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Competitive adsorption of Nickel onto *Ricinus Communis leaves* as a low cost adsorbent

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ABSTRACT

The removal of nickel from aqueous solutions was investigated using water washed raw leaves of *Ricinus communis* (RLRC). The adsorbent was characterized by Fourier Transform infrared spectroscope (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM) with an EDAX (energy dispersive analysis of X-ray), and zeta potential measurements will be carried out in order to find the iso electric point of the RLRC adsorbent. The effects of the presence of one metal ion on the adsorption of the other metal ion were investigated. The experimental results indicated that the uptake capacity of one metal ion was reduced by the presence of the other metal ion. The main focus of the work will be to recover, adsorbed the used adsorbent contaminant and regenerate the adsorbent for its reusing is of great importance for environmental and economical reasons.ie, RLRC will be recovered by desorption method by using proper desorption agent like H_2O by batch mode study. The maximum adsorption of nickel was observed at pH 6 (56.32%). The Langmuir, Freundlich, Temkin and Dubin-Radushkevich isotherm models were used to analyze the equilibrium data. The data were also fitted to kinetic models such as pseudo-first order, pseudo-second order, Intra particle and Elovich model. The adsorption equilibrium data were well fitted by the Langmuir model. Kinetic studies showed that the adsorption followed pseudo-second order model and intra particle diffusion also. According to the experimental results, the adsorbent derived from this material is expected to be an economical product for metal ion remediation from water and waste water.
Keywords: Adsorption, Desorption, Chemisorption, Langmuir model, Pseudo-second-order, Influence of other ions.

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INTRODUCTION

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities, which can be harmful to organisms and plants which live in these water bodies. The contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem (Ajmal et al. 2003). Their presence in streams and lakes has been responsible for several health problems with animals, plants and human beings. Many industries discharge heavy metals such as lead, cadmium, copper, nickel and zinc in their waste waters (Krishnani et al. 2008). Among these metals Ni is 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. The World Health Organization (WHO) recommends a maximum acceptable concentration of nickel in drinking water of 0.02 mg L^{-1}. The chronic exposure of humans to high nickel concentrations may cause cancer of lungs, nose and bone (Beliles et al. 1978). Consequently, there is a need to remove this toxic metal from wastewater effluents. The US EPA has set specific nickel limits for wastewater effluent which are 2 mg/L for short-term effluent reuse and 0.2 mg/L for long-term effluent reuse (USEPA. 2004). Therefore, the removal of such heavy metals from waste streams before discharge to public water sources is of primary concern.

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 (Liang et al 2009; Dhakal et al 2005). Recently, adsorption technology has become one of the alternative treatments in either laboratory or industrial scale (Kumar and Bandyopadhyay 2006; Singh et al. 2006). 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 (Zhang et al. 2007). 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 (Prahas et al. 2007). Several suitable agricultural by-products (lignocellulosics) including fruit stones (Malik et al. 2002), olive waste cake (Baccar et al. 2009; El-Sheikh et al. 2004), pine bark (Asheh and Duvnjak. 1998), rice husks(Ajmal et al. 1998), pistachio-nut shells (Yang and Chong Lua 2006) and wheat bran (Bulut, Z. Baysal 2006) have been investigated in the last years as activated carbon precursors and are still receiving renewed attention.

The adsorption ability of Zinc chloride chemical activated *Ricinus communis leaves was* pre-viously investigated for the adsorption of Cu^{2+} ion and Ni^{2+} ion from aqueous solution (Makeswari and Santhi 2013a; Makeswari and Santhi 2013b). The aim of the present work was to investigate the ability of Nickel sorbent by water washed raw leaves of *Ricinus communis* and

to study the effect of several parameters (solution pH, contact time, initial metal concentration, pH_{zpc} and foreign ions effect) on the adsorption efficiency of nickel from aqueous solution.

MATERIALS AND METHODS

Chemicals

All the chemicals used in this study were analytical grade and Purchased from Aluva, Edayar (specrum reagents and chemicals Pvt. Ltd). Deionized double distilled water was used throughout the experimental studies. Nickel stock standard solution (1000 mg/L) was prepared by dissolving desired amount of analytical grade Nickel sulphate hexa hydrate ($NiSO_4. 6H_2O$) standard in 1 L of distilled water. Working nickel solutions were prepared just before used by appropriate dilutions of stock solution. ACS reagent grade HCl, NaOH and buffer solutions were used to adjust the solution pH.

Preparation of Adsorbent

The l*eaves of Ricinus Communis* (LRC) were collected from the local fields of Tirupur district, TamilNadu province in India. It was air-dried and powdered in a grinder. The powered leaves of Ricinus communis were washed several times with distilled water to remove unwanted particles/powder and then were dried at 80° C for 8 h. The oven dried leaves were ground well to fine powder. This water washed LRC was named as raw leaves of Ricinus Communis (RLRC) and used in the present study. The RLRC was then stored in an air-tight container for later experimental use.

Instrumentation

A Cyber scan (EUTECH INSTRMENTS) pH meter was used for pH measurements. The pH meter was calibrated using standard buffer solutions of pH 4.0 and 10.0. A Fourier transform infrared spectroscopy (SHIMADZU, IR Affinity-1) with KBr pellet was used to study the surface functional groups of the RLRC, with a scanning range of 4000-400 cm^{-1}. The surface physical morphology of RLRC was identified by scanning electron microscope (SEM) technique (Jeol jsm-6390). The crystalline structure of RLRC 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 Ni^{2+} ions was determined using UV-vis spectrophotometer (SHIMADZU UV-2450) of 232 nm. The point of zero surface charge characteristic of RLRC was (pH_{ZPC}) determined by using the solid addition method.

