

Biosorption of Zn(II) Ions by Low-Cost Adsorbents which Containing Tannins and Thermal Properties of Adsorbents

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Abstract

A new low-cost, locally available sorbent sumac (*Rhus coriaria* L.) leaves (SL) and resins prepared from tannic acid/ gelatin (TG) and tannin from sumac leaves/ gelatin (STG) were tested for its ability to remove Zn(II) ions from aqueous solutions. The biosorption studies carried out with single metal solutions. The removal of Zn(II) from aqueous solution increased with pH and sharply decreased when pH of solution was decreased. Batch isotherm of biosorption zinc ions was investigated. The Freundlich, Langmuir and Tempkin models can describe the adsorption equilibrium of Zn(II) on SL, TG resin and STG resin. The biosorption constants were found from the Freundlich, Langmuir and Tempkin isotherms at room temperature. It is found that the biosorption data of zinc on SL, TG resin and STG resin fitted the Freundlich, Langmuir and Tempkin adsorption models. This study investigated also thermal analysis of TG and STG resins. The TGA-DTG curves of all the resins were similar and showed three steps in a similar way to a phenolic resin. This means that each resin is well cross-linked.

Keywords: Zn(II) ions; adsorption isotherm; thermal properties; tannin-gelatin resin; tannin from sumac leaves-gelatin resin

Tanen İçeren Düşük Maliyetli Adsorbanın Zn(II) İyonlarını Biyosorpsiyonu ve Termal, Adsorban Özelliklerinin İncelenmesi

Özet

Yeni, ekonomik sumak (*Rhus coriaria* L.) yaprakları (SL) ve reçineler ki bunlar tannik asit/jelatin (TG) ve sumaktan elde edilen tannin/ jelatin (STG) sulu çözeltilerden Zn(II) iyonun uzaklaştırmak kullanılmıştır. Biyosorpsiyon çalışmaları tek bir metal iyonu

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üzerinden gerçekleştirilmiştir. Çözeltilerden Zn(II) iyonu uzaklaştırmada ortamın pH değeri arttığında biosorpsiyon artmış, pH düştüğünde keskin bir düşüş gözlenmiştir. Çinko biosorpsiyonu SL, TG reçinesi ve STG reçinesi için; Freundlich, Langmuir ve Tempkin izotermi ile yorumlanmıştır. Çinko biosorpsiyonunun SL, TG reçinesi ve STG reçinesi için Freundlich, Langmuir ve Tempkin izotermine uyduğu gözlemlenmiştir. Ayrıca bu çalışmada TG ve STG reçinelerinin ısıl özellikleri incelenmiştir. Bütün reçinelerin TGA-DTG eğrileri incelendiğinde fenolik reçineler gibi üç basamaklı olduğu gözlenmiştir. Bu da reçinelerin iyi ağ örgülü yapı gösterdiğini ispatlamaktadır.

Anahtar kelimeler: Zn(II) iyonları; adsorpsiyon izotermi; termal özellikler; tannin-jelatin reçinesi; sumaktan elde edilen tannin-jelatin reçinesi

1. Introduction

Environmental pollution caused by toxic heavy metals occurs globally through industrial, military and agricultural processes as well as waste disposal. The discharge of heavy metals into the environment is a major concern because of their toxicity and is a threat to human life and to the environment. Strict environmental regulations on the discharge of heavy metals make it necessary to develop efficient technologies for their removal. The main techniques that have been used to dispose of industrial effluents include chemical precipitation, ion exchange, electrochemical processes, and adsorption onto various adsorbents and/or membrane filtration.

Although all these techniques are capable of removing heavy metals to some extent, adsorption by solid substrates is preferred because of its high efficiency, easy handling and cost-effectiveness, as well as the availability of adsorbents [1].

Zinc may be found in wastewater discharges from acid mine rainage, galvanizing plants, as a leachate from galvanized structures and natural ores, and from municipal wastewater treatment plant discharges. Zinc is not biodegradable and cycling through the food web via bioaccumulation. Therefore, there is significant interest regarding zinc removal from wastewaters and its toxicity for humans at levels of 100-500 mg/day. World Health Organization (WHO) has recommended that the maximum acceptable concentration of zinc in drinking water as 5.0 mg/L [2].

The removal of metal ions from effluents is a big concern too many countries in terms of environment and for water re-use. The application of low-cost sorbents including carbonaceous materials, agricultural products and waste by-products has been investigated [3]. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat [4], wood [5], pine bark [6], banana pith [7], rice husk [8], sawdust [9], wool [10] and leaves [11]. These studies showed that the natural products can be used as good sorbents for heavy metals.

Rhus coriaria L. (Anacardiaceae), commonly known as sumac is widely used in Turkey and the Middle East. The berries are russet colored and contain one seed. It is dried and ground leaves have been used as a tanning agent due to their high tannin content [12]. Sumac grows wild in the region extending from the Canary Island over the Mediterranean coastline to Iran and Afghanistan. It is native to the Mediterranean and

south eastern Anatolia, Turkey [13-16]. Sumac is a shrub 3-4 m in height and bears pinnate leaves with six to eight pairs of small oval leaflets of different sizes, with white flowers in terminal inflorescences. The main compounds present in Rhus family are hydrolysable gallotannins [17]. Tannins have multiple adjacent polyhydroxyphenyl groups in their chemical structure, which have extremely high affinity for proteins, metal ions, and other macromolecules like polysaccharides [18]. Tannins can probably be used as alternative, effective and efficient adsorbents for the recovery of metal ions. However, since they are water-soluble, when they are used directly as an adsorbent for recovery of metals from aqueous systems, they have the disadvantage of being leached by water [1]. To overcome this disadvantage, we synthesized the tannin/ gelatin and tannin from sumac/ gelatin resins.

Gelatin mainly contains glycine, proline and 4-hydroxyproline [19]. It is widely used in the pharmaceuticals, hard and soft capsules, microspheres, and is an adsorbent pad for surgical use [20]. It is a biodegradable, biocompatible and is a low cost biomaterial. In gelatin molecule, there are many chemical groups having strong affinity to metal ions, such as carboxyl group of the side chain, carbonyl group of the polypeptide chain and etc [21].

Biosorption is an emerging technology that uses biological materials to remove metals from solution through adsorption. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [22].

Thermogravimetric analysis (TGA), a widely used technique because of its simplicity, can be used to examine the thermal behavior of resins. The rate of weight loss as an effect of temperature at a given time can be measured to predict the thermal behavior of the materials [23].

The present research has described here was designed to test the characteristics of sorbents, prepared from leaves of sumac, tannin gelatin and tannin from sumac gelatin resins for removing Zn(II) from aqueous solutions in batch system. The important factors affecting the biosorption efficiency such as, solution pH, metal concentration and biosorbent dosage were investigated. Lastly the investigation focused on thermal properties of the resins.

2. Materials and Methods

2.1 Reagents

All chemicals used in this study were of analytical grade. Zinc stock solution (1000mg/L) was prepared from a ready made ZnCl₂ standard (Merck). Working zinc solutions were prepared just before usage by appropriate dilutions of stock solution.

