5% and 4% error was noticed.

2.4 STATISTICAL PROCEDURE

Design of experiments was carried out by using SPSS 14.0 for Windows [32] and L16 matrix by Taguchi method [33].Tannin gel was prepared according to this as taking 4 variables. Upto 16 different combinations regarding three variables were attempted. The feasible combinations were just nine of them; the rest did not gelify. As long as it is not possible to test every combination since there are some of that did not drive to a solid product, the whole system was considered as a categorical design, that is, no different variables are observed but nine different categories can be put into relationship, so an optimum point should be obtained. Table 1a and 1b shows the combinations.

Table. 1a. Design factors and levels.

Independent variables	Symbol	Range and Levels			
		1	2	3	4
Polymerization time(h)	A	8h	12h	16h	18h
Acetaldehyde dose(ml)	B	2mL	0mL	4mL	6mL
Formaldehyde dosage(ml)	C	0mL	2mL	4mL	6mL
Tannin extract(ml)	D	5g	7g	9g	11g

Table. 1b. Different combination s of reactions,

Runs	Variables				Responses
	A	B	C	D	Does it gelify?
1	1	1	1	1	Yes
2	1	2	2	2	No
3	1	3	3	3	No
4	1	4	4	4	No
5	2	1	2	3	Yes
6	2	2	1	4	No
7	2	3	4	1	No
8	2	4	3	2	No
9	3	1	3	4	No
10	3	2	4	3	No
11	3	3	1	2	No
12	3	4	2	1	No
13	4	1	4	2	Yes
14	4	2	3	1	No
15	4	3	2	4	No
16	4	4	1	3	No

2.5 Scanning electron microscopy

The SEM enables the direct observation of the changes in the surface structures of the resin. Morphological analysis of the tannin resin was performed by SEM using a Jeol JSM-6060LV. As shown in Fig 1, many small pores are seen on the surface tannin gel. Studying the SEM images, it is possible to see that the loose nature of tannin condenses as it forms into a resin. In Fig.2 the pores of TGAN are completely covered with Cu^{2+} ions.

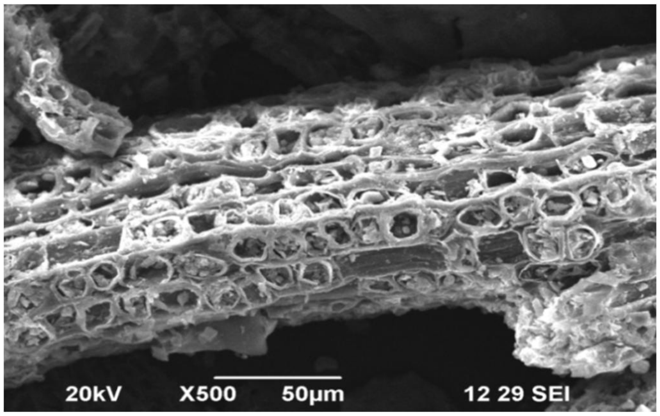

Fig. 1. SEM study before adsorption of Cu^{2+} using TGAN.

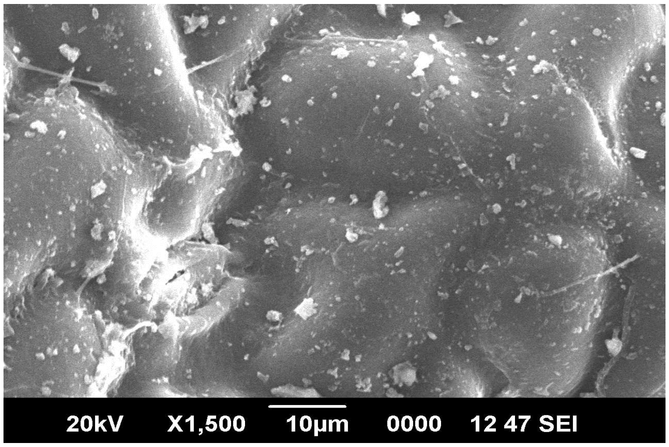

Fig. 2. SEM study after adsorption of Cu^{2+} by TGAN.

