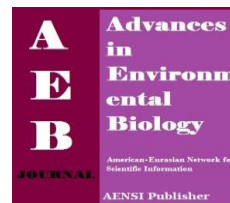




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## Simultaneous Removal of Nickel (II) and Cadmium (II) from Aqueous Solutions by Waste Tire Rubber Ash as a Low-Cost Adsorbent

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### ABSTRACT

In this study, waste tire rubber ash, characterized by FTIR and XRD studies, was applied in a batch adsorption system for simultaneous removal of Ni (II) and Cd (II) from aqueous solutions. The effects of operating parameters such: contact time, pH, adsorbent mass, temperature and 10 starting initial metal ions concentration ranging from 75-300 mg L<sup>-1</sup> were investigated. Results show that the removal of Ni (II) and Cd (II) is pH-dependent and the best results are obtained at pH 4.0. The experimental data were analysed using the Langmuir, Freundlich and Tempkin isotherms. The kinetics of adsorption process follows the pseudo-second-order model. Values of different thermodynamics parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) were determined at an initial concentration of 150 mg L<sup>-1</sup> and the results demonstrate that the adsorption process was spontaneous and endothermic. The maximum capacity of adsorbent for Ni (II) and Cd (II) are 56.50 and 58.83 mg g<sup>-1</sup>, respectively.

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## INTRODUCTION

Heavy metal pollution is one of the most important environmental problems today. Various industries produce and discharge wastes containing different heavy metals into the environment, such as electroplating, surface finishing industry, paints, fertilizer and pesticide industry and application, metallurgy, electrolysis, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation, cadmium–nickel and lead storage batteries, etc. [1, 2]. Heavy metals released into the environment have posed a significant threat to the environment and public health because [3]they are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders[4, 5]. The toxic elements discharged in the effluents will be absorbed and accumulated by microorganisms. Eventually, the toxic element will get transferred to humans via the food chain [6].

Ions of heavy metals like Cadmium and nickel are of major concern because of their frequent handling in developing countries, have a significant impact on the environment since they often detected in industrial wastewaters. Cadmium is one of the heavy metals with the greatest potential hazard to humans and the environment. Chronic exposure to elevated level of cadmium is known to cause renal dysfunction, bone degeneration, liver and blood damage[7, 8]. The drinking water guideline value recommended for this element by World Health Organization (WHO) and American Water Works Association (AWWA) is 0.005 mg cadmium per litre[9]. The chronic toxicity of nickel to humans and the environment is also well-known and high nickel concentrations cause gastrointestinal irritation and lung and bone cancers[8]. Therefore, there is a considerable need to treat industrial effluents containing such heavy metals prior to discharge to protect public health. The metal needs to be removed from industrial effluents before discharge into the environment to mitigate any impact on plant, animal and human receptors [10].

Various technologies such as reduction and precipitation, coagulation and flotation, electrochemical deposition, neutralization, reverse osmosis, ion exchange and adsorption are available for the removal of metallic pollutants from water and wastewater. That these technologies are related to high maintenance and operational cost, high energy requirements, incomplete metal removal, and the generation of toxic sludge is another major disadvantage related to these techniques. Among all methods[11, 12], The adsorption process is arguably one of the more popular methods for the removal of heavy-metal ions because of its simplicity, convenience, and high removal efficiency [13-16].In addition because adsorption is sometimes reversible,

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adsorbents can be regenerated by suitable desorption process [17]. In recent years, a variety of low-cost materials have been used as adsorbents for the removal of metal ions from aqueous solutions and wastewaters. There are some readily available waste materials that possess potentials of cheap adsorbents [18]. Discarded tires are an interesting and inexpensive medium for the adsorption of toxic pollutants from aqueous solutions [19]. Large amount of waste tires as more than  $5 \times 10^6$  tons/year, are being produced in the world [20, 21].