General procedure for adsorption

To study the effect of parameters such as adsorbent dose, metal ion concentration and solution pH for the removal of adsorbate on RLRC, batch experiments were performed. Stock solutions of nickel were prepared by dissolving $NiSO_4. 6H_2O$ in deionized water and further diluted to the 50 – 200 mg/ L concentrations for the experiments. pH was adjusted by adding

0.1 M HCl or 0.1 M NaOH into the solutions with known initial nickel ion concentrations. Batch adsorption experiments were conducted in asset of 250 mL stoppered flasks containing 200 mg of RLRC and 50 mL of metal solutions with different concentrations (50, 100, 150 and 200 mg / L) at pH 6. The flasks were agitated using a mechanical orbital shaker, and maintained at room temperature for 2 h until the equilibrium was reached. The suspensions were filtered and metal concentrations in the supernatant solutions were measured using a UV-vis spectrophotometer at 232 nm. The amount of uptake of Ni^{2+} ions by RLRC in the equilibrium (q_e) was calculated by the following mass-balance relationship,

$$q_e = \frac{(C_0 - C_e)}{W} \times V \qquad (1)$$

where C_o and C_e (mg/L) are the liquid phase concentrations of metal at initial and equilibrium, respectively. V (L) is the volume of the solution, and W (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

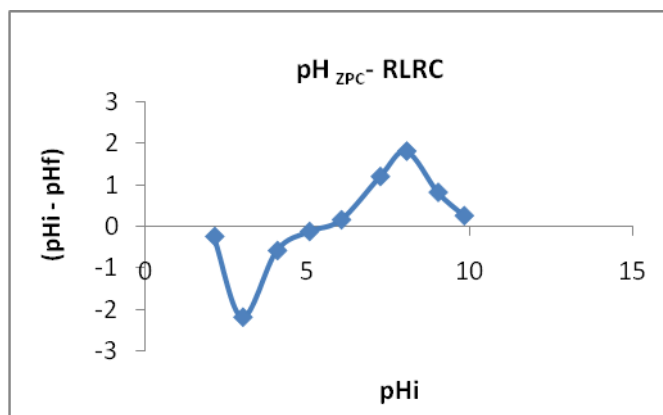### Characterizations of RLRC

Zero point charges of RLRC

Fig. **1. Zero point charges of RLRC.**

The zero surface charge characteristics of RLRC were determined by using the solid addition method (Kumar et al. 2008). The experiment was conducted in a series of 250 mL glass stoppered flasks. Each flask was filled with 50 mL of different initial pH $NaNO_3$ solutions and 200 mg of RLRC. The pH values of the $NaNO_3$ 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 150 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}.

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.e. (pH_i – pH_f) and pH_i for pH_{ZPC} measurement. The point of zero charge for RLRC is found to be 5.06. This result indicated that the pH_{ZPC} of RLRC was depended on the raw material and the activated agency. The zero point charge (pH $_{ZPC}$ = 5.06 for RLRC) is below the solution pH (pH = 6) and hence the negative charge density on the surface of RLRC increased which favours the adsorption of Ni^{2+} ions (Janos et al. 2003).
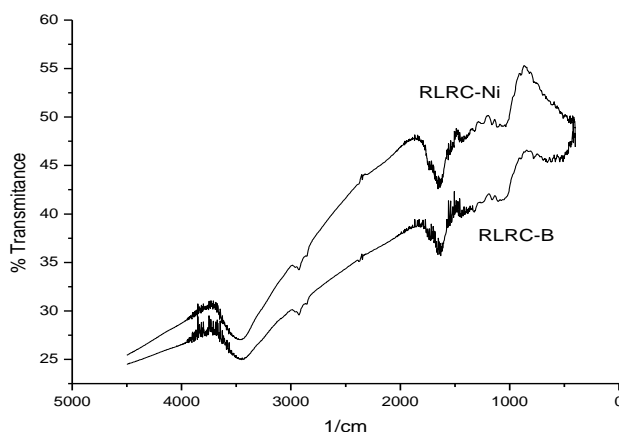
FTIR analysis of RLRC

Fig. **2. FTIR analysis spectra of RLRC before and after adsorption of Ni^{2+} ions.**

Surface functional groups were detected by Fourier-transform infrared spectroscopy. *Fig. 4.* Shows the FTIR spectra of RLRC before and after adsorption of Ni^{2+} ions from aqueous solution. These spectra contain a broad band between 3851 and 3443 cm^{-1}. This indicates the presence of hydrogen-bonded OH groups. The intense bent at about region 2929.9-2825 cm^{-1} for the precursor was attributed to the asymmetric and symmetric vibration modes of methyl and methylene group (C-H group) (Nakanishi. 1962). At wave number 1734 cm^{-1} is assigned to carbonyl group C= O group present in aldehyde, ester, ketone and acetyl derivatives. The peak around 1629 cm^{-1} can be assigned to symmetric and asymmetric stretching vibrations of the C=C group. The peak at 1096 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. The peak present at 866 cm^{-1} indicates the presence of aromatic heterocyclic molecules.

SEM analysis of RLRC

The physical morphology of RLRC-B and RLRC-Ni is observed by SEM at 1,000 magnification. As shown in *Fig. 3(a)*, the RLRC material has more fibre and more active sites. According to the micrograph, it is clear that the adsorbent has considerable number of heterogeneous pores where there is a good possibility for metal to be trapped and adsorbed.

Fig.3 (b) shows the adsorbent is covered with Ni^{2+} ions, which prove adsorption of Ni^{2+} ions by the RLRC surface. This is confirmed by the EDAX analysis of the adsorbent.