2.2 Preparation of adsorbents

2.2.1 Sumac leaves

The sumac leaves (*Rhus coriaria* L.) in this study were collected in and around Manisa city (Turkey), dried at room temperature in dark. They were grounded and sieved in the size range of 0.3 to 1.0 mm (300-1000µm) and were stored in plastic bottle for further use. For the total tannin determination Folin-Ciocalteu method was used and tannin

content was found 22.5%. Similar findings of tannin content were reported for sumac grown in Spain [24].

2.2.2 Tannin/ gelatin (TG) resin

For synthesized TG resin; the tannic acid (TA) and gelatin (G) powders purchased from E. Merck. TA powder (20 g) was dissolved in distilled water at 95-98⁰C, then solution cooled at room temperature and 37% formaldehyde solution (20 mL) added to the solution. G powder (15 g) was dissolved with distilled water at 95-98⁰C and then added to the TA/ formaldehyde solution. Concentrated hydrochloric acid (7.5 mL) was added to the mixture and heated 95-98⁰C for 12 h with a reflux condenser. TG resin was washed with distilled water, dried at 110⁰C. Dried resin was crushed into small particles [25].

2.2.3 Tannins from sumac/ gelatin (STG) resin

For synthesized STG resin; sumac tannins were obtained from the sumac leaves, gelatin (G) purchased from E. Merck. The raw leaves were dried at room temperature in dark and then ground and sieved. Tannins are extracted from sumac leaves with 1:1 (v/v) acetone/water solution (Liao et al., 2004). Tannin (T), which was extracted from sumac leaves (20 g) dissolved in distilled water at 95-98⁰C, then solution cooled at room temperature and 37% formaldehyde solution (20 mL) added to the solution. G powder (15 g) was dissolved with distilled water at 95-98⁰C and then added to the T/ formaldehyde solution. Concentrated hydrochloric acid (7.5 mL) was added to the mixture and heated 95-98⁰C for 12 h with a reflux condenser. STG resin was washed with distilled water, dried at 110⁰C. Dried resin was crushed into small particles [25].

2.3 FTIR spectrum

The surface functional groups of adsorbents were detected by Fourier transform infrared (FTIR) spectroscope (Perkin Elmer Spectrum One). The spectra were recorded from 4000 to 650 cm⁻¹.

2.4 Scanning electron microscopy

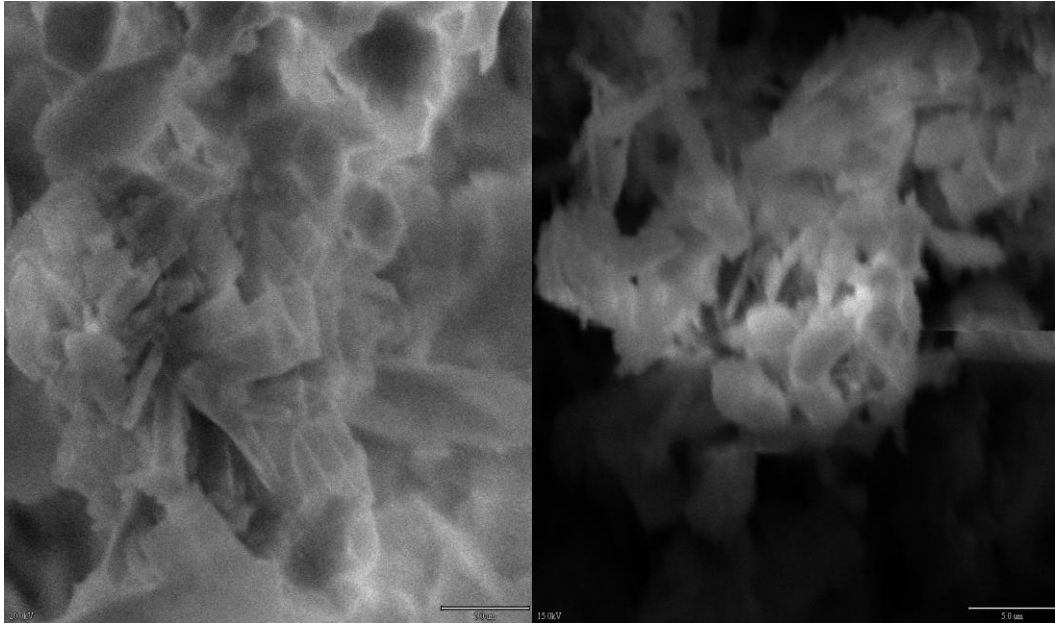
The SEM enables the direct observation of the changes in the surface structures of the resins. Morphological analysis of the TG and STG was performed by SEM using a Jeol JSM-5410LV. As shown in Fig. 1 and many small pores and particles with diameter < 5.0µm are seen on the surface TG and STG resins.

2.5 Particle size analysis

Particle size analysis of the SL, TG and STG were performed by using BT-9300H Laser particle size analyzer Beter Biate Instruments.

2.6 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a thermoanalytical method, in which the weight variation of a sample heated at a constant rate is measured continuously. From the temperature derivative of these spectra and differential thermogravimetric analysis (DTG), it is possible to obtain peak temperatures associated with a maximum rate of weight loss. Thermogravimetric analysis (TGA) was done with using a TA SDT Q600. Nitrogen gas was set to run at 20 ml/min to provide a controlled combustion environment. TGA was carried out in the temperature range of 20–750⁰C. (Merck) tannin, gelatin, sumac leaves TG, and STG resins were analyzed.



a) b)
Fig. 1. SEM images of a) STG resin, b) TG resin

2.7 Batch adsorption of Zn(II)

The range of concentrations of prepared Zn(II) solutions varied from 10 to 30 mg/L. Biosorption of Zn(II) from aqueous solution containing a single metal ion was investigated. Biosorption experiments were carried out in 100 mL Erlenmeyer flasks using 20 mL metal-bearing solution with a known quantity of the dried biosorbent. Optimum conditions (pH, contact time and temperature) for biosorption of the metals were determined. Biosorption at pH above 6.0 was not carried out to avoid any possible interference from metal precipitation. The biosorption medium was placed in a thermostated shaker bath (Memmert) and stirred for 2 h at the required temperature. Temperature was maintained at desired values using a temperature-controlled storage unit, where the experiments were conducted. The samples were taken at definite time and were filtered immediately to remove biomass by filter paper and heavy metals in the remaining solution were analyzed. The Zn(II) ions biosorption equilibrium was modeled by using the Freundlich, Langmuir and Tempkin models at the optimum pH value of solution.

The concentration of unadsorbed Zn(II) ions in the effluent was determined using an atomic absorption spectrophotometer (Nova 300 AAS).