3. RESULT AND DISCUSSION

3.1. Characterizations of Tannin gel.

3.1.1. Total phenolic contents.

Phenols, the aromatic compounds with hydroxyl groups are widespread in plants. They occur in all parts of the plants. Phenols includes an array of compounds like tannin, flavonols etc. Total-phenol estimation can be carried out with the Folin-Calteu reagent. Related to the standard value we get 490 µg/mg shows high phenolic content of the tannin extracted from *Acacia nilotica*.

3.2. FTIR spectroscopy studies

Fourier transform infrared spectroscopy (FTIR) was used to determine the vibration frequency changes in the functional groups in the resin. The spectra of gel and extract were measured by an FTIR spectrometer within the range of 400–4000 cm^{-1}wavenumber. The dry beads (about 0.1 g) was thoroughly mixed with KBr and pressed into a pellet and the FTIR spectrum of raw Tannin extract and TGAN was then recorded. The FTIR spectra of tannin extract and TGAN were shown in Fig.3 and Fig.4. Generally; wide bands in the range of 3550–3100 cm^{-1} correspond to –OH bridging groups in all systems [34] and here bands between 3304-3361 cm^{-1} and shows the presence of respective groups. The small peaks in the region of 2854-2927cm^{-1} are associated with the methylene (–CH2–) bridges of the tannin resin. The peaks at 1058-1105cm^{-1} in the spectrum of tannin extract are due to C–O stretching and CH deformation. The absorption bands between 1631 cm^{-1} and 1452 cm^{-1} are characteristic of the elongation of the aromatic –C-C– bonds. The deformation vibration of the carbon–carbon bonds in the phenolic groups absorbs in the region of 1500–1400 cm^{-1}. Between 3000 and 3200 cm^{-1} aromatic C–H peaks have increased in TGAN spectrum in contrast with the one for raw tannin extract.

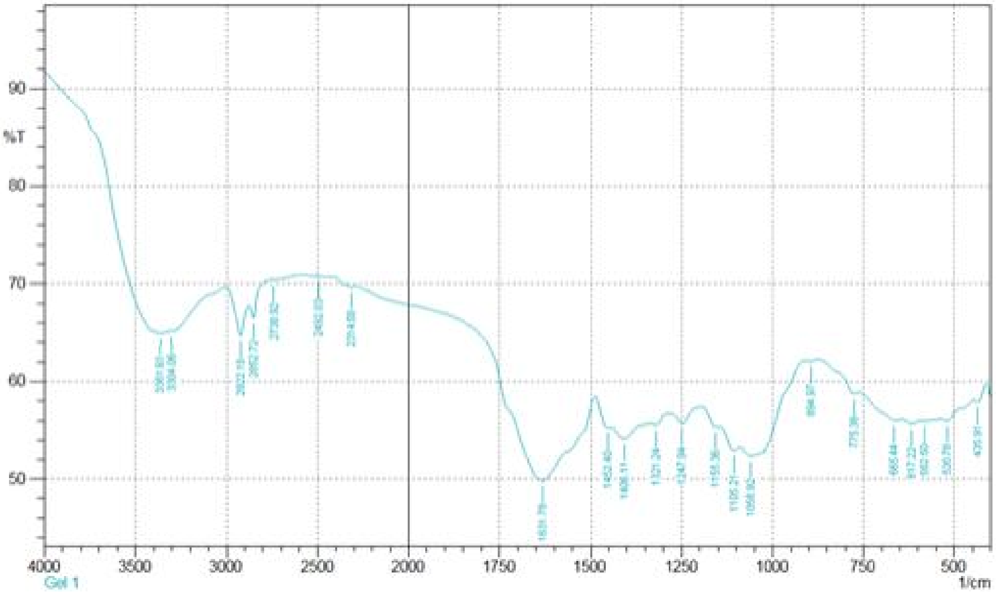

Fig. 3. FTIR result for *Acacia nilotica* tannin extract.