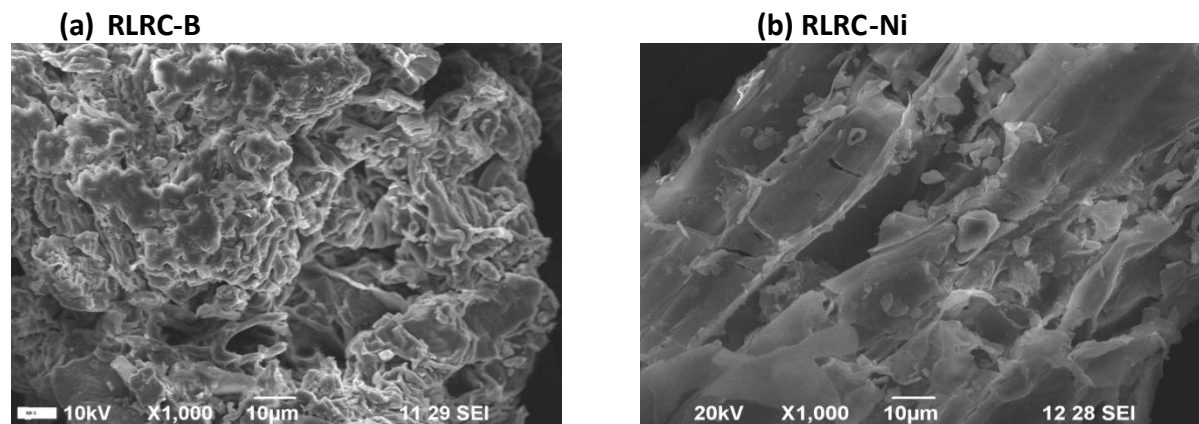**(a) RLRC-B**   **(b) RLRC-Ni.**

Fig. **3. SEM images of (a) RLRC-B and (b) RLRC-Ni.**

EDAX analysis of RLRC

Based on the EDAX results, the elementary analyses of the RLRC before and after adsorption are presented in the *Fig. 4 (a) and (b).* The elements, percentage mass of elements presented in RLRC before and after adsorption are summarized in Table 1. In *Fig. 4 (b)*, the peaks at 1 and 7–9 on the keV scale prove adsorption of Ni^{2+} ions by RLRC.

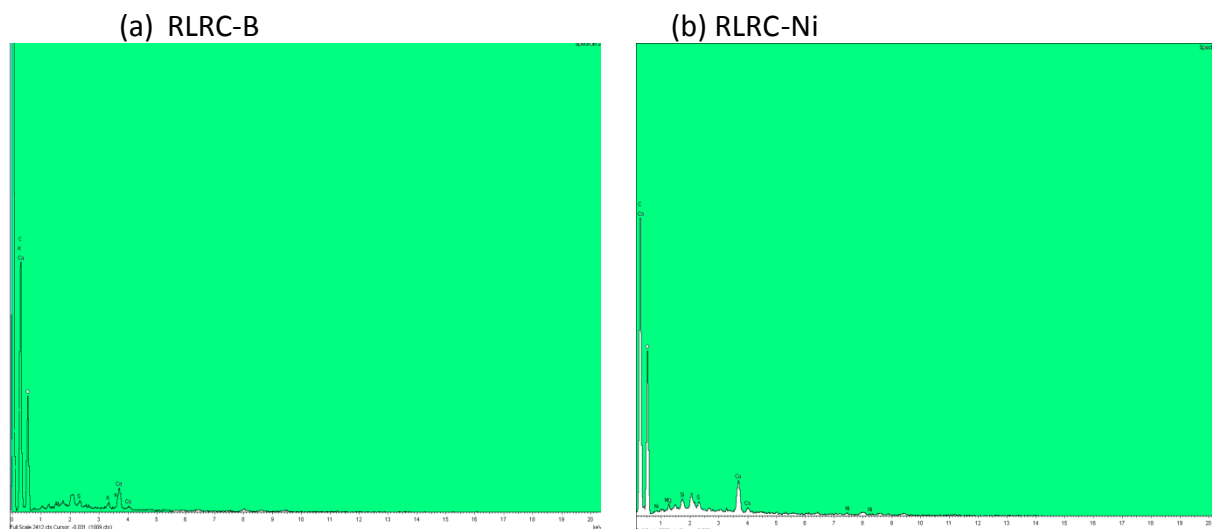(a) RLRC-B   (b) RLRC-Ni

Fig. 4. EDAX spectra of (a) RLRC-B and (b) RLRC-Ni.

Table 1 Data for the elements presented in RLRC-B and RLRC-Ni.

| Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
RLRC-B					
C K	59.82	1.1993	54.16	1.54	62.00
O K	19.64	0.4952	43.06	1.50	37.00
S K	0.41	0.9601	0.46	0.10	0.20
K K	0.43	1.0514	0.45	0.11	0.16
Ca K	1.69	0.9763	1.87	0.16	0.64
Totals			100.00		
RLRC-Ni					
C K	76.50	1.0910	49.74	0.82	57.95
O K	34.97	0.5346	46.38	0.84	40.57
Mg K	0.32	0.7135	0.32	0.09	0.19
Si K	0.58	0.8952	0.46	0.08	0.23
S K	0.57	0.9503	0.42	0.08	0.18
Ca K	3.08	0.9790	2.23	0.14	0.78
Ni K	0.49	0.7872	0.44	0.17	0.10
Totals			100.00		

XRD analysis of RLRC
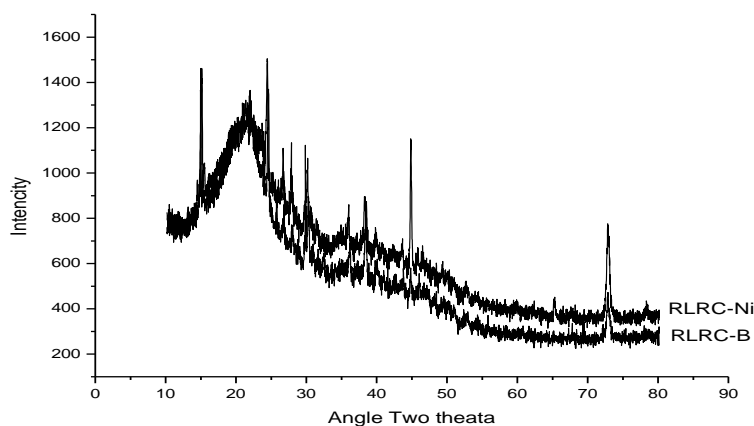
Fig: 5 XRD spectra of RLRC-before and after adsorption of Ni^{2+} ions.