Approximately 800,000 tires are reused each year, the remainder is land filled, stockpiled or illegally dumped. In turn, stockpiled scrap tires pose potentially serious health and safety problems. Whole tires serve as breeding grounds for disease carrying mosquitoes and rodents. Uncontrolled tire piles are fire hazards and, once ignited, tire piles can burn out of control for months, producing acrid black smoke and a hazardous oil residue. Widespread illegal dumping poses the same problems associated with stockpiling. These huge numbers of waste tires represent not only an enormous environmental problem, but also a cheap source for the preparation of adsorbent materials that may be useful for the removal of heavy metals from solutions [22]. Approximately 32% by weight of the waste tire is mainly constituted of carbon black in which the carbon content is as high as 70-75 wt. %. This carbonaceous adsorbent is rather similar to activated carbon and the only apparent physical difference is that carbon black has much less internal surface area. Carbon black obtained by untreated rubber tire pyrolysis may be heated in air, carbon dioxide or steam atmosphere to develop its surface area and porosity and hence to improve its adsorption behaviour [23].

The objective of the present study is using waste tire rubber ash as an adsorbent for the simultaneous removal of Nickel (II) and Cadmium (II) from aqueous solutions. Factors that considered for the study are: contact time, pH and adsorbent dosage. In addition, Langmuir, Freundlich and Tempkin adsorption isotherms have been determined and the mechanisms of adsorption and thermodynamic parameters have been discussed.

## 2. Materials and Equipment:

All chemicals are of analytical grade. Stock solutions of Nickel and Cadmium of  $1000 \text{ mg L}^{-1}$  were prepared using their nitrate salts purchased from Merck. Desired concentrations obtained by diluting the stock solutions. Deionized water was used in all experiments. pH values were controlled using a Metrohm pH meter (Model E-632). Atomic absorption analysis of the metal ions was performed with a flame atomic absorption spectrophotometer (Shimadzu AA-680/G). The surface groups of the adsorbent were analysed by using a Fourier transform infrared spectrometer (FT-IR, Shimadzu 8400S). The X-ray diffraction (XRD) of the adsorbent powder was determined by using D4 Bruker X-ray diffractometer with Cu  $K\alpha$  as the radiation source, Ni as the filter and scanning angle ( $2\theta$ ) of  $10^\circ$  -  $90^\circ$ .

## 3. Experimental:

### 3.1. Adsorbent preparation:

In the present study, Rubbers from waste old tires were used. They were initially washed with a detergent solution and after the process of size reduction, the steel thread and the textile netting had been removed. Dilute HCl was used to get rid of foreign materials and impurities such as soil debris. The size-reduced waste rubber dried for 40 min at  $105^\circ\text{C}$  to remove the moisture and then was heated at  $600^\circ\text{C}$  for 5 h in a muffle furnace to prepare the desired ash. The cooled ash was then washed with a very dilute acidic solution, such as  $0.001 \text{ mole L}^{-1}$  HCl to remove salts of metals, such as  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ , similar washing process was done by the other researchers [10]. Subsequently, the ash was washed thoroughly with deionized water and filtered. The prepared adsorbent will dry in an oven and after milling and powdering will store for future experiments.

### 3.2. Batch studies:

The adsorption of Ni (II) and Cd (II) by waste tire rubber ash was studied by batch removal experiments. In the present study, under the equilibrium condition, a  $2.4 \text{ g L}^{-1}$  adsorbent was added to a 50 mL solution of the mixture of  $100 \text{ mg L}^{-1}$  initial concentration of each metal ion at pH 4.0. The solutions were shaken and after that the adsorbent particles were separated from the liquid phase by filtration through Whatman filter. The residual concentration of Ni (II) and Cd (II) in the supernatant was measured by flame atomic adsorption spectrometry. The amounts of ions adsorbed per unit mass of the adsorbent at equilibrium  $q_e$  ( $\text{mg g}^{-1}$ ) were determined by using the following equation:

$$q_e = \frac{(C_i - C_e)}{W} V \quad (1)$$

Where  $C_i$  and  $C_e$  are the initial and the equilibrium concentrations of metal ion in solution, respectively ( $\text{mg L}^{-1}$ ),  $W$  is the mass of the adsorbent (g), and  $V$  (L) is the volume of the solution. The removal percentage of metal ions was calculated according to Equation (2) [11]:

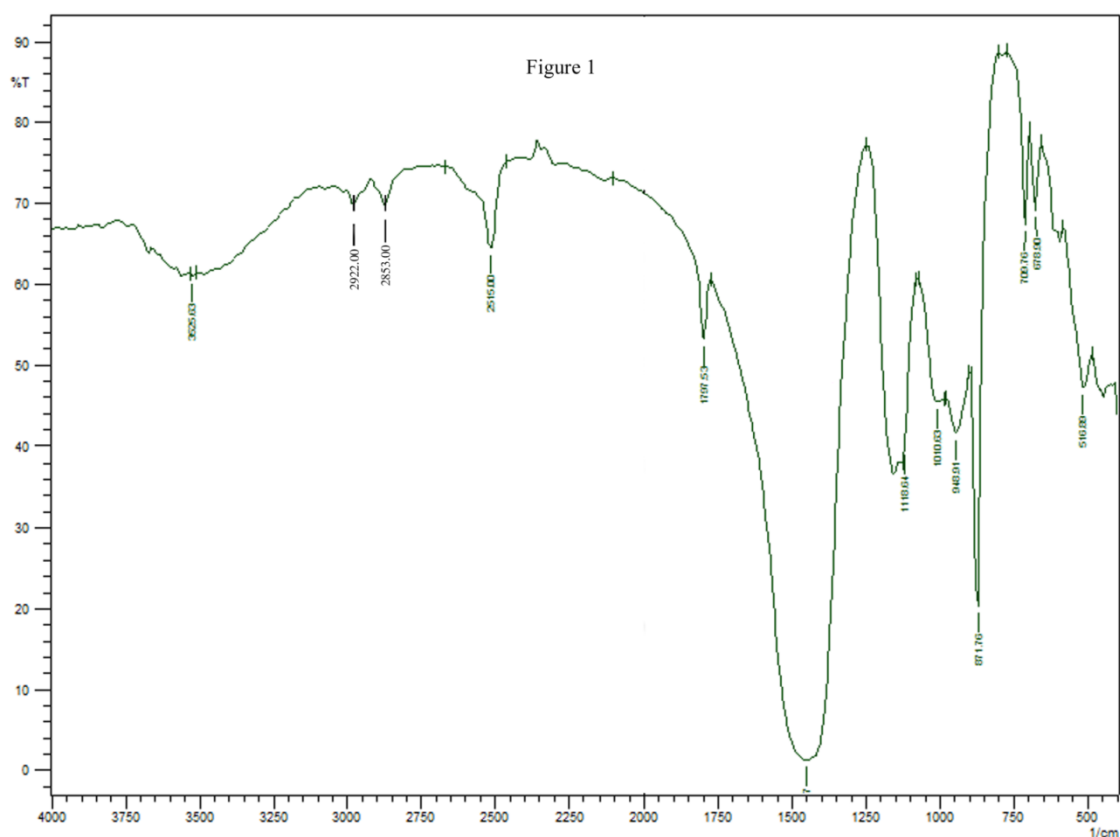
$$\%R = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

All the experiments were carried out three times and the average of values were reported.

## RESULTS AND DISCUSSION

### 4.1. Characterization of the adsorbent:

Prior to the spectra recording, the adsorbent was placed in an oven at 90 °C for 24 h. FTIR spectra were recorded in the range of 400–4000  $\text{cm}^{-1}$ , using spectroscopic quality KBr powder. The spectrum of the adsorbent displays a number of absorption peaks, which indicates the complex nature of the adsorbent (Figure 1) [24]. The bands exhibited at 3525 and 1118  $\text{cm}^{-1}$  are ascribable to O-H and C-O stretching vibrations in hydroxyl groups, respectively. They may be surface groups of carbon black and also groups formed by hydroxylation of oxides such as ZnO [25]. On the other hand the peaks at 1118 and 1010  $\text{cm}^{-1}$  can be attributed to S=O stretching vibrations. The peaks observed at 2922 and 2853  $\text{cm}^{-1}$  can be assigned to asymmetric and symmetric  $-\text{CH}_2$  groups [24]. The band at 2515  $\text{cm}^{-1}$  is attributed to  $\text{C}\equiv\text{C}$  stretching vibration in alkyne group [26]. The peak at 1797  $\text{cm}^{-1}$  is ascribed to the stretching carbonyl groups [27]. The strong band at 1450  $\text{cm}^{-1}$  may be due to the skeletal vibrations in aromatic rings [21]. The peaks at 400–1000  $\text{cm}^{-1}$  may be corresponding to the oxide composition of the adsorbent such as ZnO,  $\text{TiO}_2$  and  $\text{SiO}_2$  which absorb infrared radiation at close frequencies [25, 28].



