Effect of Batch Removal of Copper from Aqueous Solutions Using Tannin-immobilized Hide Collagen

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Authors' contributions

This work was carried out in collaboration between all authors. Author LL designed the work. Author MOO performed the statistical analysis, managed the literature search and wrote the first draft of the manuscript. Author OOA read through and made correction on the manuscript while author AOA also read through and assisted in the statistical analysis. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

This study is aimed at preparing collagen fiber from cow hide and to utilize it as cheap, effective and alternative adsorbent against the more expensive and relatively less effective techniques for the removal of Cu(II) ion from aqueous solution and to find a suitable pH, equilibrium isotherm, kinetic model and thermodynamics using a batch mode. A novel adsorption membrane was therefore prepared by immobilizing *Acacia nilotica* tannin onto hide collagen (ANTIHC). The results obtained in this study showed that the uptake of the metal ions increased with increase in initial metal ion concentration and pH. The optimum contact time of 40 min was achieved in this study. The equilibrium data fit well with the Freundlich isotherm (R^2 = 0.93) than the Langmuir isotherm (R^2 = 0.65) and the Temkin isotherm fairly described the adsorption. The results of pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion equation work showed that the pseudo-second order provides the best correlation (R^2 =1) for the adsorption process, whereas the

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Elovich equation did not fit the experimental data (0.08) Thermodynamic study showed that the reaction was non-spontaneous because the value of Gibb's free energy was positive while the value of ΔH indicate exothermic nature. Also, the adsorption increases as the temperature increases indicating that the process is chemisorptions. The adsorbents were characterized with SEM analysis which was used to obtain the characteristics of the adsorbates; EDAX analysis confirmed that immobilized tannin gained additional functional groups while the FT-IR analysis showed functional groups such as amine, hydroxyl, carbonyl and carboxyl groups that were responsible for the sorption of the metal ions onto the biomasses.

The results of this study however revealed that ANTIHC can be used as suitable biosorbent for the removal of Cu ion and it may be an alternative to more costly methods used for removal of heavy metal ions from waste waters and aqueous solution in a batch mode system. The results also showed that ANTIHC have excellent adsorption properties that are probably due to increase in surface active sites for adsorption.

Keywords: Adsorption; immobilization; collagen; copper; tannin.

1. INTRODUCTION

Heavy metals are considered as hazardous pollutants due to their toxicity even at low concentration. Toxic metals such as Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), have become an eco-toxicological hazard of prime interest and increasing significance, owing to their tendency to accumulate in vital organs in man and animals [1]. They do not degrade into harmless end products in the metabolisms and they are accumulated in the food chain, thereby posing the greatest danger to living organisms causing various diseases and disorders. The waste generated in large volumes is high in pollutant load and must be cleaned before it is released. Concern over this problem has led to the development of alternative technologies for the removal of these pollutants from aqueous effluents [2]. Among various water treatment methods, adsorption is supposed as the best one due to its inexpensiveness, universal nature and ease of operation [3,4].

The heavy metal of concern in this paper is copper. It is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives [5]. 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, gastro-intestinal irritation, and possible necrotic changes in the liver and kidney [6]. Effective methods for copper ion removal that have been used include ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption. The application of such processes is often limited because of technical or economic constraints [7].

Adsorption is a proven technology for the removal of copper, among many water treatment methods, adsorption is considered to be one of the best [8,9] ions from synthetic and real industrial effluents. The high cost of activated carbon has motivated scientists into the search for new low cost adsorption means. Inorganic pollutants, especially metal ions, are more dangerous due to their toxic and possibly carcinogenic natures [10]. In recent years, considerable attention has been focused on the removal of copper from aqueous solution using adsorbents derived from low-cost materials. Several adsorbents, such as sawdust, silica, and iron oxide [11], bagasse fly ash [12,13] spent activated clay [14] and modified goethite have been used for the treatment of copper (II) rich effluents at the solid–liquid interface [15].

A. nilotica is native to the drylands of tropical Africa and western Asia, eastwards as far as India, Myanmar and Sri Lanka. In Africa it occurs from Senegal to Egypt and southwards through eastern Africa to Mozambique and South Africa (Natal) and the Indian Ocean islands. It has been distributed throughout the tropics and became naturalized in many areas. Babul acacia (trade name); scented thorn, scented-pod acacia (English); Bagaruwa (Hausa); Iyere (Yoruba). It belongs to the family: Mimosaceae (Leguminosae - Mimosoideae). Plantations of *A. nilotica* for timber, tannin or gum production require regular weeding and thinning to maintain maximum growth and 2-3 weedings are sufficient to control weed growth. Spot sowings with 10-15 seeds per hole did not require weeding but needed early thinning and then thinning at 5-yearly intervals. For 5-year-old stands a density of 1200 trees/ha is recommended. Use of NPK fertilizers did not prove economically worthwhile

in plantations grown on a 20-25 year rotation. The pods of *A. nilotica* are used traditionally in Nigeria and other sub-Saharan countries for tanning leather and as a source of khaki-to-brown dyes if used without mordant. In contrast in India and Pakistan it is the bark, a by-product from timber plantations, which is used for tanning and dyeing leather. The tannins contribute to its many medicinal uses, the plant acting as a powerful astringent (Burkill, 1995). *A. nilotica* is a truly multipurpose tree, widely used as a timber, source of fodder, food, tannin and gum, and as a fence, shade and fuel tree. The leaves and pods are an excellent fodder, rich in protein. The flowers yield a honey of good quality. The Hausa people use roasted seeds as food flavouring. In Tanzania the inner bark and the thick fruit pulp are boiled in water and drunk as a tea. In eastern Java (Indonesia) sprouted seeds are consumed as a vegetable, and well-roasted seeds are mixed with coffee. Being easy to propagate by seed, fast growing, nitrogen fixing, tolerant of poor soils and arid conditions it will always have a role to play in the reclamation of degraded areas where fuel and timber supplies are lacking (Wulijarni-Soetjipto and Lemmens, 1991).