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 Ni^{2+} ions have been studied.

As a representative case the XRD patterns of RLRC before and after treatment with Ni^{2+} ions are shown in *Fig. 5.* The results indicated that the diffraction profiles of RLRC before and after adsorption of Ni^{2+} 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 $2\theta = 21°$, 26° and 29° which was similar to the peak of crystalline carbonaceous structure such as graphite. It is evident from the figure that the XRD pattern of RLRC loaded with Ni^{2+} ions exhibits no variation in the crystal structure and this suggests that the Ni^{2+} ions might diffuse into micropores and sorbs mostly by physisorption without altering the structure of the adsorbent. From the XRD analysis for the adsorbent (RLRC), we concluded that the adsorbent is suitable for the adsorption of Ni^{2+} ions. The above observation corroborated well with batch sorption experiments.

Batch adsorption experiments
Batch equilibrium studies

To study the effect of parameters such as adsorbent dose, dye concentration and solution pH for the removal of adsorbate on RLRC, batch experiments were performed. Stock solutions of $NiSO_4.6H_2O$ was prepared and further diluted to the 50 – 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 (50, 100, 150 and 200 mg / L) at pH 5. 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:

$$\% \ of \ Removal = \frac{(C_0 - C_f)}{C_0} \times 100 \tag{2}$$

where C_0 is the initial concentration of Cu(II) ions in mg/L and C_S is the final concentration of Ni^{2+} ions in mg/L. The results obtained in batch mode were used to calculate the equilibrium metal uptake capacity. The amounts of uptake of Ni^{2+} ions by RLRC in the equilibrium (q_e) were calculated by the following mass-balance relationship:

$$q_e = \frac{(C_0 - C_e)}{W} \times V \tag{3}$$

where q_e is the equilibrium uptake capacity in mg/g, Vis 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.

Effect of solution pH on adsorption

The zeta-potentials of the RLRC particles in water were measured at different pH. It was found that the RLRC particles are positively charged at low pH and negatively charged at high pH, having a point of zero charge (pH$_{zpc}$) at pH 5.06 for RLRC. Therefore, it can be expected that positively charged metal ions are likely to be adsorbed by the negatively charged RLRC particles at a pH > ZPC for RLRC.
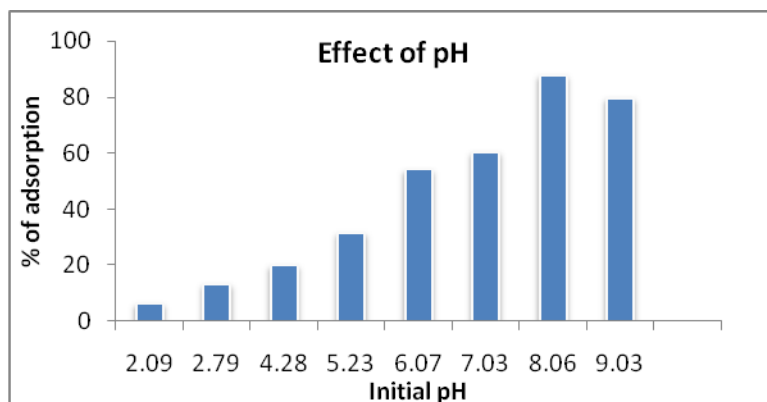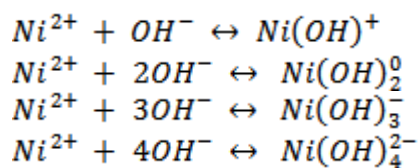

Fig. 6. Effect of pH on the adsorption of Ni^{2+} ions. Initial concentration of 100 mg /L, contact time of 70 min, adsorbent dosage 200mg/50 mL at room temperature.

Fig.6. shows that pH strongly influences the adsorption of Ni^{2+} ions. The adsorption of Ni^{2+} ions using purified RLRC shows a gradual increase from pH 2 to pH 5, then the trend changes between pH 5 and pH 6 and rises sharply between pH 8 and pH 9. Generally, are positively charged at low pH values (Lu and Chiu. 2008); this explains the electrostatic repulsions between RLRC and Ni^{2+}. These changes could be attributed to various factors such as: the surface charge of the RLRC; the degree of ionisation; and the species of Ni^{2+} available in aqueous solution (Tan et al. 2008). In fact, zeta potential results in Fig. 6 show that the surface charges of RLRC shift from being positively charged in acidic media to being negatively charged in basic media. The shift is at around neutral pH of 5.06. It has been reported that in acidic medium (up to pH 5) the predominant species of nickel is Ni^{2+} ions (Rao et al. 2007). At pH 2 the adsorption of Ni^{2+} ions is low because of the high competition between H^{+} ions from (HNO3) and Ni^{2+} ions. The slight rise in adsorption uptake observed at pH values of between pH 4 and pH 8 is therefore due to the decrease of protons (H^{+}) in solution. Hence, at higher values (pH >7) the protons are replaced by hydroxide (OH^{-}) forming species such as Ni(OH)$^{+}$ and Ni(OH)$^{0}_{2}$ (Tan et al. 2008; Wang et al. 2007). In addition the surface of RLRC is more negatively charged resulting in an electrostatic attraction of Ni^{2+} ions. The change in the surface charges of RLRC (positive to negative) observed at pH of 7.6 and shown in Fig. 6 justifies the drastic increase in removal of Ni^{2+} ions. The electrostatic interactions are more likely to be the adsorption mechanism occurring at this point. The maximum nickel removal is observed over the pH range pH 7 to pH 9, which is due to the formation of hydrolysis species, i.e., Ni(OH)$^{+}$ (Tan et al. 2008; Wang et al. 2007). Another mechanism that is likely to occur at this pH range is precipitation due to the formation of Ni(OH)$^{0}_{2}$ as shown in the following hydrolysis equations sequences (Yang et al. 2009):

$$Ni^{2+} + OH^- \leftrightarrow Ni(OH)^+$$
$$Ni^{2+} + 2OH^- \leftrightarrow Ni(OH)_2^0$$
$$Ni^{2+} + 3OH^- \leftrightarrow Ni(OH)_3^-$$
$$Ni^{2+} + 4OH^- \leftrightarrow Ni(OH)_4^{2-}$$

