

Tannin gel derived from Leaves of Ricinus Communis as an adsorbent for the Removal of Cu (II) and Ni (II) ions from aqueous solution

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ABSTRACT: The biosorption of Cu (II) and Ni (II) ions from aqueous solutions by Tannin gel derived from Leaves of Ricinus Communis was investigated as a function of pH_{ZPC} , Initial pH, adsorbent dose, contact time and metal ion concentration. The aim of this study was to prepare the adsorbent and to find a suitable equilibrium isotherm and kinetic model for the removal of Cu (II) and Ni (II) ions in a batch reactor. The maximum percentage of adsorption for the removal of Cu (II) ion was found to be 76.92% at 7.04 pH and for the removal of Ni (II) ion was 71.74% at 7.12 pH. The adsorption of Cu (II) and Ni (II) ions followed the Pseudo-second-order and Intra particle diffusion rate equations and fits the Langmuir, Freundlich and Frenkel-Halsey-Hill isotherm equations well. The effects of the presence of one metal ion on the adsorption of the other metal ion were investigated in binary and ternary mixture and then the results were compared with single system. We investigate the recovery of the used adsorbent for its reusing is of great importance for environmental and economical reasons. i.e., TGLRC will be recovered by desorption method by using proper desorption agent like H_2O by batch mode study. Activated carbon developed from Ricinus Communis leaves can be an attractive option for heavy metal removal from water and waste water since test reactions made on stimulated waste water showed better removal percentage of Cu (II) and Ni (II) ions.

Keywords: Adsorption; Tannin gel; Ricinus communis leaves; Binary and Tertiary; Desorption.

I. INTRODUCTION

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. It is well known that some metals can have toxic or harmful effects on many forms of life. Among the most toxic metals are chromium (Cr), copper (Cu), lead (Pb), zinc (Zn) and mercury (Hg), which is one of the 11 hazardous priority substances in the list of pollutants contained in the Water Framework Directive (Directive 2000/60/EC) [1]. Many industries discharge heavy metals such as lead, cadmium, copper, nickel and zinc in their wastewaters [2]. Metals such as copper and nickel are known to be essential to plants, humans and animals, but they can also have adverse effects if their availability in water exceeds certain threshold values.

Therefore, it is urgent to remove heavy metals such as copper and nickel from wastewater. Although heavy metal removal from aqueous solutions can be achieved by conventional methods, including chemical precipitation, oxidation/reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies, they may be ineffective or cost-expensive, especially when the metal ion concentrations in solution are in the range of 1–100 mg/L [3, 4]. Recently, adsorption technology has become one of the alternative treatments in either laboratory or industrial scale [5, 6]. There are many adsorbents in use. Activated carbons (AC) are known as very effective adsorbents due to their highly developed porosity, large surface area, variable characteristics of surface chemistry, and high degree of surface reactivity [7]. However, due to their high production costs, these materials tend to be more expensive than other adsorbents. This has led a growing research interest in the production of activated carbons from renewable and cheaper precursors. The choice of precursor largely depends on its availability, cost, and purity, but the manufacturing process and intended applications of the product are also important considerations [8]. Several suitable agricultural by-products (lignocellulosics) including fruit stones, olive waste cake, pine bark, rice husks, pistachio-nut shells and wheat bran have been investigated in the last years as activated carbon precursors and are still receiving renewed attention.

In recent years, considerable attention has been focused on the removal of heavy metals from aqueous solution using natural raw materials as an interesting potential source of low-cost adsorbents [9-11]. 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. During the last years, the interest on biomaterials and specifically in tannins was growing.

The term tannins cover many families of chemical compounds. Traditionally they have been used for tanning animal skins, hence their name, but one also finds several of them used as water treatment agents. Their natural origin is as secondary metabolites of plants [12], occurring in the bark, fruit, leaves, etc. While Acacia and Schinopsis bark constitute the principal source of tannins for the leather industry, the bark of other non-tropical trees such as Quercus ilex, suber, and robur, Castanea, and Pinus can also be tannin-rich.

Tannin gelification is a chemical procedure that immobilizes tannins in an insoluble matrix [13, 14] so their properties involving, e.g. metal chelation, are available then in an efficient adsorbing agent. In addition, the resulting material from gelification (sometimes called tannin rigid gel) presents interesting properties from the point of view of resistance, nonflammability or mechanical undeformability [15, 16]. Gelifications of tannins have been widely reported either in scientific literature or in patents. Experimental conditions of gelification may imply the use of formaldehyde or other aldehyde in a basic or acidic environment. Examples of basic gelification are shown in scientific literature previously [17-19] and in patents such as US patent 5,158,711 [20]. Acid gelification is also presented by other researchers [21, 22].

The chemical basis of the tannin gelification is widely reported [23]. Formaldehyde and other aldehydes react with tannins to induce polymerization through methylene bridge linkages at reactive positions on the tannin flavonoid molecules.

Agricultural by-products are high volume, low value and underutilized lignocellulosic biomaterials, and contain high levels of cellulose, hemicellulose and lignin. *Ricinus communis* is a species of flowering plant in the spurge family, Euphorbiaceae. It belongs to a monotypic genus, *Ricinus*, and subtribe, *Ricininae*.

Ricinus communis grows throughout the drier parts and near drainages of India. Annual production of *Ricinus communis* is estimated to be more than 1.0 tons globally, of which India accounts for 60% of the production. The adsorption ability of *Ricinus communis* leaves was previously investigated for the adsorption of Cu^{2+} ion and Ni^{2+} ion from aqueous solution [24, 25].

In this study, Tannin gel has been prepared from the cheap and abundantly available agricultural waste product leaves of *Ricinus communis* (TGLRC) and applied them to remove heavy metals such as Cu (II) and Ni (II) ions from waste water.

The objective of this study is to systematically examine adsorption mechanisms, adsorption isotherms, adsorption kinetics and properties of a tannin gel adsorbent synthesized from leaves of *Ricinus communis* (TGLRC) for removal of Cu (II) and Ni (II) ions from aqueous solutions.

II. MATERIALS AND METHODS

Preparation of Adsorbent

Tannin extracts

The *Ricinus communis* leaves were obtained from the agricultural form in Tirupur district (Tamil Nadu). It was air-dried and powdered in a grinder. Dried *Ricinus communis* with the mass of 100 g were mixed with 600 mL of water. Then 5 g of NaOH were added and the mixture was stirred in magnetic stirrer at 90°C for 1 h. Solids were separated by filtration and liquid fraction was dried in oven (65°C) overnight. The resultant was considered the tannin extract.