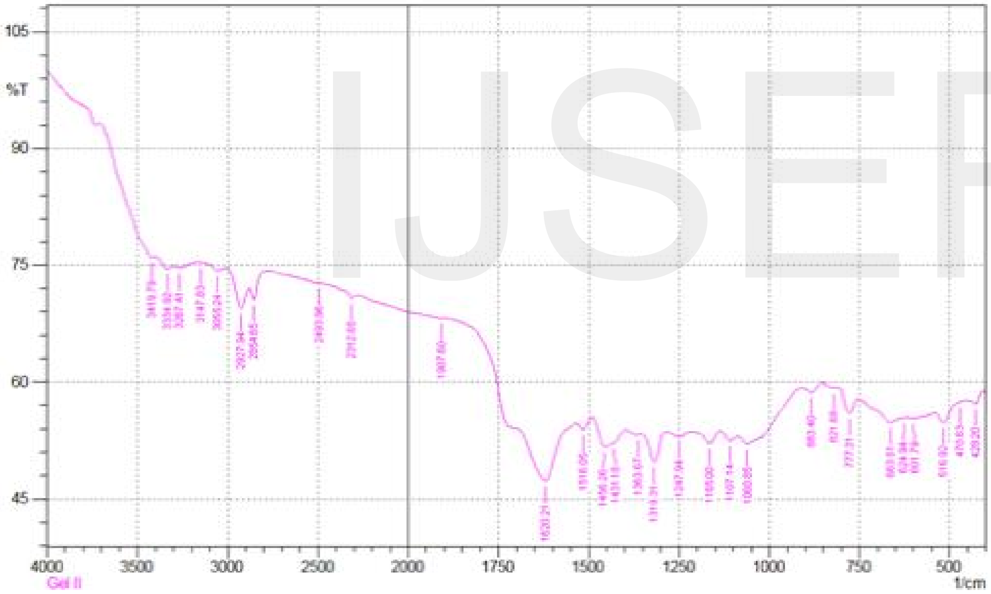

Fig. 4. FTIR results for *Acacia nilotica* tannin gel.

3.3. BATCH MODE STUDY

3.3.1. Effect of pH

The uptake of Cu^{2+} was strongly affected by solution pH. At the metal initial concentration of 100 ppm, copper removal efficiency was 13.8% at a solution of pH of 2.0. But the efficiency of removal is increased sharply when solution pH rises from 2 to 4. Fig. 5 shows that in low pH (2.0 to 3.0) leads to increase in H^+ ion concentration in the system and surface of gel acquires positive charge(pH_{ZPC} =5.12), due to electrostatic repulsion ,no adsorption takes place. Furthermore the solution pH is above the zero point charge (pH_{ZPC}=5.12) of the adsorbent (TGAN) favors the adsorption of Cu^{2+} ions due to the solution pH is above the pH_{ZPC} of the adsorbent favors the negative surface charge of the adsorbent increases the adsorption of cation(Cu^{2+}) due to electrostatic attraction. The optimum pH for the removal of Cu^{2+} onto TGAN was pH = 4. Moreover, the increasing in the adsorption of metal with increasing of pH value is also due to the attraction between metal ions and excess OH^- ions in the solution [35].

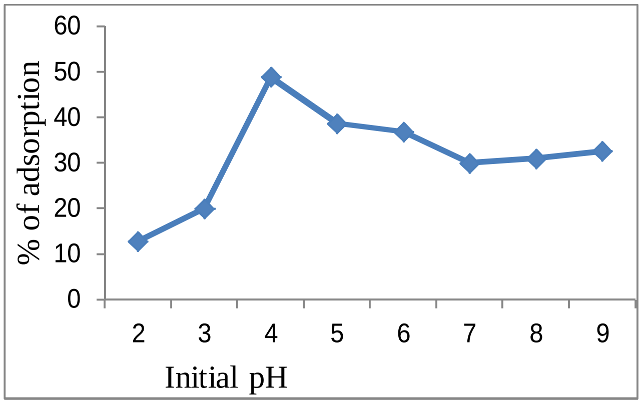

Fig. 5. Effect of pH on adsorption of copper onto TGAN.

3.3.2. Effect of initial concentration

The effect of initial concentration of Cu^{2+} ions was studied over different range (25 ppm to 200 ppm). The result obtained is shown in Fig.6. The maximum uptake of Cu^{2+} ions at equilibrium was at 48.4% at an initial Cu^{2+} concentration of 100 ppm. The initial concentration of Cu^{2+} has little influence of the time of contact necessary to reach equilibrium. The percentage of adsorption was decreased with increasing initial concentration of metal ions. Higher initial Cu^{2+} concentration resulted in lower diffusion efficiency and more competition of adsorbing ions for a fixed activated surface site.