Recently, vegetable tannins have shown to be potential alternative for the removal of heavy metals from aqueous solution, such as lead, cadmium and chromium [16-18]. Tannins exhibit extremely high metal-binding capacity because they contain abundant adjacent phenolic hydroxyls being able to chelate with metal ions [19]. However, tannin is water–soluble compound, which restricts its practical application as an adsorbent. Therefore, great efforts have been made to overcome this disadvantage, mainly by immobilizing tannins onto various water-insoluble matrices such as agarose, hydrotalcite and cellulose [20-22]. These approaches are usually complicated in procedures, and tannins are still easily leached out during adsorption process.

Collagen fiber, one of the abundant natural biomass mainly obtained from skins of animals, exhibits excellent hydrophilic ability, swelling capacity and mechanical strength [23]. The functional groups of collagen fiber, including –NH_2, -COOH and –OH, can react with many other chemicals [24]. These facts suggest that collagen fiber would be more suitable to be used as a matrix for the immobilization of tannins. Furthermore, the covalent-bond interaction between tannins and collagen fiber completely solves the problem that tannins may be leached

out during adsorption process, as compared with other tannin-immobilized approaches [25]. This work however reports the effects of batch removal of copper from aqueous solutions using tannin-immobilized hide collagen to adsorb Cu(II) ion from aqueous solutions and to evaluate their properties as adsorbents.

2. MATERIALS AND METHODS

2.1 Materials

The cowhide used in this work was obtained from abatoir at Sabo market in Zaria while bark of bagaruwa (*Acacia nilotica*) was obtained from Ahmadu Bello University, Zaria, Kaduna State, Nigeria. Collagen fiber was prepared according to a standard procedure [26]. The hide was cleaned, limed, splitted and de-limed as for leather processing in order to remove non-collagen components.

2.2 Chemicals

Sigma analytical grades of $CuSO_4.5H_2O$, HCl, HCHO, $Ca(OH)_2$, NaOH and Na_2S were purchased and prepared for the analyses.

2.3 Preparations of Tannins and Immobilized Tannins

The sample (bark of bagaruwa) was dried and ground using grounding machine. 200 g of the sample was weighed and was taken into Koch extractor and extracted with deionized water at 70°C for 4 h. The extract was concentrated under pressure at 50°C. Concentrated extract was dried by using LAB-PLANT SD-04 spray drier. At the end of the extraction total yield of 50 g was obtained for the sample. The process of immobilization prepared was according to the method of vegetable tannin-aldehyde combination tannage used in leather-making [27].

The physical appearances of cowhide and *A. nilotica* tannin before and after immobilization were determined through Physical Observations Scanning Electron Microscopy.

The IR spectra of the free and immobilized biomass were run using KBr pellets on Thermo Nicolet 6700 FTIR spectrometer in the frequency range 4000-400 cm^{-1}, 10 mg of finely ground biomass was encapsulated in 500 mg of KBr in order to prepare a translucent sample disk. The

FTIR spectrometer was turned on, initialized, aligned and before use to scan an air background followed by scanning sample spectrum.

2.4 Experimental Procedures

2.4.1 Sorption kinetics

Accurately weighed 0.5 g of the adsorbent *A. nilotica* tannin immobilized on hide collagen (ANTIHC) was suspended in 100 cm^3 of 127 mg/L Cu (II) solutions at various time intervals of 10, 20, 30, 40 and 50 min respectively. The initial pH of the solutions was adjusted to 6. The adsorption solutions were shaken on mechanical shaker at 150 rpm at room temperature according to the indicated time intervals. At the end of the predetermined time, the solutions were withdrawn, filtered separately using Whatman filter paper (No1). The filtrate containing the residual concentration of Cu (II) was determined spectrophotometrically by means of Shimadzu Model AA-680 atomic adsorption spectrophotometer at 325 nm [28].

The effects of pH and temperature on the adsorption capacity were also investigated. $0.1 moldm^{-3}$ NaOH and $0.1 moldm^{-3}$ HCl were used to adjust the initial pH value of Cu(II) solution in the experiments.

2.5 Adsorption Capacity Studies

Isotherm studies were carried out with initial concentrations of Cu(II) ranging from 13 to 414 mg/L. The initial pH of the solution was adjusted to 6.0. The procedures were similar to those of adsorption kinetic study, but the adsorption process was analyzed at the optimal time interval.

3. RESULTS AND DISCUSSION

3.1 Immobilization of Tannin on Collagen Fiber

The concentration of *A. nilotica* tannin in the residual solution of the first preparation step during immobilization was 6.67 mg/L and the concentration of the residual solution of the cross-linking reaction during immobilization was 0.9 4 mg/L. Finally, 54.26 g immobilized *A. nilotica* tannin was obtained and the ratio of tannin in the product was approximately 27.25%. The higher thermal stability comes from vegetable tanning effect and implies wider suitability of the immobilized tannins [29].

Increase in temperature from 25°C to 50°C during fixation of the cross-linking agent (formaldehyde) apparently causes other nitrogen groups apart from all histidine that have already reacted to become reactive and cause this reaction to proceed more rapidly thus making available $-NH_2$ groups for formaldehyde association. At low concentrations and high pH (8, 10) of formaldehyde the amino groups are more reactive for tannage (immobilization). The function of the high pH value also is to repress the ionization of basic group. It has been recorded in literature that immobilized collagen fiber has higher denaturing temperature (363-368K) than that of raw collagen fiber (333-338K). The improved thermal stability should be attributed to the formation of methylene bridges and a large number of hydrogen bonds [25].