The percent biosorption of Zn(II) ion was calculated as follows:

$$\text{Biosorption (\%)} = (C_0 - C_e) / C_0 \times 100 \quad (1)$$

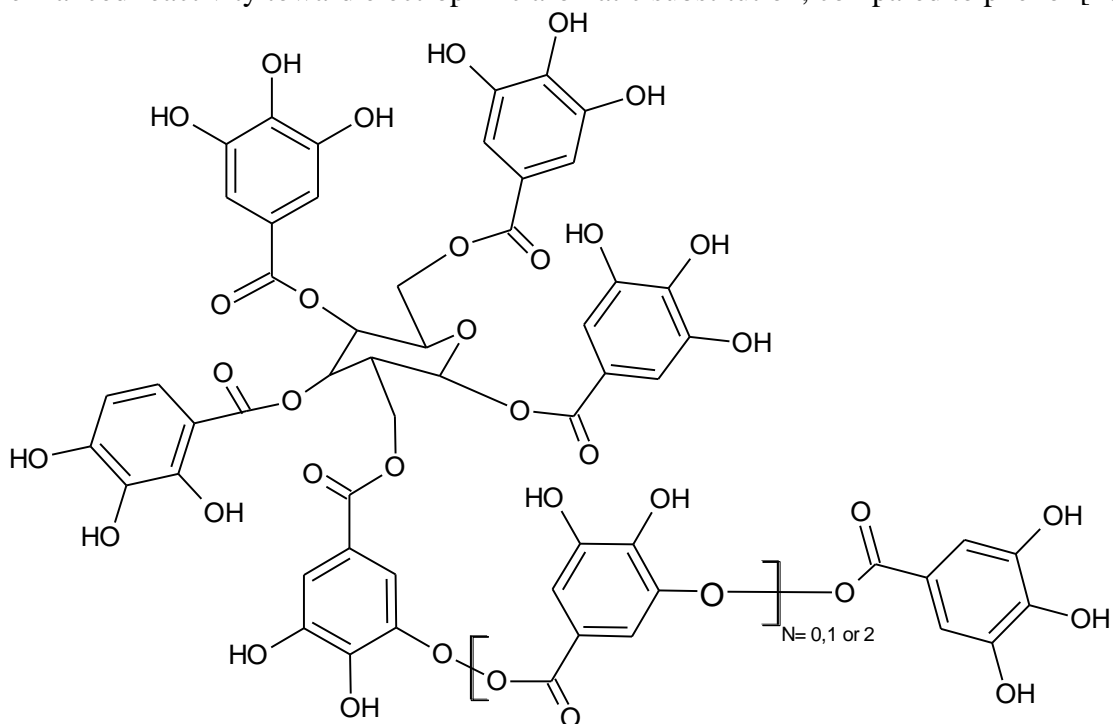
C_0 and C_e are the Zn(II) concentrations in mg/L initially and at equilibrium, respectively. The adsorption capacity of adsorbents for Zn(II) ions was calculated according to the following equation:

$$q_e = (C_0 - C_e)V/1000m, \quad (2)$$

where C_0 and C_e are the Zn(II) concentrations in mg/L initially and at equilibrium, respectively, V is the volume of Zn(II) solutions in mL, and m is the weight of sorbent in grams.

3. Results and Discussion

Tannins are made up of complex phenolic compounds of high molecular weight, ranging from 500 to 20000. They are divided into two major groups; a) condensed tannins (proanthocyanidins) and b) hydrolysable tannins (polyesters based on gallic and/or ellagic acid and their derivatives). Generally, tannins are soluble in water, with exception of very high molecular weight compounds. Turkish gallo-tannin (sumac tannin) is hexa-(or hepta)-O-galloyl- β -D-glucose and its structure is shown in Scheme1. Galloyl group in gallotannin consists of an aromatic ring bearing an esterified carboxyl group and three adjacent hydroxyl groups, leaving two free sites on the ring. Reactivity considerations show that the hydroxyl functions activate the free positions, while the remaining groups deactivate them. The overall effect is that galloyl group possesses an enhanced reactivity toward electrophilic aromatic substitution, compared to phenol [18].



Scheme1. Gallotannin structure in sumac tannin [26].

Gelatin, a polyampholyte obtained by a controlled hydrolysis of insoluble collagen, is one of the most important materials in resin production [27].

The sumac tannin dissolves in water, not after the reaction of tannin with formaldehyde and gelatin. Thus, insoluble TG and STG resins formed by the reaction of tannin with formaldehyde and gelatin show perfect adsorbent properties for the adsorption of Zn(II) ions from aqueous solutions.

3.1 Sorbent characterization

The FTIR spectra of sumac leaves, tannic acid, gelatin, TG resin, and STG resin are shown in Fig. 2. The broad peak in the region of 3400- 3200 cm^{-1} is characteristic of the -OH stretchings of the phenolic and methylol group of tannin. The small peak in the region of 3500- 3400 cm^{-1} is associated with N-H bond (from gelatin) of the TG resin and STG resin. The peaks at approximately 1300 and 1000 cm^{-1} in the spectrum of tannin belong to phenol groups [28]. The absorption bands between 1689 and 1459 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 1520-1400 cm^{-1} . The peak around 1270 cm^{-1} is associated with the -CO stretchings of the benzene ring and dimethylene ether bridges formed by reaction with the formaldehyde. The peaks at 1118-1020 cm^{-1} in the spectrums of TG and STG resins are due to C-O stretching and CH deformation. Also the FTIR spectra of TG, and STG resins have -OH and -NH peaks showed that TG, and STG resins have been synthesized properly.

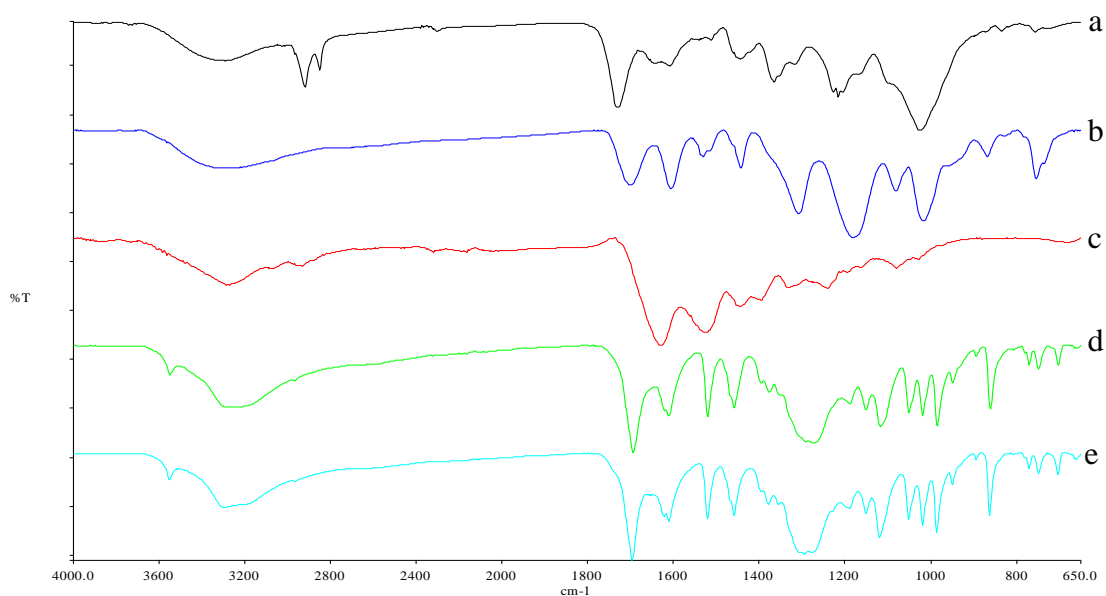


Fig. 2. FTIR spectra of a) SL b) Tannic acid (Merck) c) Gelatin d) TG resin e) STG resin

3.2 Effect of initial pH

Biosorption of Zn(II) ions onto SL, TG resin and STG resin as a function of pH was studied and the results are shown in Fig.3. The experiments were conducted at various initial zinc solution pH values of 2.0- 6.0. The metal solutions were conducted with the biosorbents (10mg/L) for 2 h at 25°C. The metal ions are best adsorbed on the biosorbents at pH 6. Similar findings were reported other types of biosorbents [29]. The uptake of metal showed a sharp increase with an increase in pH from 2.0 to 6.0. The maximum adsorption was found to be 3.27 for SL, 3.42 for TG, and 4.62 for STG at pH 6. Zn ions precipitated at pH values higher than 6.5. The optimum pH value for Zn(II) was obtained at pH 6.0 [30].