From the result it is evident that optimum pH of 6 is required for appreciable removal of Ni^{2+} ions and hence this pH is employed as an optimum pH for further studies. The obtained maximum Ni^{2+} ion uptake is 56%. The zeta potential results agree with the effect of pH on the adsorption of Ni^{2+} ions.
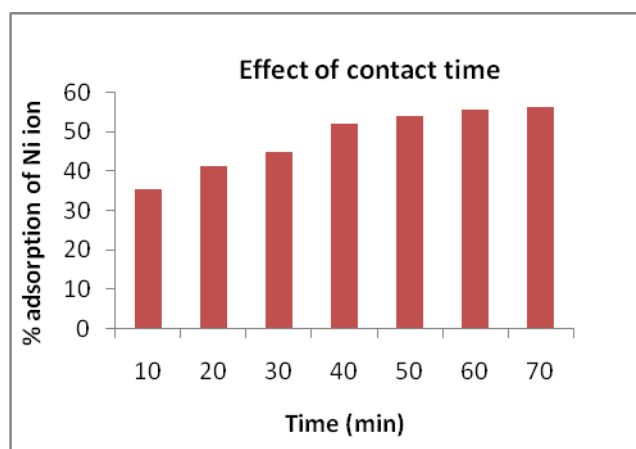
Effect of contact time

Fig. 7. Effect of contact time on the adsorption of Ni^{2+} ions. Initial concentration of 100 mg /L, pH 6.0, adsorbent dosage 200mg/50 mL at room temperature.

The effect of time on the sorption of Ni^{2+} ions by Ricinus communis leaves was studied. *Fig. 7.* indicates that the removal efficiency increased with an increase in contact time before equilibrium is reached. This may be due to the attainment of equilibrium condition at 70 min of contact time for RLRC, which is fixed as the optimum contact time. At the initial stage, the rate of removal of Ni^{2+} 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.

Batch kinetic studies

The kinetic experiments were performed using a procedure similar to the equilibrium studies. Samples containing Adsorption studies were conducted in 250 mL shaking flasks at a solution pH of 6. The adsorbent dose of 200 mg was thoroughly mixed with 50 mL of nickel solution (100 mg/L) and the suspensions were shaken at room temperature at required time intervals, filter the clear solutions and analyzed for residual nickel ion concentration in the

solutions. In order to determine the best kinetic model which fits the adsorption experimental data, the pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion model were examined.

Pseudo-first-order kinetic model

The Lagergren pseudo-first-order rate expression is given by the equation (Ho. 2004):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4)$$

where q_e (mg/g) is the amount of metal ions adsorbed at the phase of equilibrium, q_t (mg/g) is the amount of nickel ions adsorbed at time t and k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption model. The parameters were summarized in table 2. From the linear correlation coefficients (R^2), it is seen that Lagergren equation does not represent a good fit with the experimental data.

Pseudo-second-order kinetic model

The pseudo-second-order model is given by equation (Ho and Mc Kay. 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (5)$$

where k_2 (gmg^{-1} min^{-1}) is the rate constant of the pseudo-second order kinetic model. In the pseudo-second-order model chemical sorption is the rate limiting step (Wang and Sun. 2007). In reactions involving chemisorption of adsorbate onto a solid surface without desorption of products, adsorption rate decreases with time due to an increased surface coverage.

The q_e value (166.66) obtained from the second-order kinetic equation for RLRC was close to the experimental qe value (117.513), and the linear regression coefficient value R^2 value (0.988) obtained for pseudo-second-order kinetics was closer to unity than the R^2 value (0.878) for first-order kinetics. This indicates that adsorption of Ni^{2+} ions by RLRC follows pseudo-second-order kinetics.

Intra particle diffusion model

The Intra particle diffusion can be described by three consecutive steps:
(i) The transport of adsorbate from the bulk solution to the outer surface of the adsorbent by molecular diffusion.
(ii) The internal diffusion, the transport of adsorbate from the particles surface into interior sites.
(iii) The adsorption of the solute particles from the active sites into the interior surface of the pores.

The effect of intra particle diffusion resistance on adsorption can be determined by the following relationship (Gundogan et al. 2004):

$$q_t = k_{ip} t^{1/2} + C \qquad (6)$$

k_{ip} is the intra particle diffusion rate constant (mg g^{-1} $min^{-1/2}$). To follow the intra particle diffusion model, a plot of q_t against $t^{1/2}$ show yields a linear line where the slope is k_{ip}.

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 k_{dif} values were calculated by use of correlation analysis. k_{dif} = 10.77, R^2 = 0.963 for RLRC. The R^2 values were closer to unity, indicating that the application of this model is a better fit for RLRC.

The simplified Elovich equation

$$q_t = \frac{1}{\beta \ln(\alpha\beta)} + \frac{1}{\beta \ln t} \qquad (7)$$

where α (mg g^{-1} min^{-1}) is the initial adsorption rate constant and the parameter β (g mg^{-1}) is related to the extent of the surface coverage and activation energy for chemisorption (Lagergren. 1898; Elovich and Schulman. 1959). The values of α and β can be calculated from the plot of q_t against $1/\ln t$.

When the Elovich equation was used, the linear coefficient for RLRC was found to be 0.921. The Elovich constant A_E for RLRC was 0.052 mg/g min. This value was also better for RLRC, which proves the suitability of the Elovich equation for RLRC. This reveals that the presence of intra-particle diffusion process in RLRC.

Table 2. Coefficients of Kinetic parameters for Ni^{2+} ion adsorption onto RLRC.