Tannin gel preparation (TGLRC)

Tannin gels were prepared according to the basis of Nakano et al. [17]. Five grams of tannin extract were dissolved in 32 mL of NaOH (PANREAC) 0.125 mol L⁻¹ and 30 mL of distilled water at 80 °C. When mixture was homogeneous, certain amount of aldehyde (Formaldehyde) was added and reaction was kept at the same temperature for 8 h 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 to small particles. They were washed successively with distilled water and 0.01 molar HNO₃ was used to remove unreacted sodium hydroxide. Finally, the adsorbent was dried again in oven. Differences are found between this preparation way and the description made by Yurtsever and Sengil [26], mainly concerning the amount of formaldehyde.

Preparation of stock solution

Samples of potassium chromate (K_2CrO_4), copper sulphate penta hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and Nickel sulphate hexa hydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) was obtained from Aluva, Edayar (specrum reagents and chemicals pvt. Ltd). All other chemicals used in this study were analytical grade and Purchased from Aluva, Edayar (specrum reagents and chemicals pvt. Ltd)

A Stock solution of 1000 mg/L was prepared by dissolving accurately weighed amounts of potassium chromate (K_2CrO_4) in doses of 1000 mL double-distilled water. Working copper and Nickel solutions were prepared just before used by appropriate dilutions of stock solution.

Characterization of the adsorbent

The point of zero surface charge characteristic of TGLRC was (pH_{ZPC}) determined by using the solid addition method. A Fourier transform infrared spectroscopy (SHIMADZU, IR Affinity-1) with KBr pellet was used to study the functional groups available on the surface of TGLRC, with a scanning range of 4000-400 cm^{-1} . The crystalline structure of TGLRC was evaluated by X-ray diffractometer, by using Cu K_α radiation (1.54060 Å) at 45 kV and 30 mA with a scan analysis. The concentration of Cu (II) and Ni (II) ions was determined using UV-vis spectrophotometer (SHIMADZU UV-2450).

Batch adsorption studies

The adsorption experiments were carried out in a batch process to evaluate the effect of pH, contact time, adsorbent dose, adsorption kinetics, adsorption isotherm, influence of other metal ions in single and binary system and regeneration of Cu (II) and Ni (II) ions onto TGLRC.

Batch equilibrium studies

To study the effect of parameters such as adsorbent dose, metal ion concentration and solution pH for the removal of adsorbate on TGLRC, batch experiments were performed. Stock solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was prepared and further diluted to the 25 – 200 mg/ L concentrations for the experiments. pH adjustment was fulfilled by adding 0.1 M HCl or 0.1 M NaOH into the solutions with known initial metal concentrations. Batch adsorption experiments were conducted in asset of 250 mL stoppered flasks containing 200 mg adsorbent and 50 mL of metal solutions with different concentrations (25-200 mg / L) at the optimum solution pH. The flasks were agitated using a mechanical orbital shaker, and maintained at room temperature for 2 h at a fixed shaking speed of 120 rpm until the equilibrium was reached. The

suspensions were filtered and metal concentrations in the supernatant solutions were measured using a Digital photo colorimeter (model number-313). From the initial and final concentrations, percentage removal can be calculated by use of the formula:

$$\% \text{ of Removal} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of Cu (II) and Ni (II) ions in mg/L and C_f is the final concentration of Cu (II) and Ni (II) ions in mg/L. The results obtained in batch mode were used to calculate the equilibrium metal uptake capacity. The amounts of uptake of Cu (II) and Ni (II) ions by TGLRC in the equilibrium (q_e) were calculated by the following mass-balance relationship:

$$q_e = \frac{(C_0 - C_e)}{W} \times V \quad (2)$$

where q_e is the equilibrium uptake capacity in mg/g, V is the sample volume in liters, C_0 is the initial metal ion concentration in mg/L, C_e the equilibrium metal ion concentration in mg/L, and W is the dry weight of adsorbent in grams.

III. RESULTS AND DISCUSSION

Characterization of TGLRC adsorbent

Zero point charges (pH_{ZPC})

The zero surface charge characteristics of TGLRC were determined by using the solid addition method [27]. The experiment was conducted in a series of 250 mL glass stoppered flasks. Each flask was filled with 50 mL of different initial pH $NaNO_2$ solutions and 200 mg of TGLRC. The pH values of the $NaNO_2$ solutions were adjusted between 2 to 10 by adding either 0.1 M HNO_3 or 0.1 M $NaOH$. The suspensions were then sealed and shaken for 2 h at 120 rpm. The final pH values of the supernatant liquid were noted. The difference between the initial pH (pH_i) and final pH (pH_f) values ($pH = pH_i - pH_f$) was plotted against the values of pH_i . The point of intersection of the resulting curve with abscissa, at which pH of 0, gave the pH_{ZPC} .

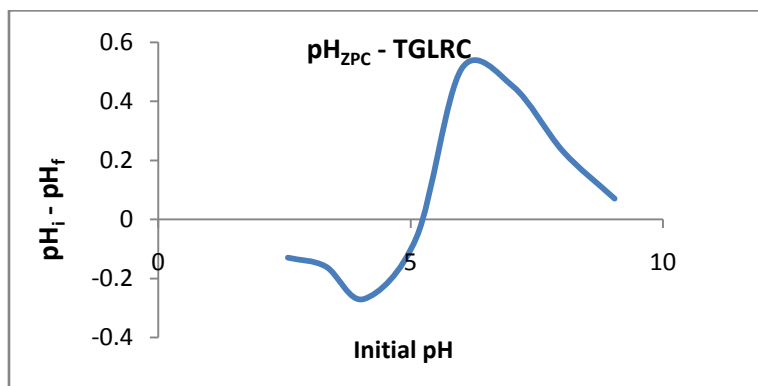


Figure. 1. Zero point charge of TGLRC.

The pH_{ZPC} of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. *Fig.1.* shows that the plot between ΔpH_i , i.e. ($pH_i - pH_f$) and pH_i for pH_{ZPC} measurement. The point of zero charge for TGLRC is found to be 5.12. This result indicated that the pH_{ZPC} of TGLRC was depended on the raw material and the activated agency. The zero point charge ($pH_{ZPC} = 5.12$ for TGLRC) is below the solution pH ($pH = 7.04$ for Cu (II) and 7.12 for Ni (II) ion adsorption) and hence the negative charge density on the surface of TGLRC increased which favours the adsorption of Cu (II) and Ni (II) ions [28].