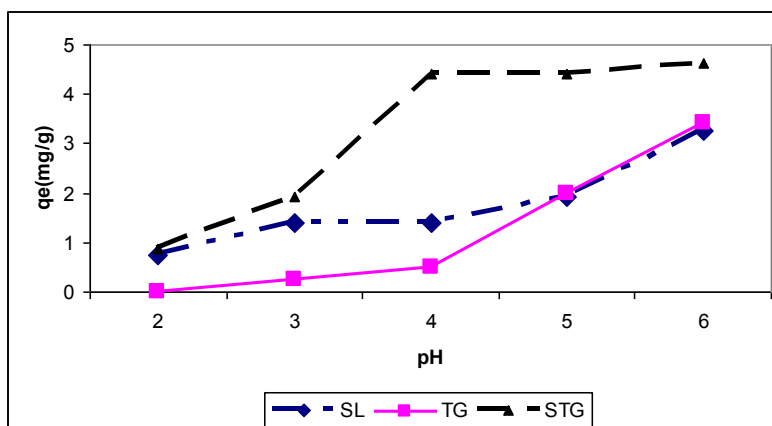
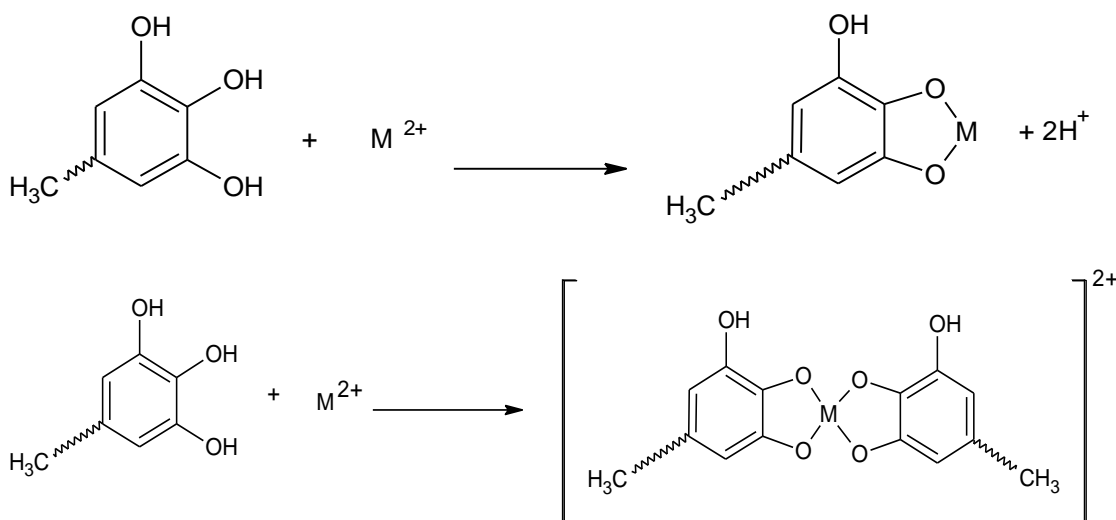


Fig. 3. The effect of pH on the adsorption of zinc(II) (adsorbent dosage: 0.2g/100ml, 10mg/L of Zn(II), 120 min)

Earlier studies on heavy metal biosorption have shown that pH was the single most important parameter affecting the biosorption process [30]. The different pH biosorption profiles for various heavy metal ions could be related to the nature of chemical interactions of each metal with the biosorbents. The metal uptake depends on active sites as well as the nature of the metal ions of solution. This can be explained by the competitive effect between the H_3O^+ and the $Zn(II)$ ions. At the low pH the H_3O^+ predominates and occupies the binding sites of the adsorbent whereas on increase in pH the concentration of H_3O^+ decreases and that of OH^- increases on the surface of the adsorbent. The surface charge of the adsorbent thus changes to negatively charged sites which results in higher attraction of cations [31]. The pH dependence of the metal uptake could be largely related to the various functional groups on the biosorbents surface and also on the metal solution chemistry. The different functional groups have a high affinity towards heavy metals so that they can complex the metal ions [32]. Hydroxyl functional group on biosorbents can play an important role for the biosorption of zinc. Biosorption mechanisms are shown in Scheme 2.



Scheme 2. Biosorption mechanisms for adsorption of divalent metal ion onto tannins [18].

3.3 Effect of temperature

The biosorption of $Zn(II)$ was carried out at three different temperatures 20, 30, and 40° C using SL, TG resin, and STG resin as biosorbents. The experimental results show that

the biosorption of Zn(II) ions onto sumac leaves, TG, and STG resins did not change significantly in this temperature range (Fig. 4). Similar findings were reported for other type of adsorbents [2,33].

3.4 Effect of initial concentration of zinc(II) on biosorption

The biosorption isotherm indicates how the adsorption molecules distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The amount of Zn(II) adsorbed (q_e) has been plotted against the equilibrium concentration (C_e) as shown in Fig 5. The equilibrium adsorption density, q_e increased with the increase in Zn(II) concentration for each adsorbent. The unit adsorption for sumac leaves was increased from 3.25 mg/g to 5.64 mg/g as the Zn(II) concentration in the test solution was increased from 10 mg/L to 30 mg/L.

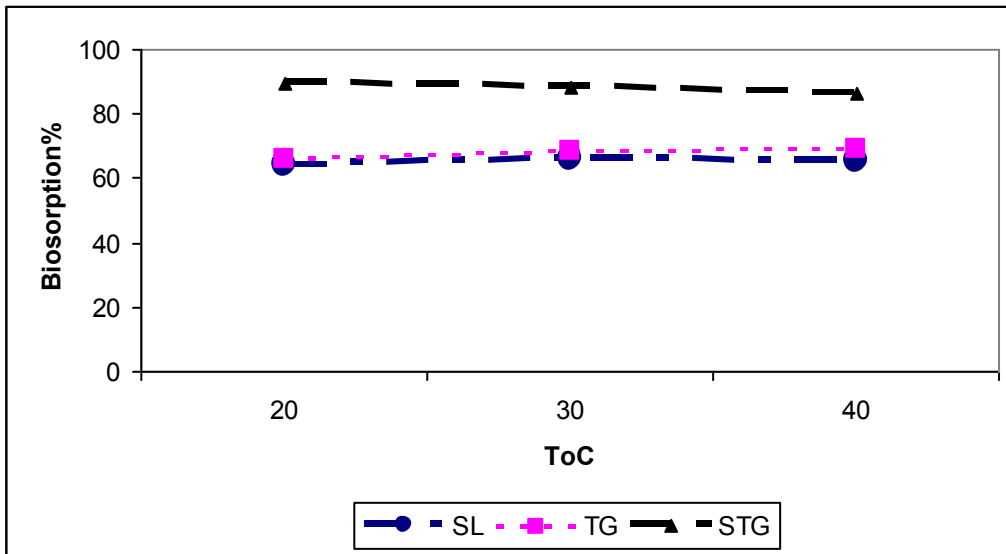


Fig. 4. The effect of temperature on the adsorption efficiency of Zn(II) onto adsorbents