Pseudo-first-order		Pseudo-second-order		Intra particle		Elovich	
$q_{e\ cal}$ (mg/g)	7.244	q_e (mg/g)	166.66	K_{dif}(mg/(g.min$^{1/2}$))	10.77	A_E (mg/(g/ min))	0.052
k_1 (min^{-1})	2.68	k_2 (g/mg/min)	6.3159×10^{-4}	C	52.94	b (g/ mg)	0.1257
$q_{e(exp)}$ (mg/g)	117.513	h	8.725	R^2	0.963	R^2	0.921
R^2	0.878	R^2	0.988				

Effect of adsorbent dosage

The influence of adsorbent dose on Ni^{2+} ion removed at a fixed initial nickel concentration of 200 mg/50 mL and pH 6 is shown in *Fig.8.* It was noticed that percentage removal of nickel ion increased from 56% to 84.05% with an increase in adsorbent dose from 200 mg to 1000 mg/50 mL. This was attributed to increased carbon surface and availability of more adsorption sites. From the result it is evident that optimum dosage of 200 mg/50 mL is

required for appreciable removal of nickel ions and hence this amount is employed as a dose for further studies.
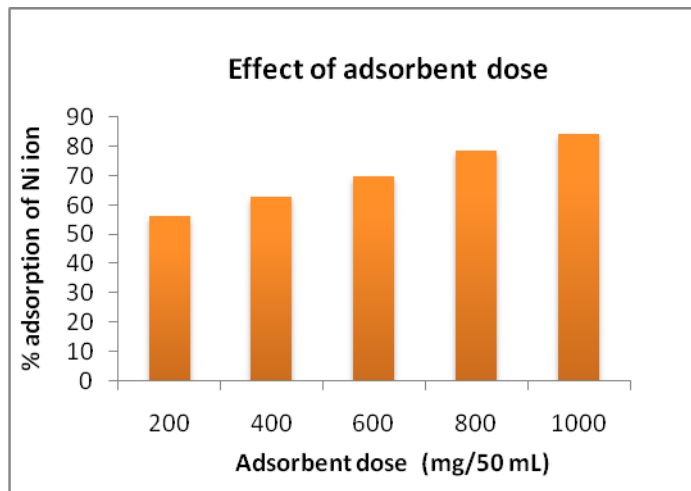

Fig. 8. Effect of adsorbent dose on the adsorption of Ni²⁺ ions. Initial concentration of 100 mg/L, pH 6.0, contact time 70 min at room temperature.

Effect of initial metal ion concentration

The experimental results of adsorptions of Ni²⁺ ions on the activated carbon at various concentrations (10, 20, 30 and 40 mg/50 mL) are shown in *Fig. 9.* It reveals that the percentage of adsorption decreased with increase in initial nickel ion concentrations from 79.86% to 24.82%. It means that the adsorption is highly dependent on initial concentration of nickel ion. It is because of that at lower concentration, the ratio of the initial number of nickel ion to the variable surface area is low subsequently the fractional adsorption becomes independent of initial concentration.
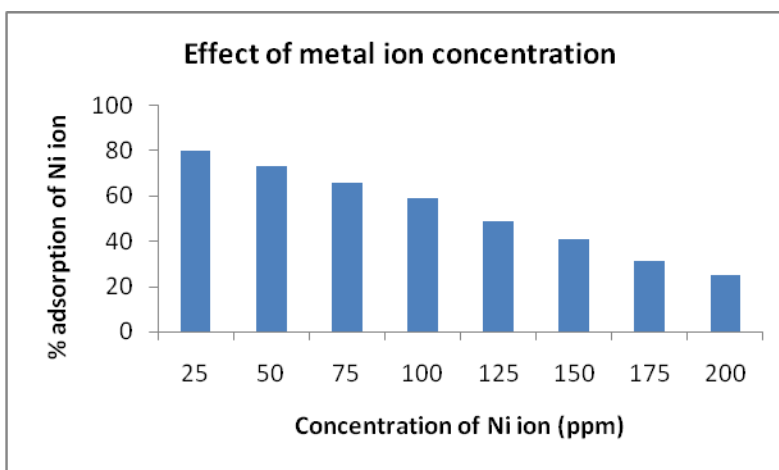

Fig. 9. Effect of Initial metal ion concentration on the adsorption of Ni²⁺ ions. Adsorbent dose 0.2 g/50mL, pH 6.0, contact time 70 min at room temperature.

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 RLRC 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 Ni^{2+} ions were analyzed by use of well-known models given by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. For the sorption isotherms, initial metal ion concentration was varied whereas solution pH and amount of adsorbent were held constant. The sorption isotherms for Ni were obtained for RLRC at solution at pH 6.0.

Langmuir isotherm

The Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. The Langmuir model is used for the fitting of a monolayer and/or chemical adsorption. It is represented as follows (Langmuir. 1918):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \tag{8}$$

where q_e (mg/g) is the amount of phosphate adsorbed at equilibrium, C_e (mg/L) is the liquid-phase phosphate concentration at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity of the adsorbent, and b (L/mg) is the Langmuir adsorption constant, respectively.

The results obtained from the Langmuir model for the removal of Ni^{2+} ions onto RLRC are shown in Table 3. The correlation coefficients reported in Table 3 showed strong positive evidence on the adsorption of Ni^{2+} ions onto RLRC follows the Langmuir isotherm. The applicability of the linear form of Langmuir model to RLRC was proved by the high correlation coefficients R2 > 0.978. This suggests that the Langmuir isotherm provides a good model of the sorption system. The maximum monolayer capacity Qm obtained from the Langmuir is 142.85mgg−1.

Freundlich isotherm

The Freundlich model is applied to describe a heterogeneous system characterized by a heterogeneity factor of 1/n. This model describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich model is expressed as follows (Freundlich. 1906):

$$log\ q_e = \frac{1}{n}\ log(C_e) + log\ K \tag{9}$$

where Ce (mgP/L) is the liquid-phase phosphate concentration at equilibrium, K is the Freundlich isotherm constant, and 1/n (dimensionless) is the heterogeneity factor, respectively.