3.2 Characterization of Adsorbent

The physical appearances of cowhide and *A. nilotica* tannin (ANT) before and after immobilization were determined through physical observation and with the aid of Scanning Electron Microscopy (SEM). The surface of the collagen fiber (cowhide) was much irregular due to fiber bundles in the collagen fiber.

In the case of Bagaruwa tannin, the loaded collagen was condensed to globular shape with regular surface thereby increasing the surface area for adsorption as observed in Plate 1.

The SEM micrographs show surface texture and porosity of the blank and loaded adsorbents. It can be inferred from these figures that the surface texture of the blank adsorbents changes drastically after the loading of the adsorbate.

Fourier transforms infrared spectroscopy (FTIR) was used to determine the vibration frequencies of the functional groups on the binding sites to compare the free biomass and the immobilized biomass with a view to understanding the multifunctional groups of the biomasses and their binding abilities. The significant spectra and bands were shown in Table 1.

The functional groups identified in the spectra include carboxylic, hydroxyl and amine groups. In Table 1, the stretched vibrations of OH group shifted from 3398 to 3400.62 cm^{-1} after Bagaruwa tannin has been immobilized onto hide. This indicates that the functional group of hydroxyl has increased, thereby creating additional sites for adsorption. The changes at all

the immobilized (loaded) samples were attributed to complexation of tannins and collagen fiber. The homogenous surfaces of the immobilized (loaded) samples provide multi-sites (i.e. carboxyl, carbonyl, hydroxyl and amine) for adsorption of the metal ions.

3.3 Effect of pH

The effect of initial pH of solution on adsorption was determined because it is known to be one of the most important factors affecting sorption [30]. It is responsible for protonation of metal binding sites on the biosorbent surface [31]. The result on the effect of pH on the adsorption of Cu^{2+} by bagaruwa tannin immobilized on collagen fiber (HB) was studied at pH ranging from 4 to 10 for the metal ion. The results were presented in Table 2. As pH increases, the deprotonation degree increases and reaches a maximum at pH 8.0 (99.41%) as equivalent H^+ was released along with the adsorption, which results in a remarkable increase in the adsorption capacity. There was a decrease in adsorption after pH 8.0. Decrease in adsorption is due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites. At higher pH, precipitate formation was observed indicating that the phenolic hydroxyl groups of the tannin have been readily oxidized [29]. At lower pH values, the active sites of the adsorbent are less available for the metal ions due to protonation of the active sites at higher H^+ concentration [32]. At low pH, the protons occupy most of the adsorption sites on the adsorbent surface and less Cu (II) ions could be sorbed because of the electric repulsion with the protons on the adsorbent. The result presented here is consistent with previous studies on adsorption of Cu (II) using tannins-immobilized on collagen by [29]. In a similar study with activated carbon from rice hulls, the optimum pH values for Cu (II) and Cd (II) adsorption was reported to be between 5 –8 [33].

3.4 Effect of Contact Time

The effect of contact time on the adsorption of Cu onto bagaruwa immobilized tannin on collagen fiber (Hide) is shown in Fig. 5. One of the important characteristics defining the efficiency of an adsorbent is the kinetics of metal ion sorption which governs the rate that determines the residence time [34]. In the result obtained from Hide Bagaruwa (HB), there was a rapid adsorption of the metal ions in the first few minutes and, thereafter, the rate of adsorption decreased gradually. The maximum removal was obtained at 90.02% and the process reach equilibrium at 20 minutes which is similar to the result obtained by Okieimen et al., [35] in the adsorption of copper(II), Okoronkwo [36] on biosorption on nickel using unmodified and modified lignin. Most reported results agree on a similar structure in the range of 20-60 min for most divalent ions [37,38]. The observed biosorption system is consistent with the biosorption of metal involving non-energy mediated reactions, where metal removal from solutions is due purely to physico-chemical interactions between the biomass and the metal solution. This agreed with some results that have been reported in many studies using different biosorbents on the uptake of different heavy metals [7,39,40].

A (Hide)
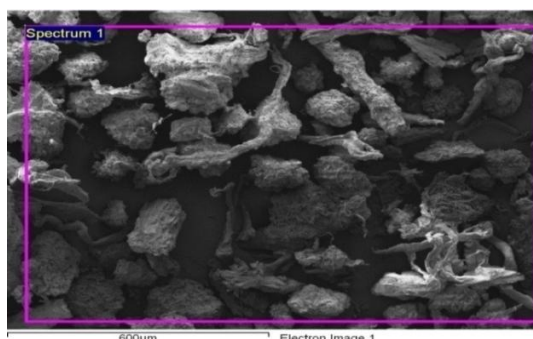
B (Bagaruwa + Hide)

Plate 1. SEM Micrographs of (A) Hide (B) Bagaruwa + Hide (HB)

Table 1. FTIR analyses of Bagaruwa tannin, cowhide and immobilized cowhide

Samples	Frequencies (cm^{-1})	Possible functional groups
Bagaruwa tannin	3398	O-H stretching vibration
	1631.83	C-C aromatic bonds
	1273.06	C-O stretching vibration
	1062.81	Cyclic O-H/Ester C-O stretch
	534.30	C-H stretching vibration
	447.50	C-H stretching vibration
Hide	3336.96	O-H stretching vibration
	2359.02	N-H bending vibration
	1631.83	N-H bending vibration
	1261.49	Ester C-O, aromatic N-H
	634.60	C-H stretching vibration
	457.14	C-H stretching vibration
Hide + Bagaruwa	3400.62	O-H stretching vibration
	1626.05	N-H stretching vibration
	1375.29	CH3 stretching vibration
	1068.60	C-O stretching vibration
	543.94	C-H stretching vibration
	461.00	C-H stretching vibration

Table 2. Effect of contact time, pH, temperature and concentration on adsorption removal at 30±2°C

Effect of contact time		Effect of pH		Effect of temperature		Effect of concentration	
Time (min)	Percentage removal (%)	pH	Percentage removal (%)	Temp (K)	Percentage removal (%)	Concentration (mg/L)	Percentage removal (%)
10	89.82	4	90.36	308	90.14	13	99.92
20	90.02	6	91.29	318	90.88	32	99.37
30	89.82	8	99.41	328	90.81	64	99.32
40	89.82	10	99.37	338	91.23	95	99.24
50	89.80			348	91.23	127	99.20

3.5 Adsorption Kinetics

The pseudo-first–order equation (Lagergren's equation) describes adsorption in solid-liquid systems based on the sorption capacity of solid (Ho, 2004). It is assumed that on Cu:

$$A + Cu^{2-}_{aq} \longrightarrow ACu \text{ solid phase} \qquad (1a)$$

Where A represents an unoccupied sorption site on the adsorbent.