Similarly, unit adsorption for TG resin was increased from 3.36 mg/g to 6.66 mg/g and STG resin increased from 5.27 mg/g to 13.61 mg/g as the Zn(II) concentration in the test solution was increased from 10 mg/L to 30 mg/L. Because the initial Zn(II) concentration provides an important driving force to overcome all mass transfer resistance. The increase of loading capacity of the adsorbents with increasing initial Zn(II) concentration may also be due to higher interaction between Zn(II) and adsorbents.

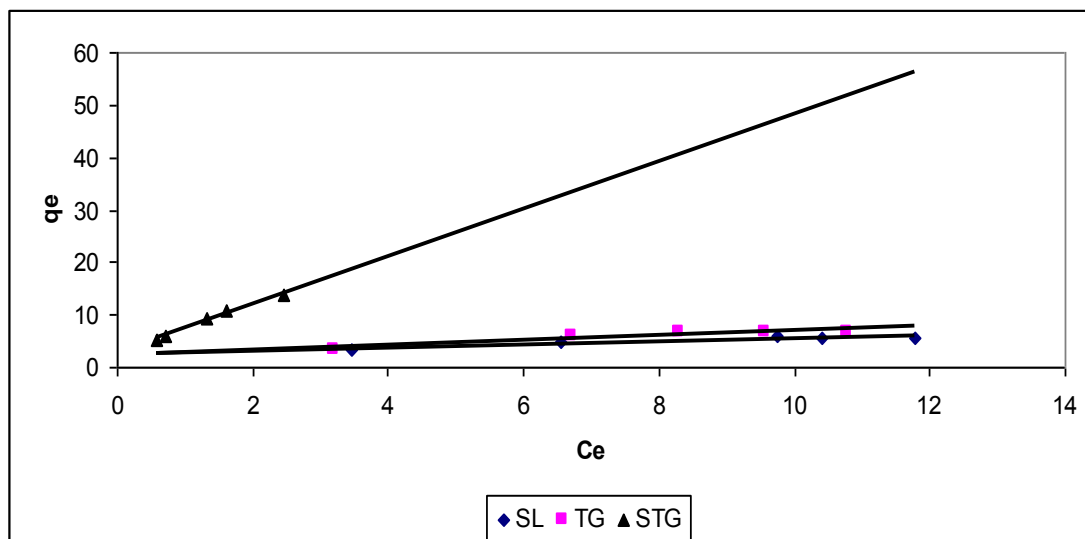


Fig. 5. The effect of equilibrium concentration on the adsorption of Zn(II) onto adsorbents (adsorbent dosage: 0.20g /100 ml of solution optimum pH, for 120 min)

3.5 Adsorption isotherms

Adsorption isotherms are important for the description of how adsorbate will interact with an adsorbent. They are also critical in optimizing the use of adsorbent. Zn(II) adsorption isotherms were obtained at constant pH, temperature and sorbent dosage. For each adsorbent, the pH value was chosen at its optimum value. To test the fit of data, the Langmuir, Freundlich and Tempkin isotherm models were applied to this study. The Langmuir, Freundlich and Tempkin isotherms are the most widely used models for studying the adsorption equilibrium between the metal solution and solid adsorbent phase [30, 34, 35]. Adsorption equilibrium data which express the relationship between mass of adsorbate adsorbed per unit weight of adsorbent and liquid-phase equilibrium concentration of adsorbate are represented by adsorption isotherms and provide important design data for adsorption system.

In this work, all models were used to describe the relationship between the amount of Zn(II) adsorbed and its equilibrium concentration.

The Freundlich isotherm model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between sorbed molecules. The Freundlich equation is expressed as

$$q_e = K_f C_e^{1/n} \quad (3)$$

K_f and n are the Freundlich constants with n giving an indication of how favorable the adsorption process is and K_f ($\text{mg/g}(\text{L/mg})^{1/n}$) is the adsorption capacity of the sorbent. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption condition. Values of K_f and n are calculated from the intercept and slope of the plot (Fig.6) are given in Table 1.

The empirical Freundlich isotherm model based on a heterogenous surface, the linear form of the equation can be written as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (4)$$

Kf and n are Freundlich constants characteristic of the system. Kf and n are indicators of adsorption capacity and intensity, respectively [36].

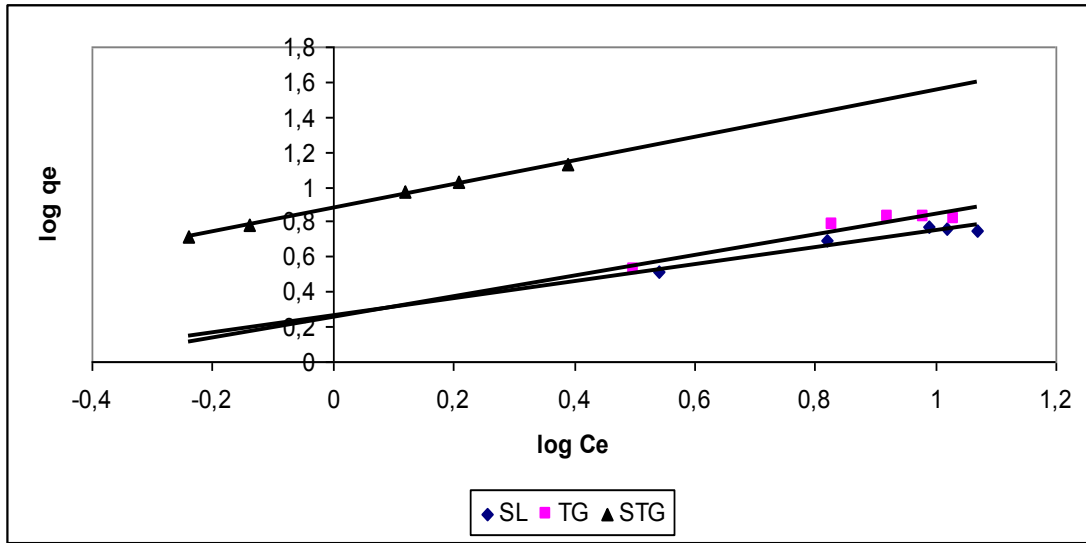


Fig. 6. Freundlich isotherms of Zn(II) adsorption onto sumac leaves, TG and STG resins

Langmuir isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. The Langmuir isotherm was used to describe observed adsorption phenomena. The Langmuir isotherm applies to adsorption on completely homogenous surface with negligible interaction between adsorbed molecules. In addition, the model assumes uniform energies of sorption onto the surface and no transmigration of the sorbate [9, 36]. The linear form of the equation can be written as:

$$C_e/q_e = 1/(b \cdot q_{max}) + C_e/q_{max} \tag{5}$$

Where C_e is the equilibrium concentration of copper, q_e is the amount of adsorption at equilibrium, q_{max} is the maximum monolayer capacity, and b is an equilibrium constant of Langmuir. The linear plots of C_e/q_e versus C_e (Fig. 7) suggest the applicability of the above model for the present system, showing formation of monolayer coverage of the adsorbate at the outer surface of adsorbent. The values of q_{max} and b were determined from the slope and intercept of the plots, respectively, and are given in Table 1.