FTIR analysis of TGLRC

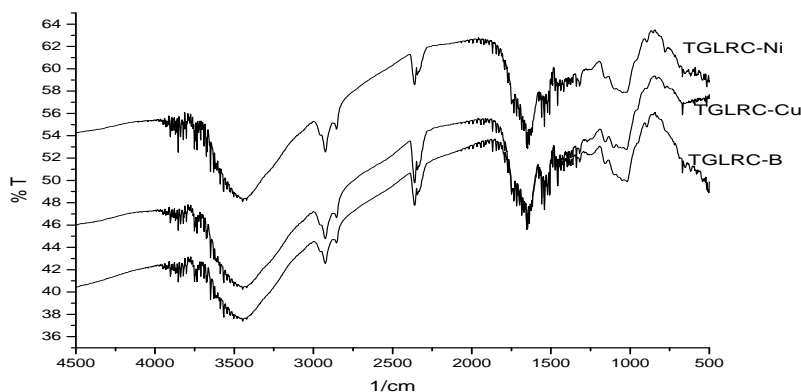


Figure. 2. FTIR spectra for TGLRC before and after adsorption of Cu (II) and Ni (II) ions.

Surface functional groups were detected by Fourier-transform infrared spectroscopy. The Fig. 2 shows the FTIR spectra of TGLRC before and after adsorption of Cu (II) and Ni (II) ions from aqueous solution. The functional groups of the adsorbents and the corresponding infrared absorption frequency are shown in Table 1. These spectra contain peaks at 3421-3462 cm^{-1} . This indicates the presence of hydrogen-bonded OH groups. The peak 3421 cm^{-1} which is originated from TGLRC before adsorption of Cu (II) and Ni (II) ions is shifted to 3462 cm^{-1} in TGLRC-Cu (after adsorption of Copper) and shifted to 3446 cm^{-1} in TGLRC-Ni (after adsorption of Nickel). The intense bent at about region 2852-2854 cm^{-1} for the precursor was attributed to the asymmetric and symmetric vibration modes of methyl and methylene group (C-H group)[29]. The peak around 1647-1653 cm^{-1} can be assigned to aromatic ring vibrations. The peak at 1018-1047 cm^{-1} is related to lignin. Therefore it is possible that cellulose, hemicelluloses as well as lignin, having many OH groups in their structure, make up most of the absorbing layer.

Table 1. The FTIR spectral characteristics of TGLRC before and after adsorption of Cu (II) and Ni (II) ions.

IR Peak	Frequencies (cm^{-1})	Assignment
1	3447	Bonded -OH groups
2	2852	Aliphatic C-H groups
3	1647	Aromatic ring vibrations
4	1022	-C-C group

X-ray diffraction analysis

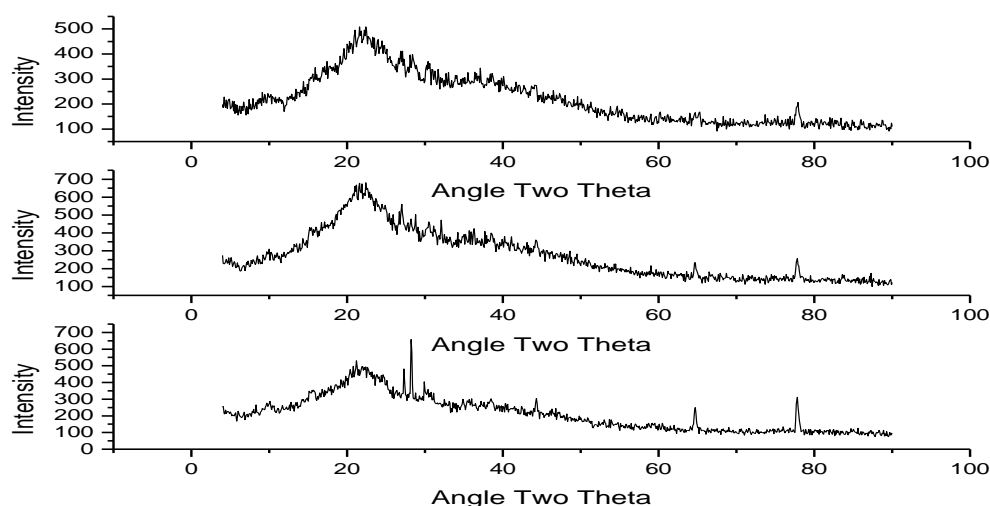


Figure 3. XRD pattern of TGLRC before and after adsorption of Cu (II) and Ni (II) ions.

Adsorption reaction may lead to changes in molecular and crystalline structure of the adsorbent and hence an understanding of the molecular and crystalline structures of the adsorbent and the resulting changes thereof would provide valuable information regarding adsorption reaction. Hence, XRD patterns of the adsorbent before and after adsorption of Cu (II) and Ni (II) ions have been studied.

As a representative case the XRD patterns of TGLRC before and after treatment with Cu (II) and Ni (II) ions are shown in Fig. 3. The results indicated that the diffraction profiles of TGLRC before and after adsorption of Cu (II) and Ni (II) ions exhibited broad peaks and the absence of a sharp peak revealed a predominantly amorphous structure, the broad peak seems to be appear at around $2\theta = 21, 22, 26$ and 28° which was similar to the peak of crystalline carbonaceous structure such as graphite. It is evident from the figure that the XRD pattern of TGLRC loaded with Cu (II) and Ni (II) ions exhibits no variation in the crystal structure and this suggests that the Cu (II) and Ni (II) ions might diffuse into micropores and sorbs mostly by physisorption without altering the structure of the adsorbent. From the XRD analysis for the adsorbent (TGLRC), we concluded that the tannin gel preparation was completed. The above observation corroborated well with batch sorption experiments.

Batch adsorption studies

Effect of solution pH

The zeta-potentials of the TGLRC particles in water were measured at different pH. It was found that TGLRC particles are positively charged at low pH and negatively charged at high pH, having a point of zero charge (pH_{zpc}) at pH 5.12 for TGLRC. Therefore, it can be expected that positively charged metal ions are likely to be adsorbed by the negatively charged TGLRC particles at a $\text{pH} > \text{ZPC}$.