The linear form of pseudo-first-order model can be expressed as:

$$\log (q_e\text{-}q_t) = \log q_e - \frac{K_1}{2.303} t \qquad (1b)$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t (h),

respectively. The value of k_1 can be obtained from the slope of the plot of log (q_e-q_t) versus t.

The first order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. The pseudo-first order rate by Lagergren has also widely been used [41,42].

The pseudo-first order rate constant K_1 value was calculated from the slope of the figure. The calculated K_1 value and the corresponding linear regression correlation coefficient values were shown in Table 1. It was observed that the rate of removal of the metal ions (copper (II) onto the adsorbent does not follow the pseudo-first-order equation because the value was low, $R^2 < 0.6$. Also the theoretical q_e^1 values found from the pseudo-first order equation did not give reasonable values. This suggests that this biosorption system is not a first order reaction.

The pseudo-second-order kinetics may be expressed as [43,44]

$$dq_t/d_t = k_2 (q_e-q_t)^2 \quad (2)$$

Where k_2 is the rate constant of adsorption ($gmg^{-1} h^{-1}$), q_e is the amount of copper ions adsorbed at equilibrium (mg/g) and q_t is the amount of copper ions adsorbed at time t (mg/g). Separating the variables in eqn (2) qives:

$$dq_t/(q_e-q_t)^2= k_2d_t \quad (3)$$

integrating this for the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t gives:

$$1/ (q_e-q_t) = 1/q_e+k_t \quad (4)$$

which is the integrated rate law for a pseudo-second-order reaction. Eqn (4) can be rearranged to obtain:

$$q_t= 1/(1/kq_e^2) +(t/q_e) \quad (5)$$

This has a linear form of:

$$t/q_t = 1/k_2q_e^2+1/q_e \quad (6)$$

While k_2 is the rate constant for pseudo-second-order adsorption ($gmg^{-1} h^{-1}$) and $k_2q_e^2$ or h ($mgg^{-1}h^{-1}$) is the initial adsorption rate, where t is the contact time (min), q_e (mg/g) and q_t (mg/g) is the amount of the solute adsorbed at equilibrium at any time t. The pseudo–second order rate

constants can be determined experimentally by plotting t/q_t against t.

The plots of the pseudo-first-order and pseudo-second-order kinetic models are shown in Figs. 1 and 2. Table 3 shows the kinetic parameters using the pseudo-first-order and pseudo-second-order. The straight lines in plot of linear pseudo-second- order equation show good agreement of experimental data with the pseudo-second order kinetic model for different initial copper concentrations.

The linear regression correlation coefficient R^2 value was higher (R^2>0.99) that is R^2 =1.0 and K_2 value was negative (-0.336) which compared well with Lawal et al., 2010 [45]. The calculated Q_e (Q_e Cal) value also agrees very well with the experimental data Q_e (Q_e Exp.). This strongly suggests that the biosorption of Cu(II) onto ANTIHC was most appropriately represented by a pseudo-second order rate process. It means that the chemisorption reaction or an activated process becomes more predominant in the rate-controlling step for the Cu system [46] which involves valence forces through sharing or exchange of electrons between adsorbent and adsorbates. It provides the best correlation of data. The same behaviour have been observed in the adsorption of copper unto agricultural waste sugar beet pulp [47], adsorption of copper onto H_3PO_4 activated rubber wood sawdust [6]; [48].
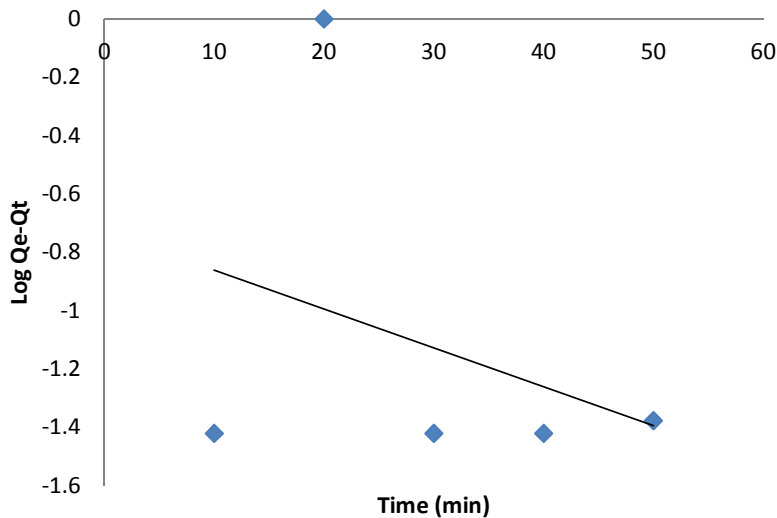