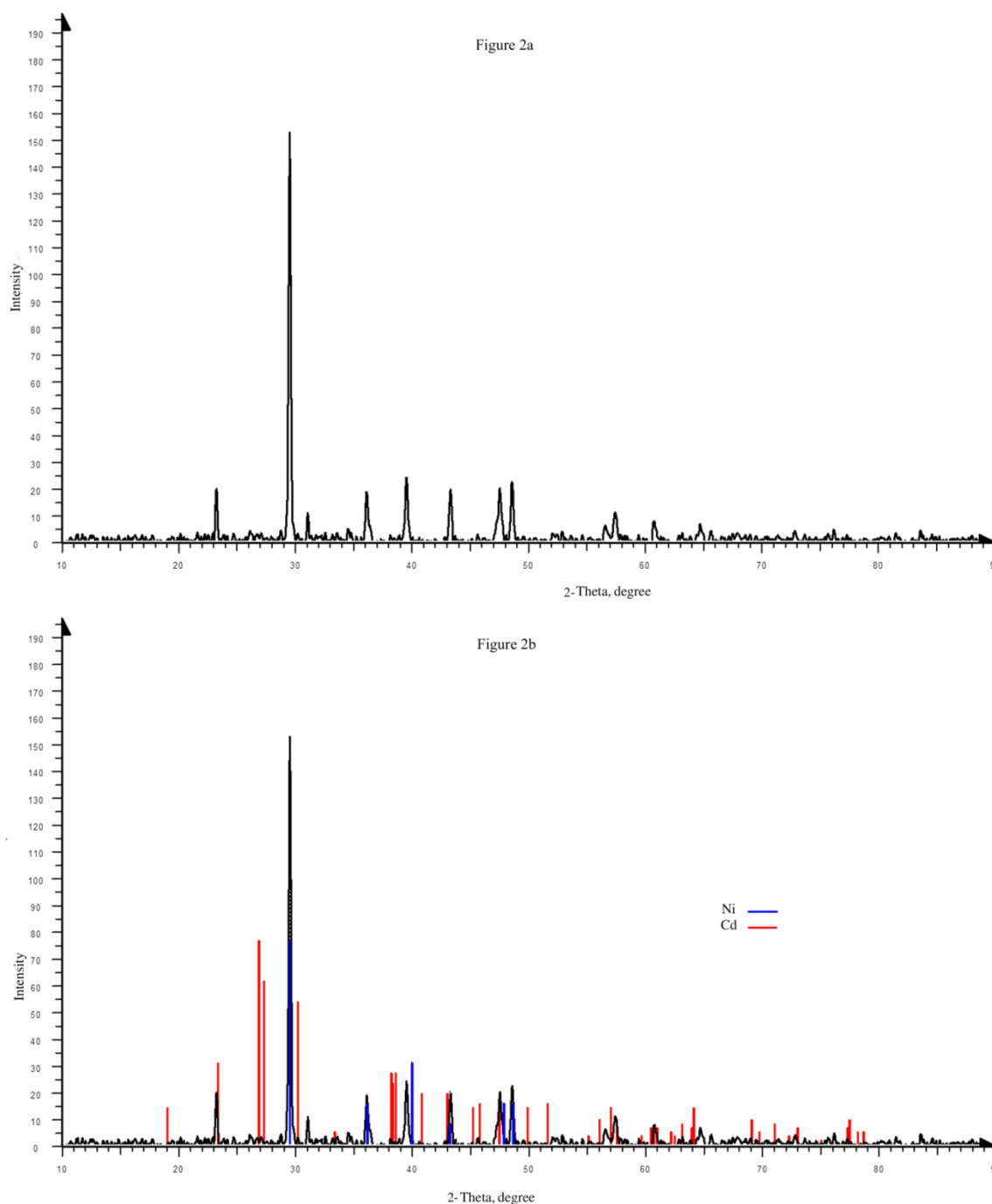
**Fig. 1:** FT- IR spectra of adsorbent.