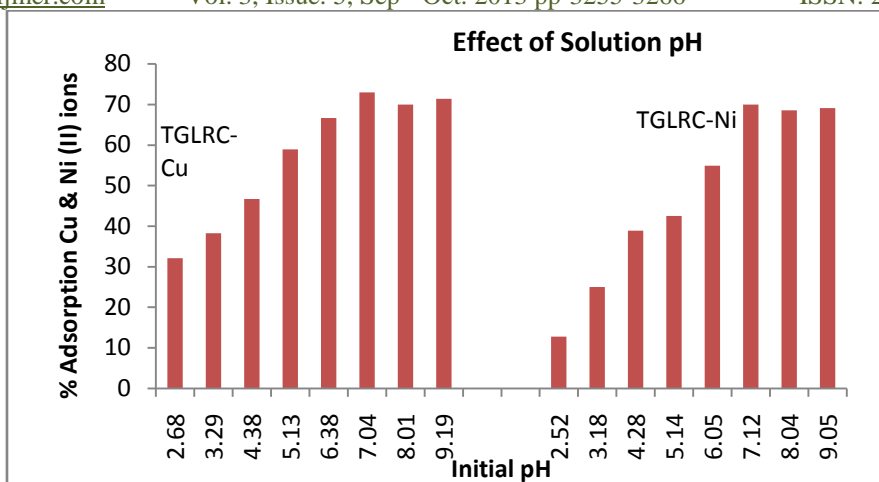


Figure. 4. Effect of solution pH on the adsorption of Cu (II) and Ni (II) ions on TGLRC.

The pH of the aqueous solution has been identified as the most important variable governing metal adsorption onto adsorbents. This is partly due to the fact that hydrogen ions themselves are a strongly competing adsorbate and because the solution pH influences the ionization of surface functional groups. In order to establish the effect of pH on the adsorption of Cu (II) and Ni (II), the batch equilibrium studies at different pH values were carried out in the range of 2–9 (Fig. 4). We note that as the pH of the solution increased from 2.0 to 9.0, the adsorption capacity of TGLRC increased up to pH 7.0 for the adsorption of Cu (II) and Ni (II) ions by TGLRC and then decreased at pH > 6.0. The amount adsorbed increased as pH increased from 2.0 to 7.0 may be due to the presence of negative charge on the surface of the adsorbent that may be responsible for metal binding. However, as the pH is lowered, the hydrogen ions compete with the metal ions for the sorption sites in the sorbent; the overall surface charge on the adsorbent becomes positive and hinders the binding of positively charged metal ions [30]. At pH higher than 7.0, the precipitation of insoluble metal hydroxides takes place restricting the true adsorption studies [31].

However, when the pH of the solution was increased, the uptake of metal ions was increased. It appears that a change in pH of the solution results in the formation of different ionic species, and different carbon surface charge. At pH values lower than 5, the metal ions can enter into the pore structure may be due to its small size. So, an optimized pH of 7.04 for the removal of Cu (II) ions and 7.12 for the removal of Ni (II) ions by TGLRC adsorbent is taken for all the adsorption experiments.

Effect of contact Time

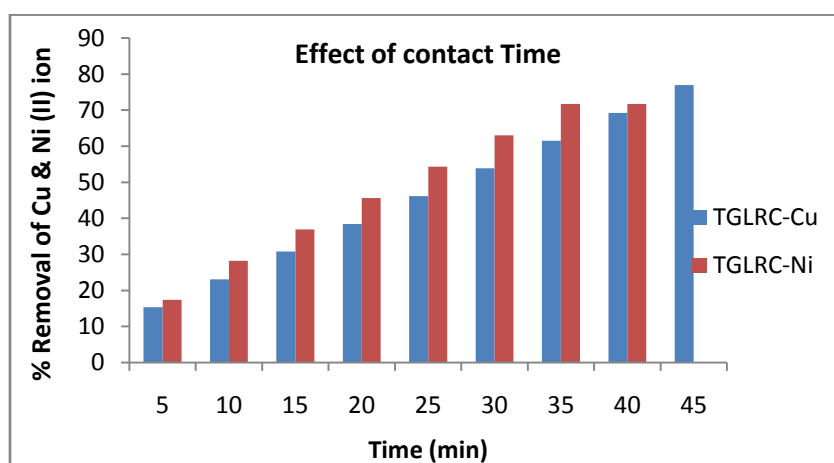


Figure. 5. Effect of Contact time on the adsorption of Cu (II) and Ni (II) ions onto TGLRC.

The uptake of Cu (II) and Ni (II) ions onto TGLRC as a function of contact time is shown in Fig. 5. The effect of contact time between the adsorbents and Cu (II) and Ni (II) ions showed that the Cu (II) was removed within 45 min by TGLRC and Ni (II) ions was removed within 40 min by TGLRC and remains almost constant even up to an hour.

This may be due to the attainment of equilibrium condition at 45 min of contact time for Cu (II) removal with TGLRC and 40 min for the removal of Ni (II) with TGLRC, which are fixed as the optimum contact time. At the initial stage, the rate of removal of Cu (II) and Ni (II) ions was higher, due to the availability of more than required number of active sites on the surface of carbons and became slower at the later stages of contact time, due to the decreased or lesser number of active sites.

Effect of adsorbent dose

The effect of adsorbent dose on the percentage removal of Cu (II) and Ni (II) ion was studied at initial Cu (II) and Ni (II) ion concentration of 100 mg/L by allowing a contact time of 60 min and at the solution pH of 7.04 for Cu (II) and 7.12 for Ni (II) ions. The results are presented in *Fig. 6*. It is showed that the percentage removal of Cu (II) and Ni (II) ion increased with increase in adsorbent dose from 200 mg/50mL to 1000 mg/50mL. This increase in Cu (II) and Ni (II) ion removal is due to the availability of higher number of Cu (II) and Ni (II) ions per unit mass of adsorbent (TGLRC), i.e., higher metal ions/ adsorbent ratio. Thus, further experiments were carried out using 200 mg of adsorbent per 50 ml of Cu (II) and Ni (II) ion solution, as it exhibits appreciable removal capacity, for the optimization of adsorption parameters.