Fig. 1. Pseudo first- order kinetics of Cu^{2+} sorption onto bagaruwa tannin immobilized onto cow (HB) collagen at pH 8.0 and 30±2°C
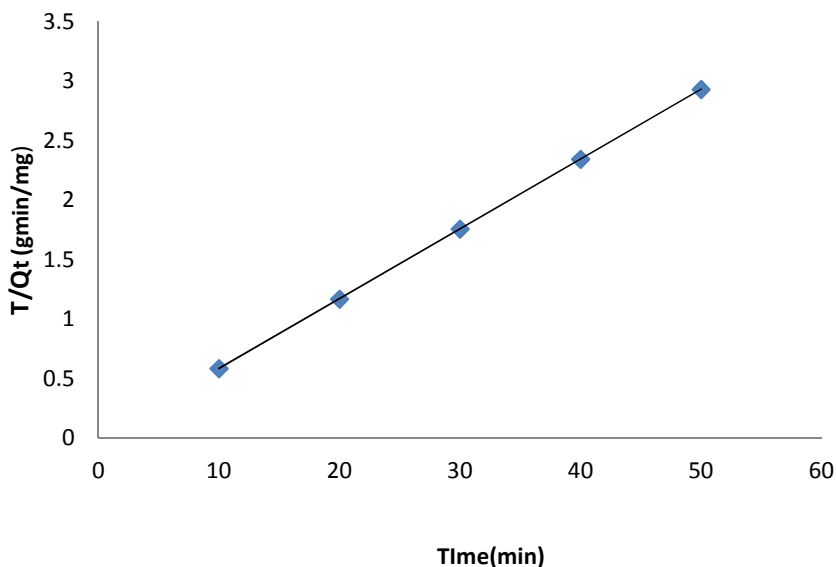
Fig. 2. Pseudo second - order kinetics of Cu^{2+}sorption onto bagaruwa tannin immobilized onto cow (HB) collagen at pH 8.0 and 30±2°C
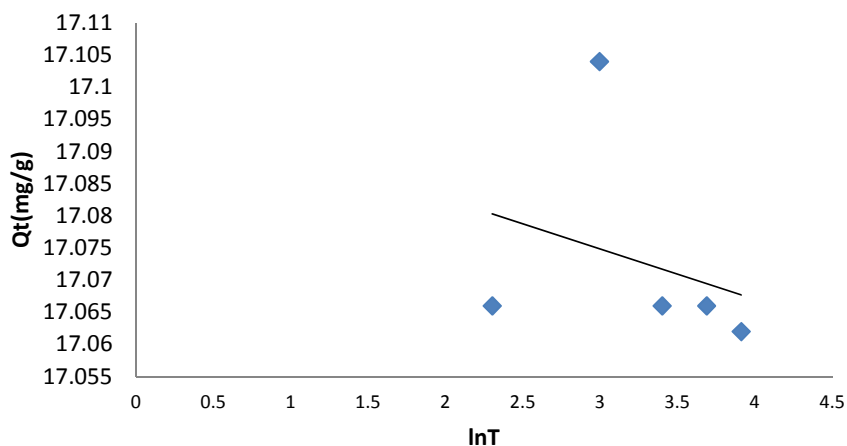

Fig. 3. Elovich plots of Cu^{2+} adsorption onto bagaruwa tannin immobilized onto cow (HB) collagen at pH 8.0 and 30±2°C

In order to gain insight into the mechanisms and controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber's intra-particle diffusion model [28]. There are different steps controlling sorption kinetic viz; transfer of solute to the sorbent particle surface, transfer from sorbent particle surface to intra-particle active sites, and retention on these active sites via sorption, complexation, and intra-particle precipitation phenomena. The kinetic results were analyzed by the intra-particle diffusion model to elucidate the diffusion mechanism. The model is expressed as:

$$Q_t = K_{id}t^{1/2} + I \qquad (7)$$

Where K_i is the intra-particle diffusion rate constant (mg/g min$^{0.5}$) and C is the intercept.

Where I is the intercept and k_{id} is the intra-particle diffusion rate constant (mg/gh ½) or pore diffusion coefficient, which can be evaluated from the slope of the linear plot of q_t versus t ½ [28] as shown in Fig. 4, q_t is the amount of solute adsorbed (mg/g) at time t (min) and $t^{1/2}$ is the square root of the reaction. The intercept of the plot reflects the boundary layer effect. The larger

the intercept, the greater the contribution of the surface sorption in the rate controlling step [49]. The calculated intra-particle diffusion coefficient k_{id} values are listed in Table 3. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step [50]. However, the linear plots at each concentration did not pass through the origin. This indicated that the intra-particle diffusion was not the only rate-limiting step. The intra-particle diffusion rate constant K, was calculated from the slopes in Fig. 4. The value of the intercept (I) provides information related to the thickness of the boundary layer [51]. The value of rate constants (K_{id}) of Cu (II) was all less than 1. The graph reflect that the pore diffusion of the metal increases within a very short period of time and then the diffusion remains almost constant, indicating the exhaustion of the pore volumes.
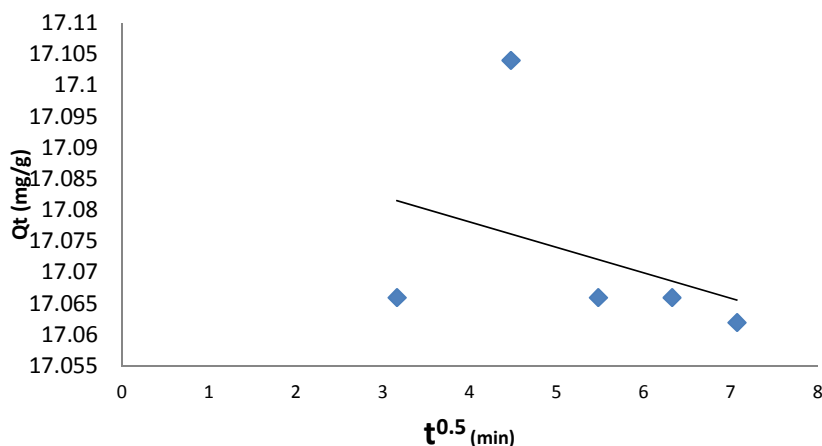