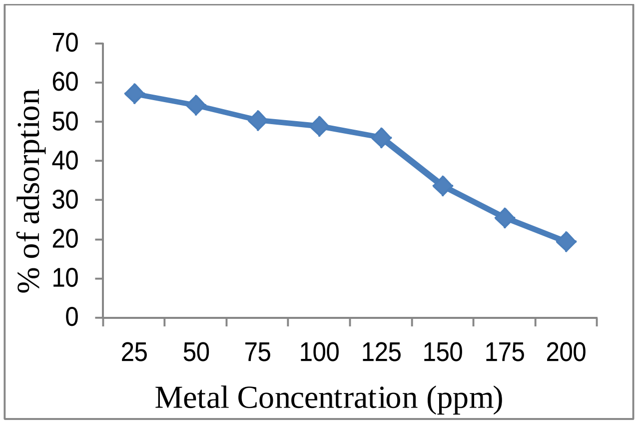

Fig. 6. Effect of initial concentration on adsorption of copper onto TGAN.

3.4.1. The Langmuir isotherm model

The Langmuir model [36] is described by the equation:

3.3.3. Effect of contact time

A series of contact time experiments have been carried out with a constant initial Cu^{2+} concentration (100 ppm). Fig.7. shows the contact time necessary for Cu^{2+} to reach saturation, the equilibrium of the % of adsorption occur at 50 minutes. The distribution of Cu^{2+} solution, when the system in a state equilibrium and is important to establish the capacity of the adsorbent for Cu^{2+}. Initial adsorption was rapid due to the adsorption of metal onto exterior surface, after that Cu^{2+} enter into pores (interior surface), and relatively slow process.

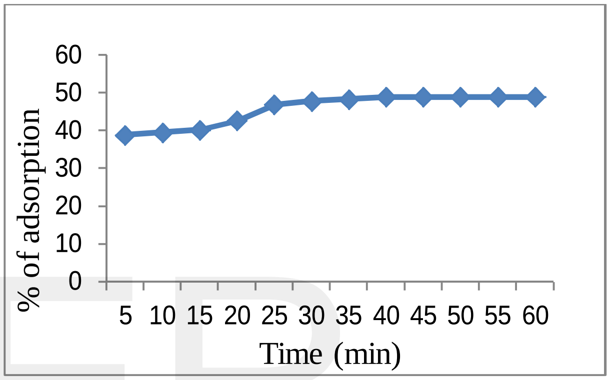

Fig. 7.Effect of contact time on adsorption of copper onto TGAN.

3.4. Equilibrium Studies

Equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of sorption systems. Adsorption isotherm is important to describe how solutes interact with adsorbent. Therefore, to optimize the design of sorption system to remove heavy metals from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. Three isotherm equations have been tested in the present study, namely, Langmuir isotherm, Freundlich isotherm and Temkin.

$$C_e/q_e = 1/K_aQ_m + (1/Q_m \times C_e) \qquad (1)$$

Where q_e and C_e are defined before in Eq. (1), Q_m is a constant and reflect a complete monolayer (mgg^{-1}) on the surface bound at high C_e; Ka is adsorption equilibrium constant(Lmg^{-1}) that is related to the apparent energy of sorption and the affinity of the binding sites. A linear plot of specific adsorption (C_e/q_e) versus the equilibrium concentration (C_e) should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_aQ_m)$.

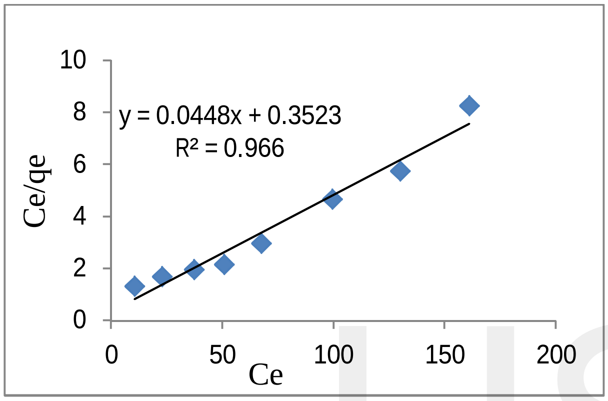

Fig. 8. Langmuir adsorption isotherm of Copper onto TGAN.