Further studies were carried out on the removal of Ni (II) and Cd (II) by waste tire ash after adsorption. Figure 2(a) and 2(b) show the XRD ( $\chi$ -ray diffraction) patterns of the adsorbent. From Figure 2(b), it can be seen that Ni (II) and Cd (II) treated with the adsorbent, well.

The pH of the adsorbent was determined by a pH meter. It was observed that the adsorbent is highly alkaline and exhibits a pH of 10.7 when added to deionized water. Similar results have been reported in literature [10, 29].

### 4.2. Effect of contact time:

The effect of contact time on the removal of Ni (II) and Cd (II) was studied in 10 min steps with the initial metal ions concentration of 100  $\text{mg L}^{-1}$ . The experiments were carried out at different time intervals ranging from 10 min to 120 min. As shown in Figure 3, the removal of metal ions increased with increasing contact time and reached a maximum value after 100 min which can be attributed to the increase in the metal ions occupancy number. Therefore, for further experiments the optimum contact time was considered to 100 min.

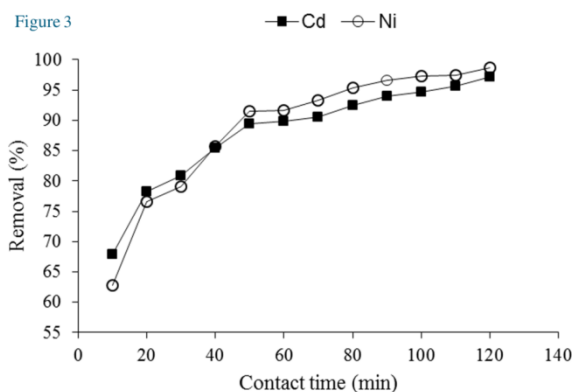


**Fig. 2:** Figure 2(a), 2(b). XRD patterns of adsorbent.

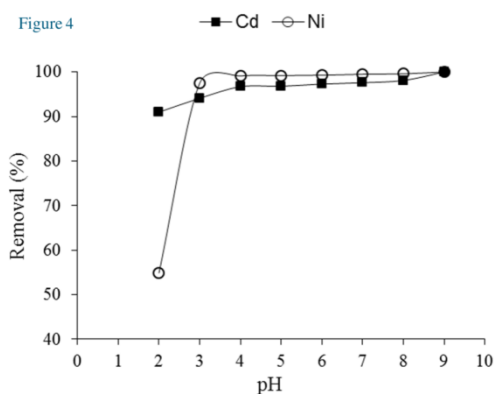
#### 4.3. Effect of pH:

pH is an important parameter influences on the removal of metal ions from aqueous solutions. The surface charge of an adsorbent could be modified by changing the pH of the solution[30]. pH also influences the degree of ionization and chemical speciation of metal ions during the reaction. So the adsorption of Ni (II) and Cd (II) depends on the species distribution of metal cations and the nature of the adsorbent surface in the aqueous solution.