Fig. 4. Intraparticle diffusion plots of Cu^{2+} adsorption onto bagaruwa tannin immobilized onto cow (HB) collagen at pH 8.0 and 30±2°C

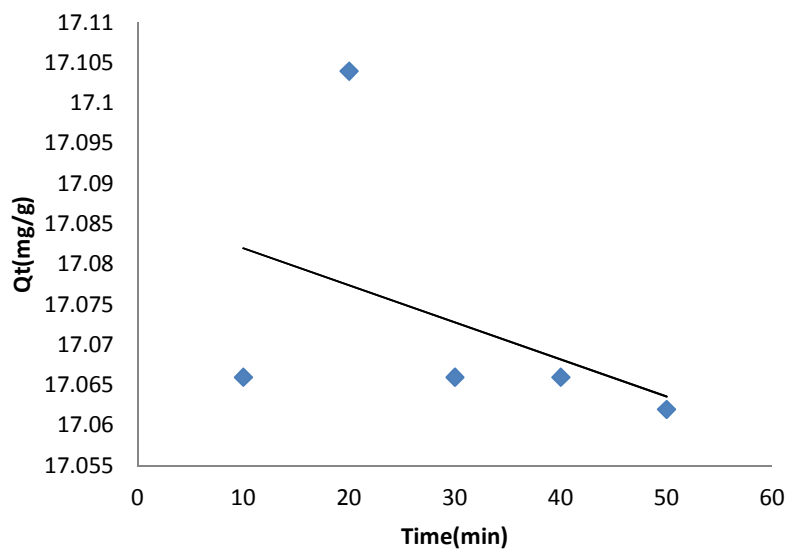**Fig. 5. Time dependence study for Cu^{2+} adsorption onto bagaruwa tannin immobilized onto cow (HB) collagen at pH 8.0 and 30±2°C**

Table 3. Comparison of Pseudo-first order and Pseudo-second order kinetic models, intraparticle diffusion and Elovich equation for Cu adsorption by ANTIHC at 30±2°C

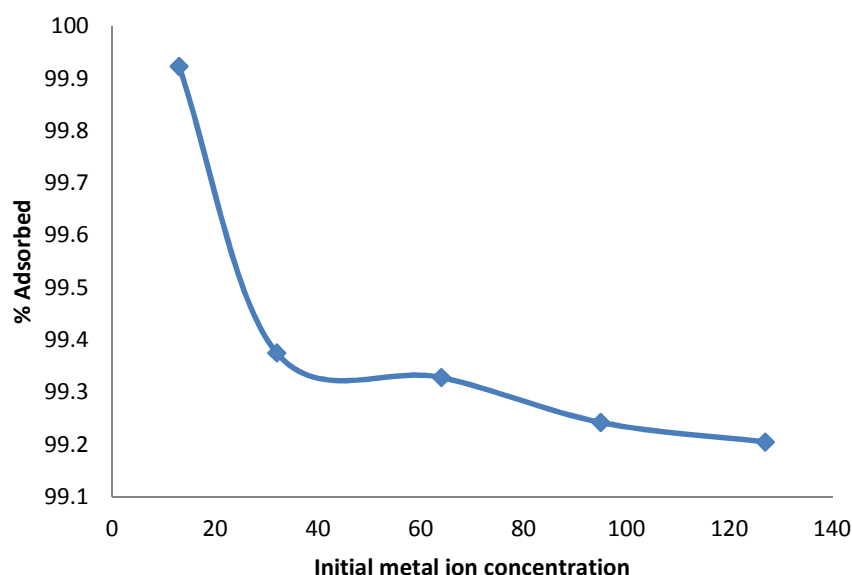| Pseudo-first order		Pseudo-second order		Intraparticle diffusion		Elovich constant	
Q_e(mg/g) Exp.	17.104	Q_e (mg/g) Exp.	17.104	K_{id} (mg/gh$^{1/2}$)	-0.004	α (mg/gmin)	6.20
K_1 (min^{-1})	0.003	K_2 (g/mgmin)	-0.336	I (mg/g)	17.09	β (g/min)	-142.86
R^2	0.111	R^2	1.000	R^2	0.13	R^2	0.080
Q_e(mg/g) Cal.	0.188	Q_e (mg/g) Cal	17.241				

Fig. 6. Effect of initial metal ion concentration on the percentage removal of copper by bagaruwa tannin immobilized onto cow (HB) collagen at pH 8.0 and 30±2°C

A widely used equation to describe the kinetics of chemisorption of gas on solids was proposed by Elovich [52]. The Elovich equation was derived from the Elovich kinetic equation:

$$\frac{dq}{dt} = ae^{-bq} \tag{8}$$

$$q = \frac{1}{b}\ln(1 + abt) \tag{9}$$

or

$$q = \frac{1}{b}\ln(ab) + \frac{1}{b}ln(t - t_o). $$

3.6 Elovich Equation

The Elovich Equation is generally expressed as presented below (Ketcha and Bougo, 2010):

$$\frac{dQ_t}{dt} = α\exp(-βQ_t) \tag{10}$$

where α is the initial sorption rate (mg^{-1}.g.min^{-1}) and β is the desorption (g.mg^{-1}) during any one experiment, it is also related to the extent of surface coverage and activation energy for chemisorptions. The integrated and simplified equation is

$$Q_t = \frac{1}{β}\ln(αβ) + \frac{1}{β}lnt \tag{11}$$

Fig. 3 shows a plot of the Elovich equation for the same data. In this case, a linear relationship was obtained between metal ions (Cu^{2+}) biosorbed, q_t, and lnt over the whole biosorption period, with correlation coefficient (R^2) of 0.080 (Table 3). In the case of using the Elovich equation, the correlation coefficient (R^2) was lower than 0.9

therefore cannot be used to describe the kinetics of biosorption of Cu(II) onto ANTIHC.