Table 1. Freundlich, Langmuir and Tempkin isotherm constants for adsorption of Zn(II) onto sumac leaves, TG and STG resins

Adsorbent	Freundlich constants			Langmuir constants			Tempkin constant		
	Kf	n	R ²	q _{max} (mg/g)	b(L/mg)	R ²	B	A	R ²
Sumac leaves	1.83	2.05	0.94	8.53	0.19	0.96	2.14	1.39	0.95
TG resin	1.79	1.69	0.93	11.82	0.14	0.92	2.92	1.05	0.95
STG resin	7.60	1.50	0.99	27.55	0.40	0.99	5.81	4.01	0.99

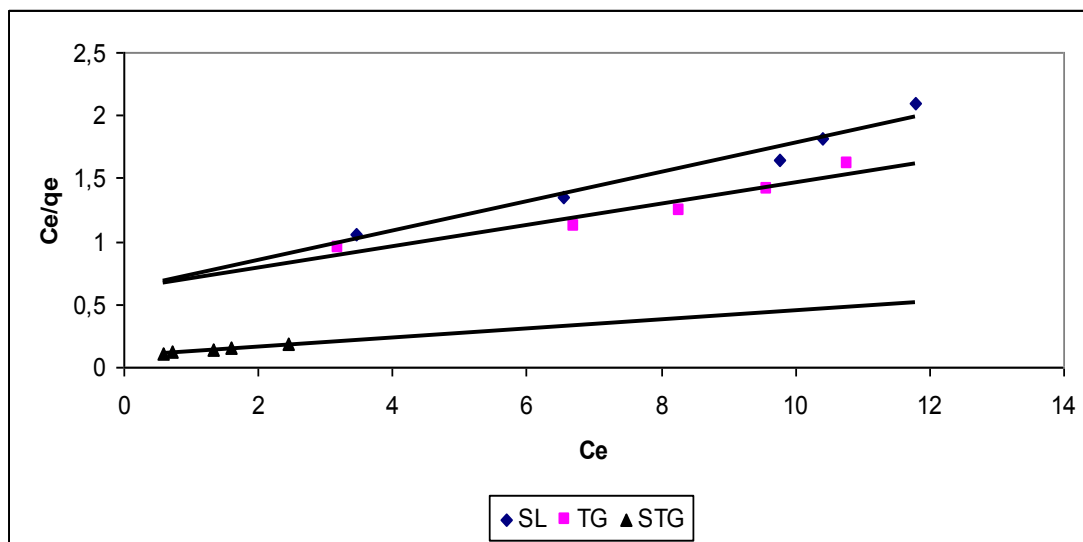


Fig. 7. Langmuir isotherms of Zn(II) adsorption onto sumac leaves, TG and STG resins

Furthermore, the essential characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor called equilibrium parameter R_L [37],

$$R_L = 1/(1+bC_0) \quad (6)$$

b is the Langmuir constant (L/mg) and C_0 is the initial Zn(II) ions concentration (mg/L). R_L value indicates the type of isotherm. An R_L value between 0 and 1 indicates a favorable adsorption. For our system, R_L values are 0.34, 0.42 and 0.20 for SL, TG resin and STG resin respectively.

As seen from Fig.6, the Freundlich adsorption model was suitable for describing the short-term sorption of Zn(II) by sumac leaves, TG and STG resins. As seen from Fig.7, the Langmuir adsorption model was suitable for describing the short-term sorption of Zn(II) by sumac leaves, TG and STG resins. Table 1 shows the model constants along with correlation coefficients for adsorption of zinc on adsorbents.

The K_f values obtained from the Freundlich model, suggest that the metal binding affinity was in the order of STG resin > sumac leaves > TG resin. The experimental values of the maximal adsorption capacities (q_{max}) of adsorbents were 9.53 mgg^{-1} for SL, 10.41 mgg^{-1} for TG resin and 28.48 mgg^{-1} for STG resin respectively. As seen in Table 1 and Fig 7 and 8, the maximum adsorption capacities for Zn(II) on SL, Tg resin and STG resin adsorbent at 303 K temperature were found to be 8.53 mgg^{-1} , 11.82 mgg^{-1} , and 27.55 mgg^{-1} , respectively.

The equilibrium data were also subjected to the Tempkin isotherm model to consider the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. So the equilibrium data suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The linear form of the Tempkin isotherm equation is:

$$q_e = B \ln A - B \ln C_e \quad (7)$$

$$B = (RT)/b \quad (8)$$

The adsorption data can be analyzed according to the equation above. A plot of q_e versus $\ln C_e$ enables the determination of the constants A and B. The constant B is related to the heat of adsorption.

The Tempkin isotherm model fitted the equilibrium data since the R^2 value was found to be 0.95 for sumac leaves biosorption, 0.95 for TG resin biosorption and 0.99 for STG resin biosorption (Fig. 8).

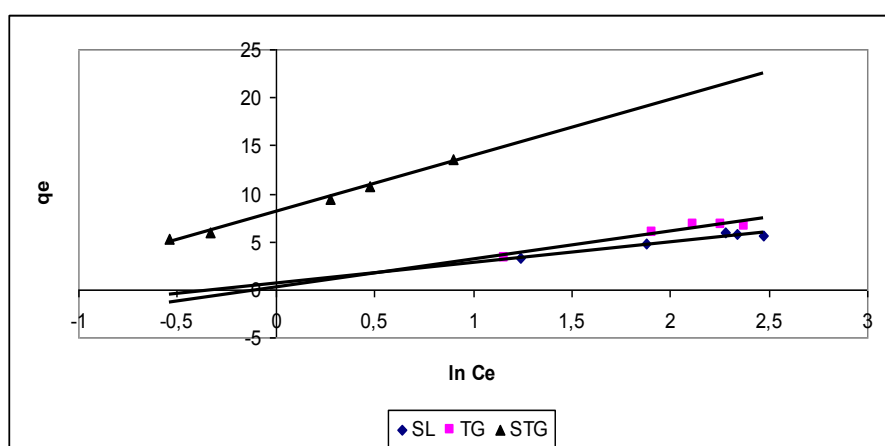


Fig. 8. Tempkin isotherms of Zn(II) adsorption onto sumac leaves, TG and STG resins

Table 2 lists a comparison of maximum monolayer adsorption capacity of Zn(II) ions with various adsorbents. Table 2 shows that the sumac leaves, TG and STG resins studied have large adsorption capacity which shows that our findings are good.