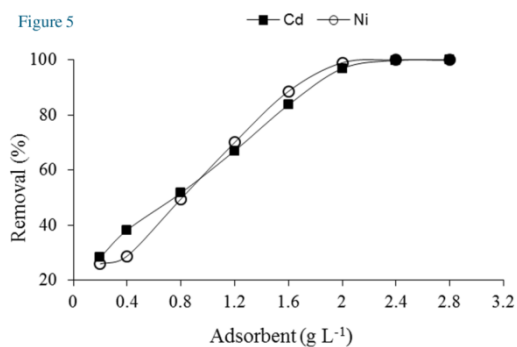
In order to evaluate the influence of pH on the removal of Ni (II) and Cd (II), the experiments were carried out with the pH range of 2.0–9.0 at a constant initial concentration of  $100 \text{ mg L}^{-1}$  Ni (II) and Cd (II) and the amount of adsorbent  $2.0 \text{ g L}^{-1}$  at 500 rpm agitation speed. The pH range was adjusted to different values by adding the required amount of dilute  $\text{HNO}_3$  or NaOH solutions. Figure4 demonstrates that the optimum pH of the solution was 4.0 for effective removal of Ni (II) and Cd (II). It was found that the removal percentages of metal ions enhanced with increasing pH from 2.0 to 4.0 and remained nearly constant up to pH 9.0. Since the adsorbent surface was negative, there is a strong electrostatic attraction between metal ions and surface groups.



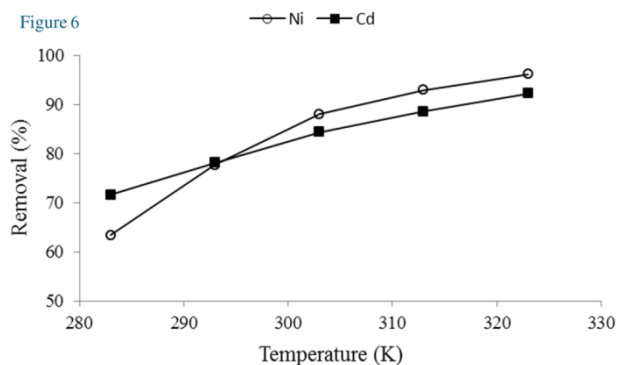
**Fig. 3:** Effect of contact time on the removal of Ni<sup>2+</sup> and Cd<sup>2+</sup> on to adsorbent; sorbent conc. 100 mg L<sup>-1</sup>, temp. 25 °C, adsorbent dose 2.0 g/L.



**Fig. 4:** Effect of pH on the removal of Ni<sup>2+</sup> and Cd<sup>2+</sup> on to adsorbent; sorbent conc. 100 mg L<sup>-1</sup>, temp. 25 °C, adsorbent dose 2.0 g/L.



**Fig. 5:** Effect of adsorbent dose on the removal of Ni<sup>2+</sup> and Cd<sup>2+</sup> on to adsorbent; sorbent conc. 100 mg L<sup>-1</sup>, temp. 25 °C, pH 4.



**Fig. 6:** Effect of temperature on the removal of Ni<sup>2+</sup> and Cd<sup>2+</sup> on to adsorbent; sorbent conc. 150 mg L<sup>-1</sup>, adsorbent dose 2.4 g/L, pH 4.

At low pH values, there is a strong competition between protons and metal cations for the active sites of the adsorbent; therefore the negative charge intensity on the sites was reduced. Optimum pH to achieve high efficiency was found to be 4.0 for subsequent experiments.

#### 4.4. Effect of adsorbent dose:

To evaluate the optimum dosage of adsorbent, eight different doses ranging from 0.2 to 2.8 g L<sup>-1</sup> were used. The pH was adjusted to 4.0 and the experiments were conducted at a fixed metal ions concentration of 100 mg L<sup>-1</sup> for 100 min. From the figure it can be observed that increasing the dose of adsorbent would increase the number of available adsorption sites or surface area, thereby resulting in the increase in removal percentage of Ni (II) and Cd (II) to 2.4 g L<sup>-1</sup>; afterwards, the removal efficiency remained constant even if more adsorbent was added. It may be due to the interface of active sites at a higher dosage or aggregation which resulting from high adsorbent dose. Such aggregation would lead to a decrease in total surface area of the adsorbent and an increase in diffusional path length [31, 32]. Figure 5 indicates that a concentration of 2.4 g L<sup>-1</sup> would insure the best removal percentage and the best adsorbent capacity for the next experiments.