3.7 Effect of Initial Metal ion Concentration

Initial metal ion concentration provides the necessary driving force to overcome resistance of mass transfer between metal ions in the aqueous phase and adsorbents [53]. Adsorption efficiency decreased with the increment of initial heavy metals ion concentration [54]. Increase in initial concentration from 13 to 127 mg/L decreased the percentage removal for Cu(II) ion on ANTIHC from 99.92% to 99.20%. An increase in adsorption capacity with increase in metal ion concentration was recorded (2.59 – 25.19)mg/g which is similar to what was obtained by Madu et al., 2011 [55] on biosorption of Cr^{3+}, Pb^{2+} and Cd^{2+} ions from aqueous solutions using modified and unmodified millet chaff. This increment is obvious because more efficient utilization of the adsorptive capacities of the adsorbent is expected due to a greater driving force (by a higher concentration gradient pressure) [56].

3.8 Adsorption Isotherms

Equilibrium data analysis is important for developing an equation that can be used to compare different adsorbents under different operational conditions and to design and optimize an operating procedure. Adsorption information for a wide range of adsorbate concentrations are most frequently described by adsorption models such as Langmuir or Freundlich isotherm which relates adsorption density (q_e); metal uptake per unit weight of adsorbent to equilibrium concentration (C_e) in the bulk fluid [57]. In this study, the Langmuir, the Freundlich, and the Temkin models were used to establish the most appropriate correlation for the equilibrium curves in order to optimize the design of sorption system to remove Cu(II) from aqueous solution as shown in Table 4.

The Langmuir model essentially describes the monolayer type of adsorption. Its advantages hinge on the availability of interpretable parameters. However, it is limited in application as it is structured and it can only be applied for the monolayer adsorption.

It is represented by the expression below;

$$q_e = \frac{Q°bC_e}{(1+bC_e)} \qquad (12)$$

And, the linear form of the equation can be written as

$$\frac{C_e}{q_e} = \frac{1}{bQ°} + \frac{C_e}{Q°} \qquad (13)$$

Where q_e is the amount of heavy metal ions adsorbed per unit mass of adsorbent (mg/g) at equilibrium liquid phase concentration of heavy metal ion (mg/L). Q° and b are Langmuir constants indicating monolayer adsorption capacity (mg/g) and free energy adsorption (L/mg) respectively. The Langmuir model assumes that the uptake of metal ions occurs on completely homogenous surface by monolayer adsorption without any interaction between adsorbed ions.

The plot of C_e/q_e versus C_e at different concentrations for Langmuir was linear. The parameters Q° (q_m), R^2 and b have been calculated and the results are represented in Table 4. In adsorption of Cu(II) ion, the adsorption did not conformed to Langmuir model with the correlation coefficient $R^2 = 0.76$. The fact that q_e (equilibrium metal uptake) has greater value than q_m (monolayer maximum adsorption capacity) indicate that the adsorption is a multilayer type. More also, the value of R_L (dimensionless constant separation factor) was < 0 indicating that the shape of isotherm is unfavorable which is similar to Liao et al., (2004) [29] on the adsorption of Cu(II) using immobilized tannin. The adsorption isotherm is similar to Gulipalli et al., [58] on batch study, equilibrium and kinetics of adsorption of selenium using rice husk ash.

The Freundlich model is also an empirical equation like the Langmuir model. It is used to estimate the adsorption intensity of the sorbent towards the adsorbate and it is given by the equation:

$$Q_e = K_F Ce^{1/n} \qquad (14)$$

n represent the Freundlich constant (dimensionless), it is related to the adsorption intensity.

K_F is the Freundlich adsorption constant related to the adsorption capacity.

The linearized form of Eq. (14) is given by Eq. (15):

$$\log q_e = \log K_F + 1/n \log C_e \qquad (15)$$

A plot of log q_e against log C_e gives a straight line graph with (1/n) as the slope and log K_F as the intercept. Both K_F and n determine the curvature and the steepness of the isotherm [59].

The Freundlich parameters and the correlation coefficient R^2 for the fitting of the experimental data are represented in Table 4. By comparing the results of the values of correlation coefficient, it was found that the adsorption of Cu(II) ions on ANTIHC was better fitted experimentally to Freundlich isotherm model. Langmuir isotherm corresponds to a dominant ion exchange mechanism while the Freundlich isotherm shows adsorption-complexation reactions taking place in the adsorption process. The 1/n value greater than 1.0 $(0<1/n_F$ or n<1) confirmed the heterogeneity and conformation to Freundlich model. The n values obtained in this work are less than unity (<1) which indicates that the process is a chemisorption.

In the adsorption of Cu(II) ions showed that the adsorption conformed to the Freundlich model by their linearity correlation Coefficient R^2 = 0.93.T()he report agrees with Lokeshwari and Joshi, [60] on biosorption of heavy metal (Chromium) using biomass.

Temkin isotherm is given as

$$q_e = B \ln(K_T C_e) \qquad (16)$$

It can be expressed in the linear form as

$$q_e = B_T \ln K_T + B \ln C_e \qquad (17)$$

A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B and K_T from the slope and the intercept, respectively. Temkin constants are given in Table 4. K_T is the equilibrium binding constant corresponding to the maximum binding energy and constant B is related to the heat of adsorption [61]. The data were listed in Table 4. The good value of correlation coefficient (0.73) for Temkin isotherm allowed to say that it describes fairly well the nature of the adsorption of Cu(II) ion by ANTIHC. The positive value of sorption energy (Table 4) indicate that the adsorption of Cu(II) ion by ANTIHC is endothermic and the fact that the sorption energy(B_T) value is less than 8KJ/mol also indicate the weak interaction between the adsorbent and the Cu(II)ions [62]. The Linear plot for Temkin adsorption isotherm also indicate chemisorption of an adsorbate onto the adsorbent [63]. This further supports the findings

that the adsorption of Cu(II) onto ANTIHC is chemisorption process.