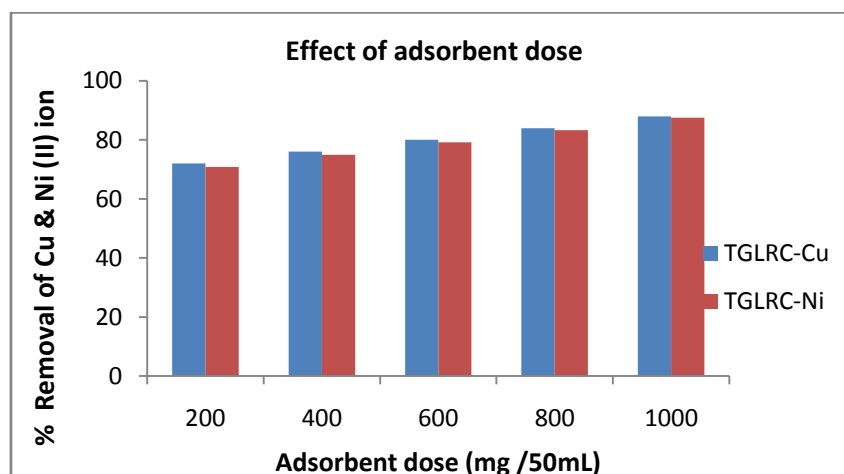


Figure. 6. Effect of adsorbent dose on the adsorption of Cu and Ni (II) ions by TGLRC.

Effect of metal ion concentration

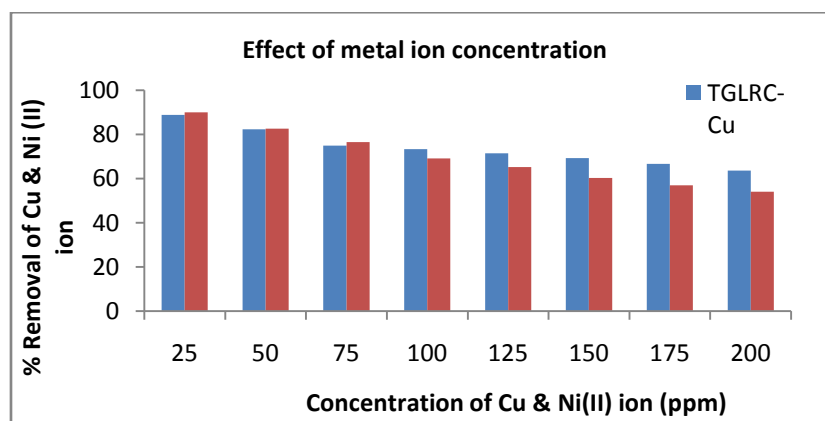


Figure. 7. Effect of metal ion concentration on the adsorption of Cu (II) and Ni (II) ions by TGLRC.

The effect of initial metal ion concentration on adsorption capacity of TGLRC was carried out at a carbon dosage of 200 mg/ 50 mL, pH 7.04 for Cu (II) ion removal and 7. 12 for Ni (II) ion removal by TGLRC, contact time 1 h, temperature 303K for different initial metal ion concentration from 25 to 200 mg/50mL and is shown in *Fig. 7*. As shown, the amount of metal uptake per unit weight of the adsorbent increases with increasing initial metal ion concentration showing the maximum adsorption capacity of 5.48 mg /50mL to 31.32 for Cu (II) ion removal and the maximum adsorption capacity of 5.53 mg/50mL to 26.57 mg/50mL for Ni (II) ion removal by TGLRC. This is because at higher initial concentrations, the ratio of initial number of moles of metal ions to the available adsorption surface area is high. This may be attributed to an increase in the driving force of the concentration gradient with increase in the initial metal ion concentration [32].

Adsorption isotherms

Adsorption isotherm is the most important information which indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when adsorption process reaches on Equilibrium state. When the system is at Equilibrium is of importance in determining the maximum sorption capacity of TGLRC towards metal solution. Equilibrium data are a basic requirement for the design of adsorption systems and adsorption models, which are used for the mathematical description of the adsorption equilibrium of the metal ion by the adsorbent. The results obtained for adsorption of Cu (II) and Ni (II) ions were analyzed by use of well-known models given by the Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Harkin-Jura and Frenkel-Halsey-Hill adsorption isotherm models [34 - 38]. For the sorption isotherms, initial metal ion concentration was varied whereas solution pH and amount of adsorbent were held constant. The sorption isotherms for Cu (II) and Ni (II) ions were obtained for TGLRC at solution pH 7.04 and pH 7.12, respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad \text{Langmuir model} \quad (4)$$

$$\log q_e = \frac{1}{n} \log(C_e) + \log K \quad \text{Freundlich model} \quad (5)$$

$$q_e = \beta \ln \alpha + \beta \ln C_e \quad \text{Temkin model} \quad (6)$$

$$\ln q_e = \ln Q_m - K\varepsilon^2 \quad \text{Dubinin - Radushkevich model} \quad (7)$$

The mean adsorption energy, E (kJ/mol) is calculated with the help of following equation:

$$E = \frac{1}{\sqrt{-2Y}} \quad (8)$$

$$\frac{1}{q_e^2} = \left(\frac{B_2}{A}\right) - \left(\frac{1}{A}\right) \log C_e \quad \text{Harkin - Jura model} \quad (9)$$

$$\ln q_e = \frac{1}{n} \ln K - \frac{1}{n} \ln C_e \quad \text{Frenkel - Halsey - Hill model} \quad (10)$$

where C_e is the Cu (II) and Ni (II) ion concentration in the solution (mg/L), q_e is the Cu (II) and Ni (II) concentrations in the solid adsorbent (mg/g), q_m is the maximum adsorption capacity (mg/g), K_f is a constant related to the adsorption capacity ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$), b is a constant related to the energy of adsorption (L/g), n is a constant related to the energy of adsorption, α (L/g) is Temkin constant representing adsorbent-adsorbate interactions and β (mgL-1) is another constant related with adsorption heat, ε is the Polanyi potential ($\text{kJ}^2 \text{mol}^2$) and E (kJ/mol) is the mean adsorption energy. B_2 is the isotherm constant, represented by Harkin-Jura isotherm model. The adsorption isotherm parameters for all the six isotherm models are calculated and the values are summarized in *Table 2*.

Table 2. Adsorption isotherm parameters for the adsorption of Cu (II) and Ni (II) ions.