3.4.2. The Freundlich isotherm model

The Freundlich [37] model can be described by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (2)$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed onto TGAN (mg/g), and K_f and 1/n are Freundlich constants. The K_f is related to the bonding energy and can be defined as the adsorption or distribution coefficient and represents the quantity of metal adsorbed onto TGAN for unit equilibrium concentration.

Eq. (2) can be linearized in the logarithmic form (Eq. (3)) and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (3)$$

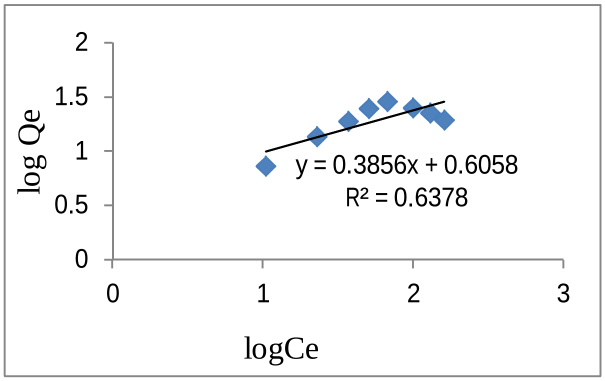

Fig. 9. Freundlich adsorption isotherm of Copper on TGAN.

3.4.3. The Temkin isotherm model

Temkin and Pyzhev [38] considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm has been used in the following form:

$$q_e = \frac{RT}{b}\ln(AC_e) \qquad (4)$$

The Temkin isotherm Eq. (4) can be simplified to the following equation:

$$q_e = \beta\ln\alpha + \beta\ln C_e \qquad (5)$$

$$\beta = (RT)/\mathrm{b} \qquad (6)$$

where the constant b (L/ mg) is related to the heat of adsorption and the constant α is the equilibrium binding constant.

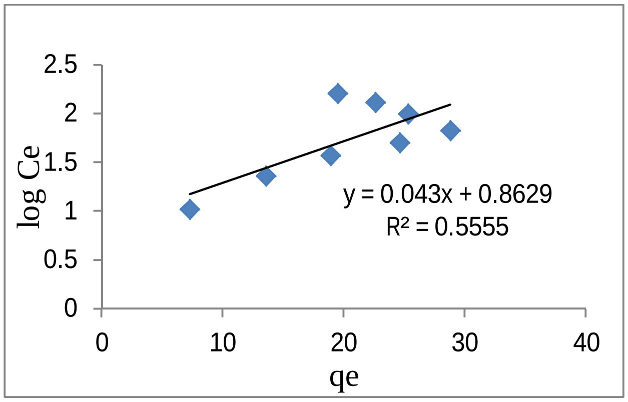

Fig. 10. Temkin isotherm for Copper onto TGAN.

The outcome values of parameters Q_m, K_a, K_f, n, b, β,α and R_2 for all the experiments for removal of Cu^{2+} are presented in Table.3. Results from Table. 3 shows that the maximum monolayer adsorption capacity (Q_m) =22.72 is mg/g. The Langmuir equation is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites. The Langmuir equation represents the better fit of experimental data than the Freundlich and Temkin isotherm equation.

Langmuir			Freundlich			Tempkin		
Q_m (mgg-1)	b (Lmg^{-1})	R^2	1/n	K_f (mgg^{-1})	R^2	α (Lg^{-1})	β (mgL^{-1})	R^2
22.72	0.125	0.966	2.59	4.027	0.637	465.02	0.043	0.555

Table. 3. Langmuir, Freundlich and Temkin isotherm constants.

3.5. Kinetics Studies.

The kinetics of metal ions sorption is an important parameter for designing sorption system. It helps to select the optimum operating conditions for full scale batch metal removing process. The amount of Cu^{2+} biosorbed increases in contact time and reached equilibrium after 50 minutes. In order to examine the mechanism of biosorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data.