The data obtained from linear Freundlich isotherm plot for the adsorption of the Ni^{2+} ions onto RLRC is presented in Table 3. The correlation coefficients (>0.712) showed that the Freundlich model is comparable to the Langmuir model. The 1/n is lower than 1.0, indicating that Ni^{2+} ions are favorably adsorbed by RLRC.

Temkin isotherm

Temkin adsorption isotherm is expressed as:

$$q_e = B \ln A + B \ln C_e \tag{10}$$

where *A* is Temkin constant representing adsorbent–adsorbate interactions and *B* is another constant related with adsorption heat (Tan et al. 2007). Temkin isotherm takes into account the adsorbing species–adsorbent interactions. Isotherm constants *A* and *B* can be determined from plot of *q*e versus ln *C*e. The constant b is related to the heat of adsorption.

The adsorption data were analyzed according to the linear form of the Tempkin isotherm Eq. (10). Examination of the data shows that the Tempkin isotherm not fitted well the Ni^{2+} ion adsorption data for RLRC. The linear isotherm constants and coefficients of determination are presented in Table 3. The heat of Ni^{2+} ion adsorption onto RLRC was found to 0.0921. The correlation coefficients R^2 obtained from Tempkin model were comparable to that obtained for Langmuir equations, which explain the applicability of Tempkin model to the adsorption of Ni^{2+} ions onto RLRC.

Dubinin–Radushkevich (D–R) isotherm model

To determine the adsorption occurred is physical or chemical in nature, the equilibrium data were applied to D–R model (Dubinin et al. 1947). The linearized form of the D–R model is given below:

$$\ln C_{ads} = \ln C_m - {}'Y\varepsilon^2 \tag{11}$$

where C_{ads} is the adsorbed metal ions on the surface of adsorbent (mg/L), C_m is the maximum adsorption capacity (mg/g), 'Y is the activity coefficient related to mean adsorption energy (mol^2/J^2) and ε is the Polanyi potential $(kJ^2\ mol^2)$.
Polanyi potential (Polanyi. 1932) can be calculated by using the following equation:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{12}$$

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

$$E = \frac{1}{\sqrt{-2'Y}} \tag{13}$$

The calculated value of D–R parameters is given in Table 3. The saturation adsorption capacity Q_m obtained using D–R isotherm model for adsorption of Ni^{2+} ions onto RLRC is 132.703mgg^{-1} at 0.2g50mL^{-1} adsorbent dose, which is close to that obtained (142.85mgg^{-1}) from Langmuir isotherm model (Table 3). The values of E calculated using Eq. (13) is 2.8868 kJ mol^{-1}, which indicating that the physico-sorption process plays the significant role in the adsorption of Ni^{2+} ions onto RLRC.

Table 3. Coefficients of isotherm parameters for Ni^{2+} adsorption onto RLRC

Langmuir		Freundlich		Temkin		Dubinin-Radushkevich	
Q_m(mg/g)	142.85	1/n	0.271	α (Lg-1)	0.6075	Q_m (mgg^{-1})	132.703
b (Lmg-1)	0.7777	K_f (mgg^{-1})	41.4954	β (mgL-1)	24.62	K (x10^{-5}mol^{2}kJ^{-2})	0.06
R^2	0.978	R^2	0.712	b	92.19	E(kJmol-1)	2.8868
				R^2	0.693	R^2	0.893

Influence of other ions from binary and ternary metal solutions

Effects of the presence of Cu^{2+} and Cr^{3+} ions on the adsorption of Ni^{2+} ions were investigated by varying the concentrations of Cu^{2+} and Cr^{3+} ions from 10 mg/L to 40 mg/50 mL. A comparison of the adsorption percentage of Ni^{2+} ions at equilibrium between the solutions with Ni^{2+} ions present as the single and with the presence of increasing concentration of Cu^{2+} and Cr^{3+} ions was given in *Fig. 10*.
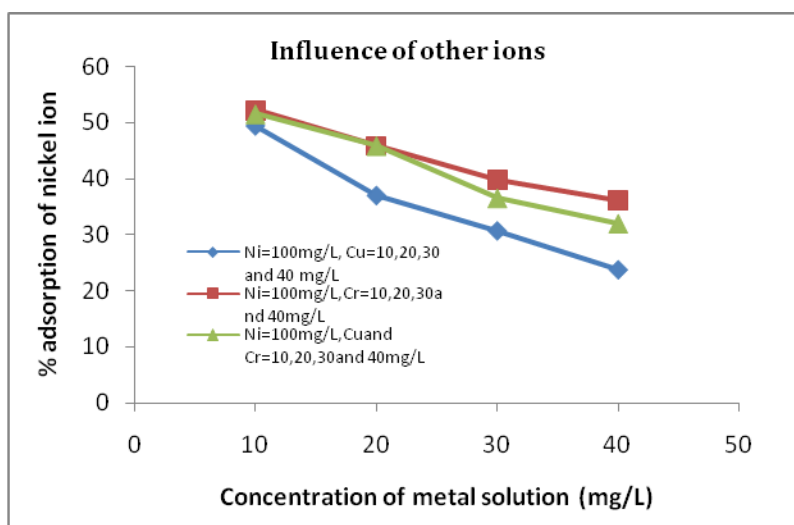

Fig. 10. Influence of other ions on the adsorption of Ni^{2+} ions. Initial concentration of 100 mg /L, pH 6.0, contact time 70 min, adsorbent dose 0.2 g/50mL at room temperature.