Isotherm model	Parameters	Cu (II) ion	Ni (II) ion
Langmuir	Q_m (mgg ⁻¹)	43.47	30.303
	b (Lmg-1)	0.0160	0.0201
	R^2	0.9390	0.9790
Freundlich	n	1.8382	2.3364
	K_f (mgg ⁻¹)	3.0690	3.8994
	R^2	0.9950	0.9960
Temkin	α (Lg-1)	0.1093	0.3424
	β (mgL-1)	8.0810	5.8130
	b	311.73	433.36
	R^2	0.9230	0.9690
Dubinin-Radushkevich	Q_m (mgg ⁻¹)	21.019	19.005
	K (x10-5mol2kJ-2)	0.2	0.2
	E (kJmol-1)	0.625	0.625
	R^2	0.685	0.728
Harkin-Jura	A	47.619	58.823
	B	1.7142	1.8823
	R^2	0.840	0.812
Frenkel-Halsey-Hill	$1/n$	0.544	0.428
	K	0.7231	1.1577
	R^2	0.943	0.996

In the present investigation, the equilibrium data were analyzed using the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Harkin-Jura and Frenkel-Halsey-Hill isotherm models. To optimize the design of an adsorption system, it is important to establish the most appropriate isotherm model. The mono-component equilibrium characteristics of adsorption of Cu (II) and Ni (II) ions by TGLRC were described by these six different isotherm models. The experimental equilibrium adsorption data were obtained by varying the concentration of Cu (II) and Ni (II) ions with 200mg/50 mL of TGLRC.

The adsorption data obtained by fitting the different isotherm models with the experimental data are listed in *Table 2*, with the linear regression coefficients, R^2 . As seen from *Table 2*, the Langmuir, Freundlich and Frenkel-Halsey-Hill

isotherms were generate a satisfactory fit to the experimental data as indicated by correlation coefficients. This shows the heterogeneity of the surface of TGLRC and the multilayer adsorption nature of the Cu (II) and Ni (II) ions on TGLRC.

TGLRC have a homogeneous surface for adsorption of metal ions. The Langmuir isotherm equation is therefore expected to best represent the equilibrium adsorption data. The R^2 values for the Langmuir model are closer to unity than those for the other isotherm models for TGLRC for both Cu (II) ion removal ($R^2 = 0.939$) and for the removal of Ni (II) ($R^2 = 0.979$). Therefore, the equilibrium adsorption of Cu (II) and Ni (II) ions on TGLRC can be represented appropriately by the Langmuir, Freundlich and Frenkel-Halsey-Hill isotherm models in the concentration range studied.

Adsorption kinetics

The kinetics of adsorbate uptake is important for choosing optimum operating conditions for design purposes. In order to investigate the mechanism of adsorption and potential rate controlling steps such as chemical reaction, diffusion control and mass transport process, kinetic models have been used to test experimental data from the adsorption of Cu (II) and Ni (II) ions onto TGLRC. These kinetic models were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion models, which were respectively presented as follows in Eqs. (11) – (14) [39 – 41]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Pseudo first order model} \quad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Pseudo second order model} \quad (12)$$

$$q_t = k_{id} t^{1/2} + C \quad \text{Intra particle diffusion model} \quad (13)$$

$$q_t = \frac{1}{\beta \ln(\alpha\beta)} + \frac{1}{\beta \ln t} \quad \text{Elovich model} \quad (14)$$

where t is the contact time of adsorption experiment (min); q_e (mg/g) and q_t (mg/g) are respectively the adsorption capacity at equilibrium and at any time t ; k_1 (1/min), k_2 (g/mg min), α (mg/g min), β (g/mg), k_{id} (mg/g min^{1/2}) are the rate constants for these models, respectively. The correlation coefficients for all the four kinetic models were calculated and the results are shown in Table 3.

Table 3. Comparison of the correlation coefficients of kinetic parameters for the adsorption of Cu (II) and Ni (II) ions onto TGLRC.

Models	Parameters	Cu (II) ion	Ni (II) ion
Pseudo first-order model	k_1 (min ⁻¹)	0.1658	0.1496
	q_e (mg/g)	173.78	64.71
	R^2	0.677	0.644
Pseudo second-order model	k_2 (g/mg/min)	0.0004	0.0005
	q_e (mg/g)	41.66	38.46
	h	0.7005	0.8613
	R^2	0.9920	0.973
Intra particle diffusion model	k_{dif} (mg/(g.min ^{1/2}))	3.411	3.510
	C	5.044	4.063
	R^2	0.983	0.989
Elovich model	A_E (mg(g/ min))	0.1452	0.1453
	b (g/ mg)	0.3928	0.6071
	R^2	0.9110	0.9530

The adsorption process of Cu (II) and Ni (II) ions can be well fitted by use of the pseudo-second order rate constant for TGLRC. The linear regression coefficient value $R^2 = 0.992$ for Cu (II) and $R^2 = 0.973$ for Ni (II) obtained for pseudo-second-order kinetics was closer to unity than the R^2 value (0.677 = Cu (II) ions and 0.644 = Ni (II) ions) for first-order kinetics. This indicates that adsorption of Cu (II) and Ni (II) ions by TGLRC follows pseudo-second-order kinetics.

In the intra particle diffusion model, the values of q_t were found to be linearly correlated with the values of $t^{1/2}$. The linear regression coefficient value $R^2 = 0.983$ for Cu (II) and $R^2 = 0.989$ for Ni (II) obtained for Intra particle diffusion model was closer to unity. The k_{dif} values were calculated by use of correlation analysis. $k_{dif} = 3.411$ for the removal of Cu (II) ions

and $k_{\text{dif}} = 3.510$ for the removal of Ni (II) ions. The data indicates that the adsorption kinetics follows the pseudo-second-order rate with intraparticle diffusion as one of the rate determining steps.

Influence of other metal ions on the adsorption of Cu (II) and Ni (II) ions.