Table 2. Previously reported adsorption capacities of various low-cost adsorbents for Zn(II)

Low-cost adsorbents	Adsorption (mg/g)	Reference
<i>Pinus sylvestris</i> L.	26.39	[2]
Tree fern	7.58	[38]
Jute fibres (modified by reactive orange 13)	5.95	[39]
Jute fibres (unmodified)	3.55	[39]
Jute fibres (modified by hydrogenperoxide)	8.02	[39]
Groundnut shells (modified by reactive orange 13)	9.57	[40]
<i>Rhizopus arrhizus</i>	12.78	[29]
<i>Botrytis cinerea</i>	12.98	[41]
<i>Penicillium simplicissimum</i>	25.54	[42]
<i>Tectona grandis</i> L. F. leaves	16.42	[43]
Sumac leaves	8.53	This study
TG resin	11.82	This study
STG resin	27.55	This study

3.6 Adsorption thermodynamics

The Standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) thermodynamic parameters have been estimated to evaluate the feasibility of the adsorption process. The positive value of change in enthalpy (ΔH°) indicates that the adsorption is an endothermic process, while positive value of change in entropy (ΔS°) reflects the increased randomness at the solid/ solution interface.

The Langmuir constant $b(\text{L/mg})$ was used to calculate the Gibbs free energy change (ΔG°) according to the following equation,

$$\Delta G^\circ = -RT \ln b \quad (9)$$

R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K). Standard enthalpy and entropy change were obtained from the plot of ΔG° versus T and the equation is as follows,

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

In order to determine thermodynamic parameters, batch experiments were carried out at different temperatures in the range of 293- 313 K for Zn adsorption.

The values of ΔS° and ΔH° are calculated from the slope and intercept of the plots of ΔG° versus T. The results are shown in Table 3. The Gibbs free energy change (ΔG°) negative values increased with temperature, indicating the feasibility and spontaneity of the adsorption process of Zn(II) ions on SL, TG resin and STG resin. The positive ΔH° indicated the endothermic nature of the adsorption process and the positive ΔS° an increase in the randomness in the system interface solid/ solution during the adsorption process.

Table 3. Thermodynamic parameters for Zn(II) ions adsorption on SL, TG resin and STG resin (for SL, TG and STG resins pH=6, Co=10mgL⁻¹)

SL	Temperature		
	293	303	313
$\Delta G^\circ(\text{kJ/mol})$	-4.05	-4.18	-4.32
$\Delta H^\circ(\text{kJ/mol})$	0.09		
$\Delta S^\circ(\text{j/molK})$	0.01		
TG resin			
$\Delta G^\circ(\text{kJ/mol})$	-4.79	-4.95	-5.12
$\Delta H^\circ(\text{kJ/mol})$	0.05		
$\Delta S^\circ(\text{j/molK})$	0.02		
STG resin			
$\Delta G^\circ(\text{kJ/mol})$	-2.23	-2.31	-2.38
$\Delta H^\circ(\text{kJ/mol})$	0.03		
$\Delta S^\circ(\text{j/molK})$	0.01		

3.7 Thermal properties

Fig. 9 shows the thermogravimetric (TGA) curves of tannin (purchased from Merck Company), gelatin (purchased from Merck Company), TG resin and STG resin. The results show that tannin, in any form had lost up to 10% of its weight by the time it reached 200°C. Fig. 9 shows the results of thermogravimetric analysis of tannin, gelatin,

TG resin, and STG resin. Beyond 750°C gelatin showed the least thermal stability while the TG resin showed the highest thermal stability. The thermal stabilities of the TG and STG resins were investigated by thermogravimetric analysis (TGA) in a nitrogen stream at a heating rate of 20°C min⁻¹. The figs. 10 and 11 shows the thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves of two types of tannin resins. The decomposition of these systems essentially occurs in three stages. The first stage covers the postcuring, thermal reforming, and preliminary oxidation steps. The second stage depends mainly on the stripping of the ring, chain cleavage, and elimination of volatile fractions. In the third stage, oxidative degradation takes place at markedly higher temperatures. TGA curves of TG resin show these three stages. The first stage corresponds to the elimination of water, in which a nearly 11% weight loss has occurred; while in the second stage, the decomposition temperature range of 150-300°C could be the result of the partial breakdown of the intermolecular bonding and the 5% weight loss that has already occurred. The third stage occurs in the temperature range of 300-750°C, which may be due to the fragmentation of the intermolecular forces, and the molecule as a whole is decomposed with 59% weight loss.

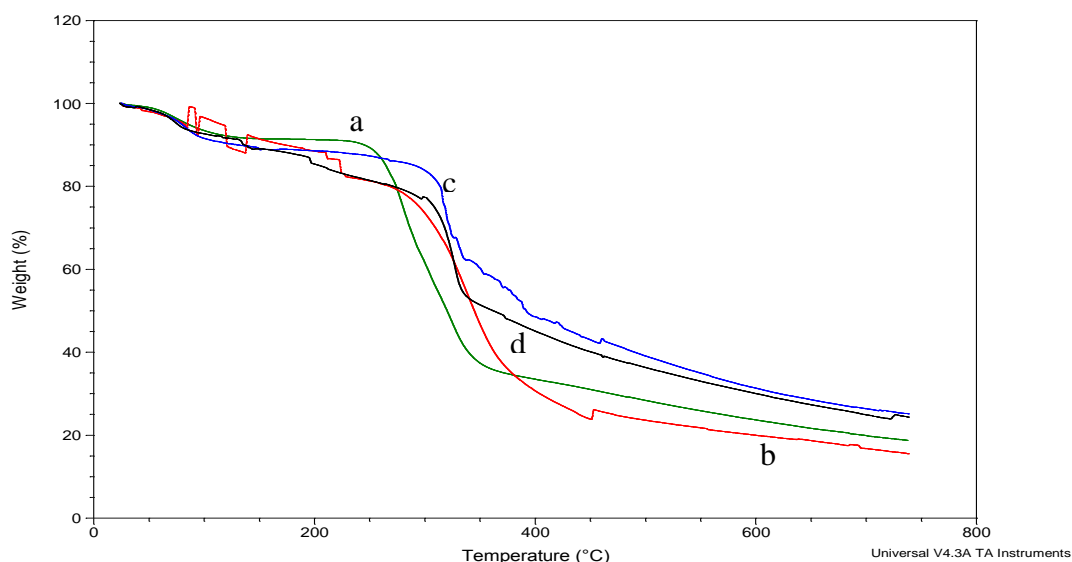


Fig. 9. TGA analysis of a-tannin (purchased from Merck company), b-gelatin (purchased from Merck company), c-TG resin and d-STG resin (Heating rate 20°C/min)

TGA curves of STG resin show these three stages. The first stage corresponds to the elimination of water, in which a nearly 11% weight loss has occurred; while in the second stage, the decomposition temperature range of 150-300°C could be the result of the partial breakdown of the intermolecular bonding and the 12% weight loss that has already occurred. The third stage occurs in the temperature range of 300-750°C, which may be due to the fragmentation of the intermolecular forces, and the molecule as a whole is decomposed with 53% weight loss. In addition, at 750°C, the residue of the TG resin weighs 1% more than the STG one. This showed that the thermal stability of TG resin was higher than the STG resin.