As shown in *Fig. 10*, the results indicated that the equilibrium uptake of Ni^{2+} ions decreased with increasing concentration of Cu^{2+} and Cr^{3+} ions from 10 to 40 mg/50 mL. In the single ion situation, the maximum uptake obtained at initial concentration of Ni^{2+} ions 100 mg/50mL, pH 6 was found to be 56.32 %, while the uptake obtained in the binary (Ni-Cu and Ni-Cr) metal solutions at the same initial concentration of Ni^{2+} ions was found to be 49.32%, 36.96%, 30.69% and 23.78% when the initial concentration of Cu^{2+} ion was 10, 20, 30 and 40 mg/L, respectively. Cr^{3+} ion in the binary solution slightly affect Ni^{2+} ion uptake on the RLRC as much as Cu^{2+} ions (Fig 10). The maximum Ni^{2+} uptake obtained at the same conditions was found to be 52.22%, 45.93%, 39.87% and 36.16 % when concentration of Cr^{3+} ions was 10, 20, 30 and 40 mg/L, respectively. As shown in *Fig. 10*, the adsorption capacity of RLRC for the ternary system with initial concentrations Ni^{2+} : 100 mg/L, Cu^{2+} : 10-40 mg/L and Cr^{3+} :10-40 mg/L remained lower than that for the single metal ions and could be ascribed to the overlapping of biosorption sites of respective metal ions. The effect on the adsorption of other ions in ternary system of Ni^{2+} ion was found to be 51.55%, 45.88%, 36.51% and 31.98% when the concentration of Cu^{2+} and Cr^{3+} ions was 10, 20, 30 and 40 mg/L.

A fixed quantity of RLRC could only offer a finite number of surface binding sites, some of which would be expected to be saturated by the competing metal ions, especially at relatively high concentration of them, and this was indeed observed (Ayhan Sengil and Mahmut Ozacar. 2009). 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.
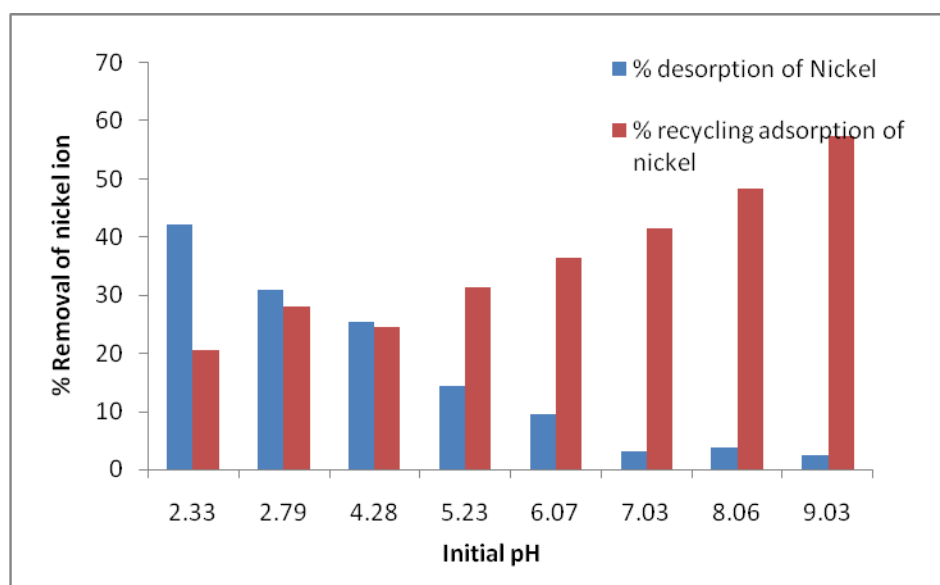
Regeneration studies

Fig. 11. Effect of pH on regeneration of Ni^{2+} ions. Adsorbent dose 200 mg/50mL, Initial concentration of 100 mg/L, contact time 70 min at room temperature.

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. 11.* If the adsorbed nickel ion can be desorbed using neutral pH water, then the attachment of the nickel ion of the adsorbent is by weak bonds. To study the effect of solution pH on nickel ion desorption, 50 mL of distilled water at different pH values (2 - 9) was agitated with 200 mg of RLRC 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 43.44 % of adsorbed nickel ion for 3 pH water onto RLRC, after 2 h of contact time between the loaded matrix and the desorbing agents.

After desorption, the adsorbents were further used for adsorption of Ni^{2+} ions. The percentage removal of Ni^{2+} ions was found to be 36.4 % for RLRC at pH 6 (*Fig. 11)*. The increase in removal of Ni^{2+} ions at pH 7 may be because of precipitation of metal ions in alkaline medium rather than adsorption.

CONCLUSION

Leaves of *Ricinus Communis* precursors were found to be a good raw material for the adsorption of Ni^{2+} ions. The present investigation shows, the RLRC is an effective adsorbent for the removal of Ni^{2+} ions from aqueous solutions. The surface morphology and functional groups involved in the adsorbents were determined by analyzing through pH_{ZPC}, SEM-EDAX, XRD and FTIR. Adsorption capacity of the adsorbents was highly dependent on the initial concentrations of metal ion, carbon dosage, contact time and solution pH.

According to the pH_{ZPC} (5.06) obtained for RLRC, the pH of the adsorbate solution must be 6.03 for RLRC so as to ensure that the surface of the adsorbent will be more favorable for the adsorption of positively charged metal ions. The optimum pH corresponding to the maximum adsorption was found to be 6.03 for RLRC. The efficiency of Ni^{2+} ion adsorption increased with an increase in the adsorbent dosage but it decreases with the increase in the initial concentration of the adsorbate solution.

The adsorption data were well fitted by the Langmuir isotherm model; this is indicative of monolayer adsorption by RLRC. Among the kinetic models tested, the adsorption kinetics was best described by the pseudo-second order equation for both the adsorbents. The adsorption process was found to be controlled by intra particle diffusion. Adsorbed Ni^{2+} ions can be desorbed from the adsorbent by use of double distilled water — 43.44 % of adsorbed Ni^{2+} ions were recovered from RLRC at pH 3.

Percentage adsorption of Ni^{2+} ions on RLRC was higher in the single-ion systems (Ni^{2+} ions only) than in binary and ternary systems (containing Cu^{2+}, Ni^{2+}, and Cr^{3+} ions), which is indicative of competitive adsorption among the metal ions. The experimental studies showed that leaves of *Ricinus Communis* could be used as an alternative, inexpensive and effective material to remove Ni^{2+} ions from aqueous solutions.

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