Effect of Ni (II) ions and Cr(III) ions on adsorption of Cu (II) and Ni (II) ions (binary system)

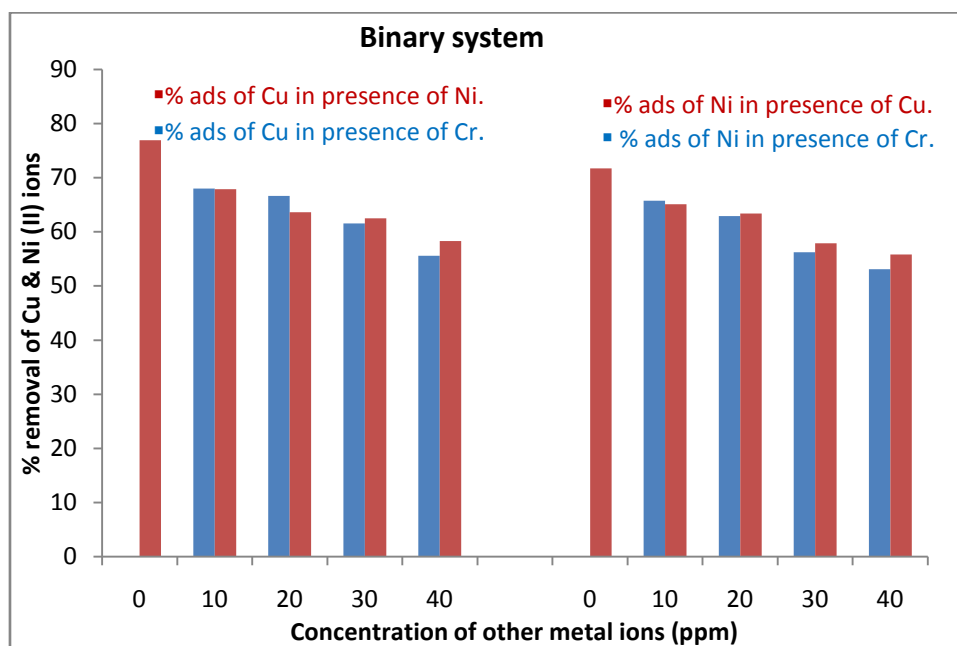


Figure. 8. Effect of other metal ions in binary system on the adsorption of Cu (II) and Ni (II) ions onto TGLRC.

The concentration of the Cu (II) ion solution was kept as 100 ppm. The concentration of Ni (II) ion was varied as 10, 20, 30, and 40 ppm. Each solution was placed in a bottle with TGLRC and the pH was adjusted to 7.04. After shaking for 60 min percentage adsorption was calculated. Percentage adsorption decreased from 76.92 to 55.56 % as the concentration of Ni (II) solution was increased. This showed competitive adsorption was, to some extent, taking place between the Cu (II) ions and the Ni (II) ions. The same procedure was repeated for Cu (II) ions in presence of Cr(III) ions. The percentage adsorption of Cu (II) ions decreased to 76.92–58.33% in the presence of Cr(III) ions. This is clearly shown in Fig. 8 for TGLRC. When the same procedure was repeated for the adsorption of Ni (II) ions onto TGLRC at pH 7.12, adsorption decreased to 71.73–53.13 % in the presence of Cu (II) ions and to 71.73–55.81% in presence of Cr(III) ions. This is clearly shown in Fig. 8.

Effect of Cu (II), Ni (II) and Cr(III) ions on the adsorption of Cu (II) and Ni (II) ions (tertiary system)

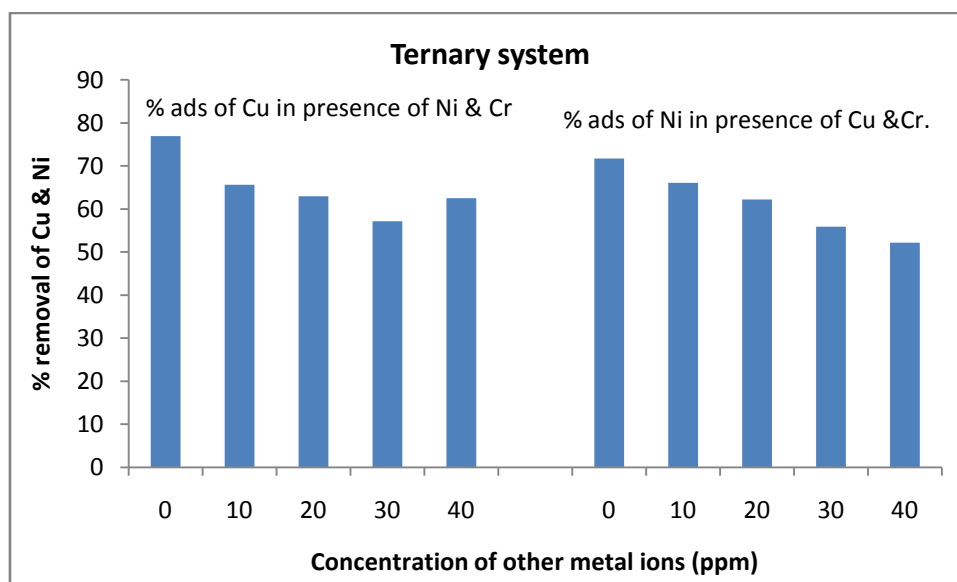


Figure. 9. Effect of other metal ions in tertiary system on the adsorption of Cu (II) and Ni (II) ions onto TGLRC.

The concentration of Cu (II) ion solution was kept as 100 ppm. The concentrations of Ni (II) and Cr(III) ion solutions were varied as 10, 20, 30, and 40 ppm. Solutions of both Ni (II) ions and Cr(II) ions were added to Cu (II) solution in a bottle with TGLRC and the pH was adjusted to 7.12. After shaking 1 h percentage adsorption was calculated. Percentage adsorption decreased from 76.92 to 62.5 % as the concentrations of Ni (II) ions and Cr(III) ions were increased. This showed competitive adsorption was, to some extent, taking place between the Ni (II) ions, the Cu (II) ions, and the Cr(III) ions. Percentage adsorption of Cu (II) was reduced in the presence of the other metals, as is clearly shown in Fig. 9. The same procedure was repeated for the adsorption Ni (II) ions onto TGLRC at pH 7.12 and percentage adsorption decreased from 71.71-52.17%, as the concentration of Cu (II) and Cr(III) was increased from 10-40 ppm, as illustrated in Fig. 9.

A fixed quantity of Cu (II) ions and Ni (II) ions onto TGLRC could only offer a finite number of surface binding sites, some of which would be expected to be saturated by the competing metal solutions. The decrease in sorption capacity of same activated carbon in target metal solution than that of single metal may be ascribed to the less availability of binding sites. In case of binary and ternary metal solution, the binding site is competitively divided among the various metal ions.