3.9 Thermodynamics

The equilibrium uptake of Cu, by ANTIHC was affected by temperature (Table 2). It was indicated that the removal increased with increase in temperature. The increase in adsorption with the rise of temperature may be due to increase in swelling of the adsorbent allowing more active sites to become available for ANTIHC. The effect of temperature was studied to calculate the percentage removal and the thermodynamic parameters such as the enthalpy ($\Delta H°$) and the entropy ($\Delta S°$) (Table 4) by using the following equation:

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (18)$$

Where, T is the temperature in K, R is the ideal gas constant having value as $8.314 Jmol^{-1}K^{-1}$ and K_c is the thermodynamic equilibrium constant. The negative value of $\Delta H°$ shows the exothermic nature of adsorption [64]. The $\Delta G°$ value for the adsorbent in Table 4 for Cu(II) is shown and was found to be positive [65] indicating that the adsorption process was less feasible and less spontaneous. The entropy of activation measures the width of the ''saddle point of energy'' over which reactant molecules must pass as activated complexes [66]. The negative value of $\Delta S°$ showed the decrease in degree of randomness at the solid/solution interface during the adsorption of Cu(II) ion on ANTIHC, which also reflects that there is little or no affinity of the adsorbent material for Cu(II) ion. The value of $\Delta H°$ was not high enough to ensure strong interaction between Cu(II) ion and the adsorbent. The Freundlich model explains the adsorption process better than the other models on the basics of the correlation factor R^2 (0.92-0.99). The factor R^2 values obtained suggests that multilayer sorption takes place on the surface of biomass and that the adsorbents were fully covered by the metal ions, while the n< 1 confirm the heterogeneity of the adsorbents, this trend is similar to cases reported in literature [31]; [58]. The fitness of the adsorption data of Cu(II) ions to Freundlich isotherm implies that the binding energy on the whole surface of the adsorbents were non-uniform. It also indicates that the adsorbed metal ions interact or compete with each other and that they are adsorbed by forming a multilayer. The study indicates that the adsorbent tested is an encouraging biosorbent for Cu(II) ions removal from aqueous solution.

Table 4. Langmuir, Freundlich, Temkin Isotherms and Thermodynamic parameter for Cu (II) Adsorption by ANTIHC at 30±2°C

	Isothermic parameters											Thermodynamic parameters	
	Langmuir constants				Freundlich constants			Temkin constants					
q_{exp} mg/g	q_{max} (mg/g)	$K_{L\,(-)}$ L/mg	$R_L(-)$ x 10^{-4}	R^2	$K_{F\,(L/g)}$	n_F	R^2	B_T (KJ/mol)	K_T (L/mg)	R^2		$\Delta H°$ (J/mol)	$\Delta G°$ (J/mol)
32.65	0.05	128.21	1.0	0.65	0.60	0.51	0.93	4.23	97.71	0.73		-2700.39	6818.49

4. CONCLUSION

Novel adsorbent was prepared by immobilizing tannins onto collagen fiber matrix. The process of immobilization is the same as for the vegetable tannin-aldehyde combination tannage used in leather-making. The immobilized tannin adsorbents from literature have satisfactory chemical and thermal stabilities. The adsorption capacity of immobilized tannins is related to the molecular structure of tannins that is, the chelating ability of tannins to metal ions originates from its adjacent phenolic hydroxyls.

Experimental data indicate that the adsorption efficiency is dependent on operating variables such as contact time and initial metal ion concentration. Under batch conditions, equilibrium was attained within 20 minutes after which adsorption decreased. Biosorption efficiencies increased with increasing contact time and initial metal ion concentration. All these are comparable to other adsorbents reported in literature for Cu (II) adsorption. The uptake of Cu (II), ions by ANTIHC was increased by increasing the metal ion concentration and the adsorbent concentration. The increase of initial concentration led to increase of adsorption capacity, but prolonged the time to attain adsorption equilibrium, indicating that the adsorption of tannins onto collagen fibers is multi-layer adsorption. In Cu(II) adsorption, the time taken for the adsorbent to attain adsorption equilibrium at 95 mg/L was 20 minutes.

The pseudo second order kinetic model accurately described the adsorption kinetics. The adsorption mechanism was found to be chemisorption and the rate-limiting step was mainly surface adsorption. The Freundlich isotherm showed a better fit than the Langmuir isotherm, thus, indicating the applicability of multi-layer coverage and also connotes the heterogeneity of Cu(II) ions on ANTIHC. The equilibrium data described by Temkin equation further supports Cu adsorption on ANTIHC as a chemisorption process.

Results obtained from the equilibrium and kinetic studies revealed that ANTIHC can be used as a suitable biosorbent for the removal of Cu ions and it may be an alternative to more costly methods such as active carbon adsorption, reverse osmosis, solvent extraction, reduction and oxidation to mention a few for removal of heavy metal ions from waste waters/aqueous solution in a batch mode system. Immobilized tannin has excellent adsorption properties.

In this study, the results obtained from the equilibrium and kinetic studies revealed that ANTIHC showed higher adsorption. Also, SEM was used to obtain the characteristics of the adsorbates and the EDAX analysis confirmed that immobilized tannin gained additional functional groups. Moreover, FTIR was used to determine the type of functional groups present in the adsorbate. The functional groups were presented by the peak at different wave numbers from the analysis. It hence revealed that the functional groups such as amine, hydroxyl, carbonyl and carboxyl present in the adsorbents were responsible for the sorption of the metal ions onto the biomass.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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