3.5.1. The linear pseudo-first -order equation

The linear pseudo-first-order equation is given as follows [39]

$$\frac{dq_t}{d_t} = K_1(q_e - q_t) \qquad (7)$$

Where qt and qe, are the amounts of Cu^{2+} adsorbed at time t and at equilibrium (mmol g^{-1}), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). Fig. 11 shows a plot of log ($q_e - q_t$) vs t for biosorption of Cu^{2+} for the pseudo-first-order equation. The values of pseudo-first order rate constants (k1), and equilibrium biosorption capacities (q_e), for each initial copper concentration were calculated from slopes and intercepts of straight lines in Fig. 11.

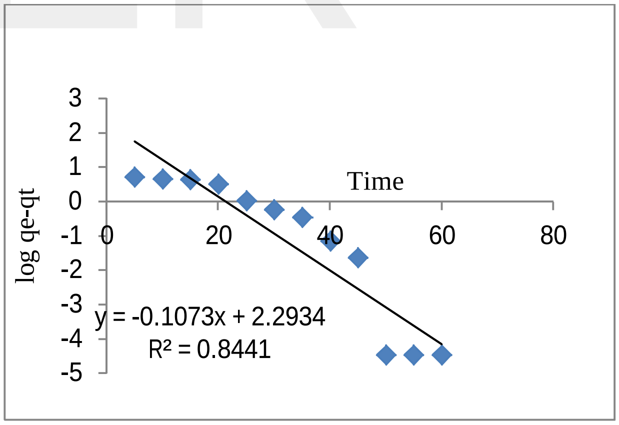

Fig. 11. Plot of the pseudo-first-order equation for the biosorption kinetics of Copper onto TGAN.

The values of pseudo-first-order equation parameters together with correlation co-efficient are given in Table. 4. The correlation co-efficient for the pseudo-first order equation is low. Also the theoretical q_e values found from the pseudo-first-order equation did not given reasonable values. This suggests that this biosorption system is not a first-order reaction.

3.5.2. The linear pseudo – second order model

The adsorption kinetics may be described by the pseudo-second- order model [40]. The differential form of the pseudo-second order equation is generally given as follows:

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \qquad (8)$$

Eq. (8) can be rearranged and linearized to obtain:

Where k_2 (g (mg min) $^{-1}$) is the second - order rate constant of adsorption.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t) \qquad (9)$$

The second - order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = K_2 q_e^2 \qquad (10)$$

Fig.12 shows typical plots of pseudo-second-order equation for the copper–TGAN system as t/qt vs t.

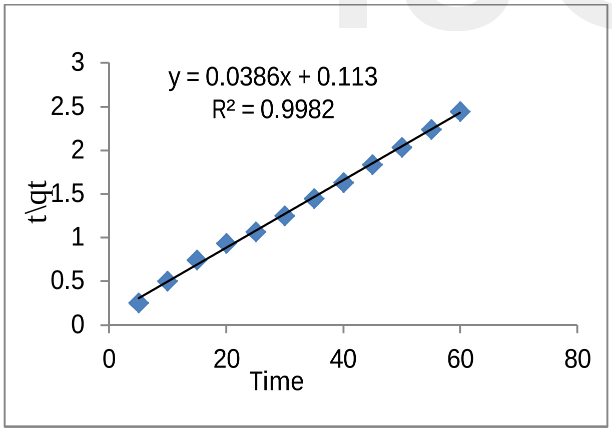

Fig. 12. Plot of the pseudo-second-order equation for the biosorption kinetics of Copper onto TGAN.

The straight lines in plot of linear pseudo-second-order equation shows good agreement of experimental data for for the adsorption copper onto TGAN. The values of pseudo-second-order equation parameters together with correlation coefficients are listed in Table. 4. The correlation coefficients for the pseudo-second-order equation were 0.998 for all concentrations. The calculated q_e values also agree very well with the experimental data. This strongly suggests that the biosorption of Cu^{2+} onto TGAN is most appropriately represented by a pseudo-second-order rate process.