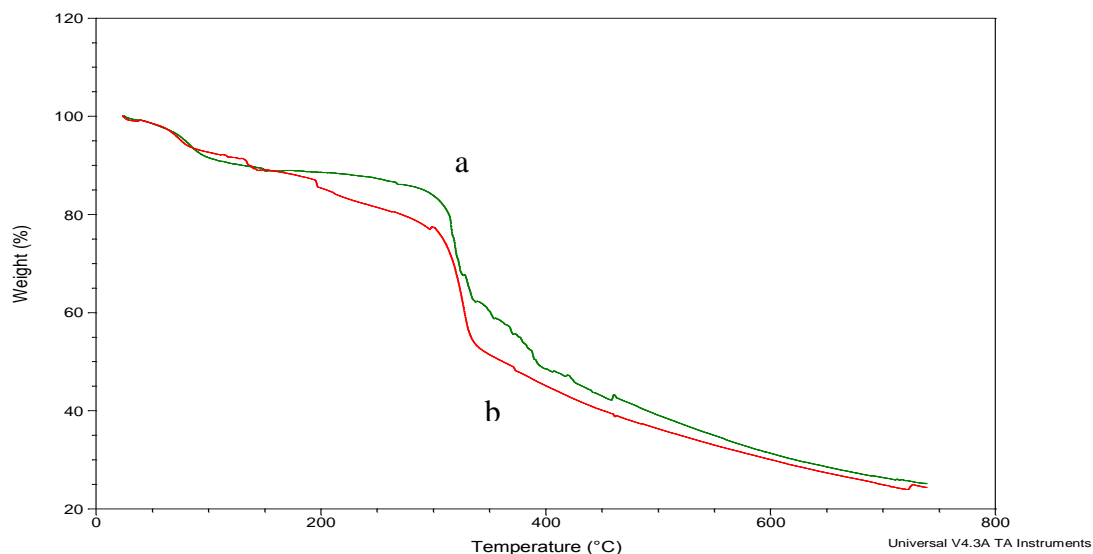


Fig. 10. Comparison of TGA thermograms between STG and TG resins (Heating rate 20°C/min)(a-TG resin b- STG resin)

According to the literature, the thermal decomposition mechanism of a phenolic resin includes three steps [44, 45]. The first step is the increase in the cross-linking density, which occurs from 300 to 500°C, as reported by Trick and Saliba [45]. The second step is from 400 to 750°C, which involves increasing vibrations of the molecule with temperature. At this step, the cross-linking network is broken. The third step is from 560 to 750°C. This involves the cleavage of the C-H groups in phenol and the formation of hydrogen gas. Although, as deduced Figs 9, 10 and 11, tannin is similar to phenol in structure, hence TG and STG resins are similar to phenol and show similar thermal behavior.

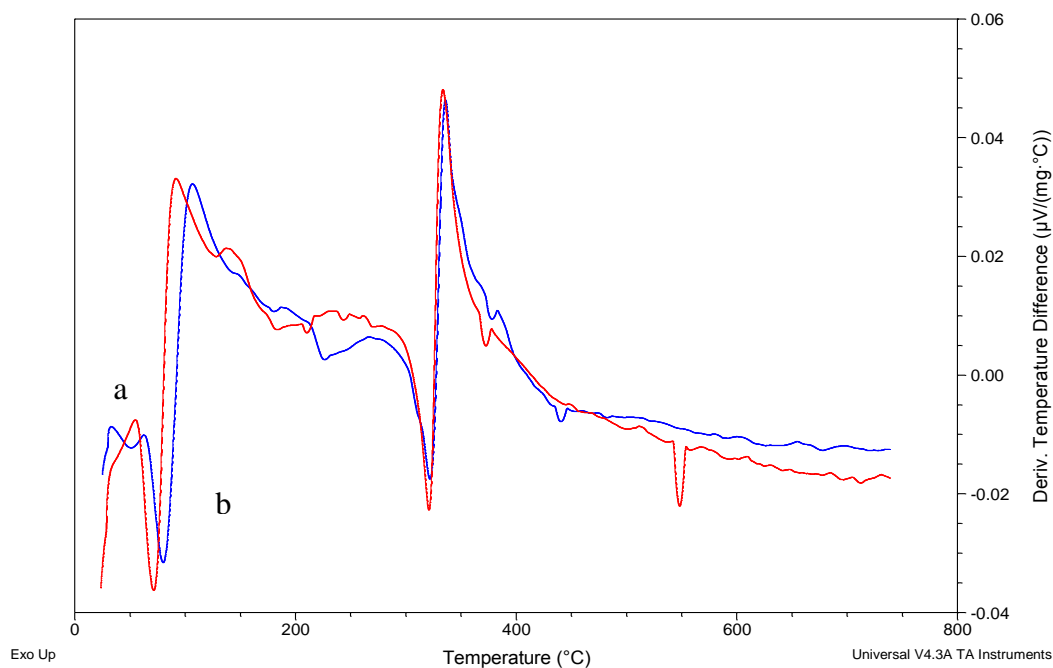


Fig. 11. Comparison of DTG thermograms between STG and TG resins (Heating rate 20°C/min), (a- TG resin b- STG resin)

4. Conclusion

In this work, SL, TG resin and STG resin as sorbents have been proposed to be an efficient and economical alternative in Zn(II) ion removal from water. The findings clearly show that:

- Batch sorption studies of zinc ions showed that the SL, TG resin and STG resin can be successfully used to remove Zn(II) ions from aqueous solution.
 - Langmuir model describes the zinc adsorption process and experimental data fitted to Langmuir isotherm. Using the Langmuir model equation, the monolayer adsorption capacity of SL, TG resin and STG resin were found to be 8.53, 11.82, 27.55 mgg^{-1} , for Zn(II) ions.
 - R_L value between 0 and 1 indicates a favorable adsorption. For our system, R_L values are 0.34, 0.42 and 0.20 for sumac leaves, TG resin and STG resin respectively. The process was a favorable adsorption from the values of a dimensionless factor (R_L) which is an essential characteristic of Langmuir model.
 - The K_f values obtained from the Freundlich model, suggest that the metal binding affinity was in as follows: STG resin > sumac leaves > TG resin.
 - The Tempkin isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.95 for sumac leaves adsorption, 0.95 for TG resin adsorption and 0.99 for STG resin adsorption.
 - The thermodynamic parameters ΔG° , ΔH° and ΔS° determined, indicated spontaneous endothermic and increasing randomness sorption process.
 - Beyond 750 °C gelatin showed the least thermal stability while the TG resin showed the highest thermal stability.
 - Thermal analysis of TG and STG resins: The TGA-DTG curves of all the resins were similar and showed the three steps in a similar way to a phenolic resin. This means that each resin is well cross-linked.
- (10) From Figs 9,10 and 11, it can be deduced that tannin is similar to phenol in structure and therefore TG and STG resins are similar to phenol and show similar thermal behavior.

Given the obtained results, it is apparent that sumac leaves, TG resin and STG resin can serve as appropriate adsorbents in removal process of Zn(II) ions from aqueous solution in terms of its high sorption capacity, naturality and abundance.

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