It is generally complicated to find a common rule to identify how metal properties affect the competitive sorption. Among various factors that affect the sorption preferences of a sorbent, binding of metal ions on material largely depends on physicochemical properties of metals.

The HSAB (hard and soft acids and bases) theory developed by Pearson [42] and extended to activated carbons adsorption by Alfarra et al, [43]. Once acids and bases have been classified as hard or soft, a simple rule of the HSAB principle can be given: hard acids prefer to bond to hard bases, and soft acids prefer to bond to soft bases. Generally, the C–O or C=O bonds are more polar and less polarizable, hence harder than the C–C or C=C bonds. In this concept, the oxygen surface groups of TGLRC are the hard sites that fix hard metal ions. According to this theory, Ni (II), Cu (II) and Cr(III) cations are borderline acids [42]. Changing the experimental conditions, metal ions with a borderline hardness can be biosorbed by the hard sites of TGLRC. The cationic exchange between the oxygenated surface groups (hard base) of TGLRC and borderline acids gives ionic bonds which are more easily dissociated. But the competitive process cannot be explained exactly by the hardness of cations because other effective factors and hardness values of Ni (II), Cu (II) and Cr (III) borderline acids are close each other.

Desorption and Reusability

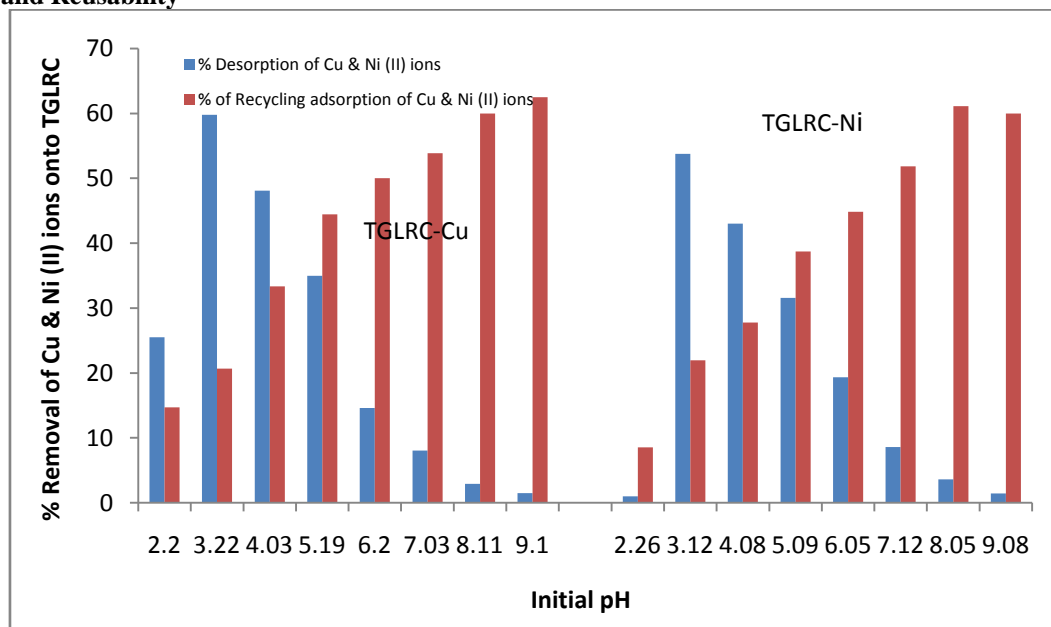


Figure. 10. Effect of pH on the desorption and recycling adsorption of Cu (II) and Ni (II) ions.

To investigate the possibility of repeated use of the adsorbent, desorption experiments were conducted under batch experimental conditions and desorption efficiencies were showed in Fig. 10. If the adsorbed Cu (II) ion and Ni (II) ion can be desorbed using neutral pH water, then the attachment of the copper and nickel ion of the adsorbent is by weak bonds. To study the effect of solution pH on Cu (II) and Ni (II) ion desorption, 50 mL of distilled water at different pH values (2 - 9) was agitated with 200 mg of TGLRC in a mechanical orbital shaker at room temperature. The pH was adjusted with 0.1 M NaOH and 0.1 M HCl solutions. We could get maximum removal of 59.77% of adsorbed Cu (II) ion for 3.22 pH water and 53.77% of adsorbed Ni (II) ion for 3.12 pH water onto TGLRC, after 2 h of contact time between the loaded matrix and the desorbing agents.

After desorption, the adsorbents were further used for adsorption of Cu (II) and Ni (II) ions. The percentage removal of Cu (II) ions was found to be 53.85% for TGLRC at pH 7.04 and the removal of Ni (II) ion was found to be 51.85 % for TGLRC at pH 7.12 (Fig.10). The increase in removal of Cu (II) and Ni (II) ions at pH 8 may be because of precipitation of metal ions in alkaline medium rather than adsorption.

IV. CONCLUSION

In this work, Tannin gel derived from *Ricinus Communis* leaves as a sorbent has been proposed to be an efficient and economical alternative in Cu (II) and Ni (II) ion removal from water. The findings herein made us conclude that:

- (1) Batch sorption studies of Cu (II) and Ni (II) ions showed that the TGLRC can be successfully used to remove Cu and Ni (II) ions from aqueous solution.
- (2) The adsorption data were well fitted by the Langmuir isotherm model; this is indicative of monolayer adsorption by TGLRC.
- (3) By applying the kinetic models to the experimental data, it was found that the kinetics of Cu and Ni (II) ion adsorption onto TGLRC followed by the pseudo-second order rate equation and intra particle diffusion is one of the rate limiting step. Results of kinetic studies demonstrated that the Cu and Ni (II) ion adsorption was rapid and efficient.
- (4) Percentage adsorption of Cu (II) and Ni (II) ions on TGLRC was higher in the single-ion systems than in binary and ternary systems, which is indicative of competitive adsorption among the metal ions.
- (5) Adsorbed Cu (II) and Ni (II) ions can be desorbed from both the adsorbents by use of double distilled water — 59.7 % of adsorbed Cu (II) ions were recovered from TGLRC and 53.7 % of adsorbed Ni (II) ions were recovered from TGLRC at pH 3.22 and pH 3.12, respectively.
- (6) The experimental studies showed that Tannin gel prepared from leaves of *Ricinus Communis* could be used as an alternative, inexpensive and effective material to remove high amount of Cu (II) and Ni (II) ions from aqueous solutions.

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