3.5.3. Elovich equation

The adsorption data may also be analyzed using the Elovich equation [41], which has the linear form:

$$\frac{dq_t}{dt} = B_E \exp(-A_E q_t) \qquad (11)$$

Where B_E is the initial adsorption rate (mg (g min) $^{-1}$) and A_E is the desorption constant (g mg^{-1}) during any experiment. It is simplified by assuming $A_EB_Et \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (11) becomes

$$q_{t=\frac{1}{A_E}} \ln(B_E A_E) + \frac{1}{A_E}\ln(t) \qquad (12)$$

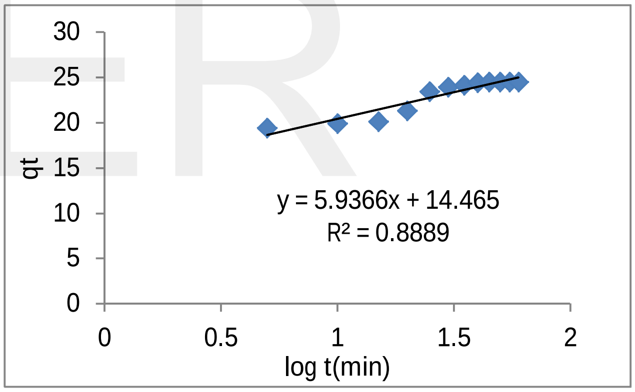

Fig. 13. Plot of the Elovich equation for the biosorption kinetics of Copper onto TGAN.

In the case of using the Elovich equation, the correlation coefficients are lower than those of the pseudo-second-order equation. It cannot be used to describe the kinetics of biosorption of Cu^{2+} onto TGAN.

3.5.4. Intraparticular Diffusion

Because Eqs. (7) and (11) cannot identify the diffusion mechanisms; the intraparticle diffusion model was also tested Fig.14 shows a plot of the linearized form of the intraparticle diffusion model at all concentrations studied.

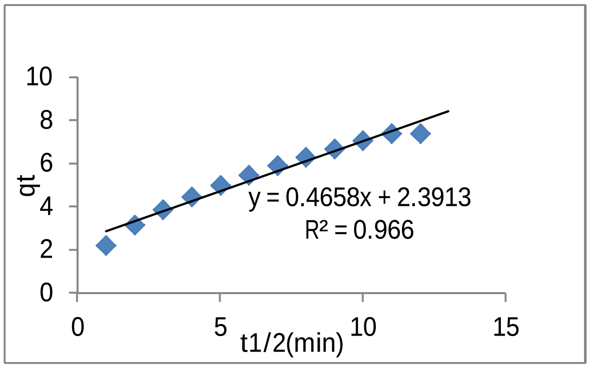

Fig. 14. Plot of the Intraparticular diffusion equation Copper onto TGAN.

Pseudo first order			Pseudo second order			Elovich equation			Intraparticular diffusion		
K_1 min^{-1}	q_e (mg/g)	R^2	K_2 (gmg^{-1} min^{-1})	q_e mg/g	R^2	A_E	B_E	R^2	C_e	K_{diff}	R^2
0.246	196.3	0.844	0.0049	26.31	0.998	0.1684	11.32	0.888	14.46	0.465	0.966

Table. 4. Kinetic parameters for the sorption of Cu^{2+} on TGAN.

The Langmuir isotherm and pseudo-second-order kinetic model provide best correlation with the experimental data for the adsorption of copper ions onto TGAN.

3.6. Binary and Tertiary solutions

As showing in the Fig. 15, the results indicated that the equilibrium uptake of Cu^{2+} ions decreased with the increasing concentration of Ni^{2+} ions. In single-ion-system, the maximum uptake obtained at initial concentration of Cu^{2+} at 100 ppm, pH=4 was found to be 48.93%, while uptake in binary metal solutions at the same initial concentration of Cu^{2+} ions and biosorption condition was found to be 39.52%, 38.50%, 34.55% and 31.48% when concentration of Ni^{2+} ions was 10 ppm, 20 ppm, 30 ppm and 40 ppm respectively. This is because of fixed quantity of TGAN could only after a finite number of surface binding sites, some of which would be expected to be saturated by the competing metal ions especially at relatively high concentration of them and this was indeed observed.

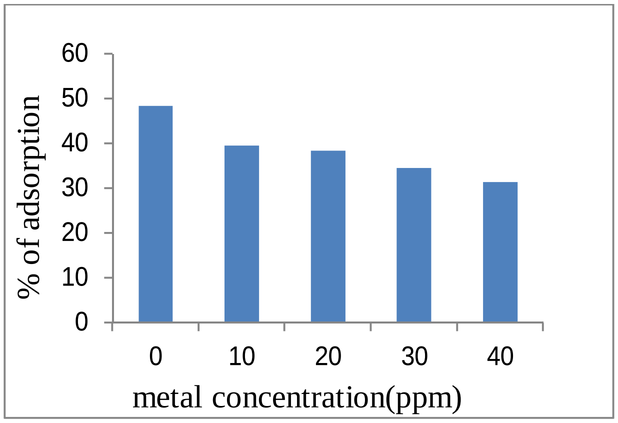

Fig. 15. Binary solutions of Cu^{2+} and Ni (II).

As shown in the Fig. 16, the result of binary solution of copper and chromium indicated that the adsorption of Cu^{2+} ions increased slightly with the increasing concentration of Cr (VI) ions as compared with the single-ion-situation. This is may be because of the formation of chromium cyanide complex which is used as a complexing reagent for copper.

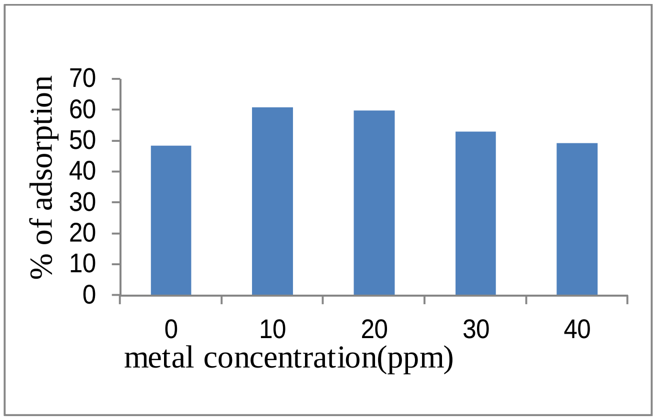

Fig. 16. Binary solution of Cu^{2+} and Cr (VI).

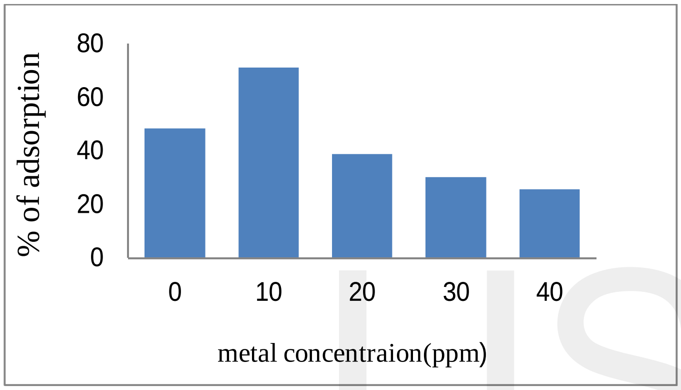

Fig. 17. Tertiary solution of Cu (II), Ni (II) and Cr (VI).

The decrease in adsorption capacity of same biomass in tertiary solution than that of single metal ions may be due to the less availability of binding sites. In case of multi-metal solution, the binding site is competitively divided among the various metal ions, Cu (II), Cr (VI) and Ni (II).

4. CONCLUSION

The aim of the work was to find the possible use of *Acacia nilotica* tannin gel as a sorbent for the removal of Cu^{2+} from aqueous solution. Experiments were performed as a function of initial pH, contact time and initial concentration. Adsorption at pH 4 enhanced the efficiency of adsorption process. Increasing the time, the adsorption yield also increases. Equilibrium data of adsorption were correlated with Langmuir, Freundlinch, Temkin, Intraparticular diffusion and Langmuir model was found to provide the best fit of experimental data. According to the Langmuir model, the maximum Cu^{2+} adsorption capacity of TGAN was 22.75 mg g^{-1}. The suitability of the pseudo-first-order, pseudo-second order and particle-diffusion type kinetic models for the sorption of Cu^{2+} onto TGAN for all situations was also discussed. The results showed that pseudo-second-order kinetic model was found to be in good agreement with the experimental results. Results obtained from this study showed that TGAN can be used as an adsorbent for the removal of Cu^{2+} from the aqueous solution by using a batch mode system.

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