#### 4.5. Effect of temperature:

Most of the adsorption processes are exothermic in nature, but in some cases endothermic adsorption is reported [33]. The effect of temperature on the removal of Ni (II) and Cd (II) was investigated by performing batch experiments at 283, 293, 303, 313 and 323 K, initial metal ion concentration of 150 mg L<sup>-1</sup> and the fixed equilibrium conditions. Figure 6 depicts that the removal percentage was increased for both of metal ions with increasing in temperature of solution. It revealed that adsorption is endothermic in nature so the higher values of temperature would be favourable for ions removal from aqueous solutions and cause to increase in the ions migration from the bulk phase to the solid phase.

#### 4.6. Adsorption isotherms:

Adsorption isotherm is an equilibrium data that describes the relationship between the amount of adsorbate adsorbed per unit mass of adsorbent ( $q_e$ , mg/g) and the concentration of the adsorbate in bulk solution ( $C_e$ , mg/L) at a given temperature under equilibrium conditions. It is very useful in giving information on adsorption mechanisms, surface properties and affinity of an adsorbent towards heavy metal ions [34].

In this study, metal ions adsorption isotherm is presented as a function of the equilibrium concentration of Ni (II) and Cd (II) in the aqueous solution at room temperature and in the equilibrium conditions. To obtain the maximum sorption capacities for the interested metal ions, the initial concentration was increased from 75 to 300 mg L<sup>-1</sup> for mixed Ni (II) and Cd (II). Different sorption isotherms, namely, Langmuir, Freundlich and Tempkin were investigated.

##### 4.6.1. Langmuir isotherm:

The non-linear Langmuir equation is:

$$q_e = \frac{K_L q_{max} C_e}{1 + K_L C_e} \quad (3)$$

Where  $q_e$  is the amount of metals adsorbed at equilibrium (mg g<sup>-1</sup>),  $K_L$  is the equilibrium constant (L mg<sup>-1</sup>),  $q_{max}$  the maximum adsorption capacity (mg g<sup>-1</sup>) of adsorbent and  $C_e$  the equilibrium concentration (mg L<sup>-1</sup>). Also, the adsorption data were analysed according to the linear form of the Langmuir isotherm (Figure 7) as follows [35]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}} \quad (4)$$

##### 4.6.2. Freundlich isotherm:

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [36]. This isotherm is suitable for a highly heterogeneous surface. The application of the Freundlich equation suggests that sorption energy exponentially decreases on completion of the sorptional centres of an adsorbent. The non-linear form of isotherm is expressed by the following equation:

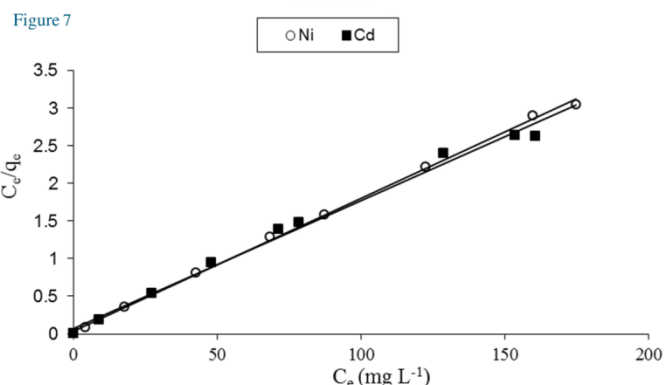
$$q_e = K_F C_e^{1/n} \quad (5)$$

The Linear form of Freundlich model can be expressed as Equation (6)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where  $q_e$  is loading of adsorbate on adsorbent at equilibrium (mg g<sup>-1</sup>),  $K_F$  is indicator of sorption capacity (mg<sup>1-n</sup> L<sup>n</sup> g<sup>-1</sup>),  $n$  is adsorption energetics and  $C_e$  is aqueous concentration of adsorbate at equilibrium (mg L<sup>-1</sup>) [32, 37]. Figure 8 shows the Freundlich isotherm.





**Fig. 7:** Langmuir plots for the removal of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  on to adsorbent; adsorbent dose 2.4 g/L, temp. 25 °C, pH 4.

#### 4.6.3. Tempkin isotherm:

This model assumes that the heat of adsorption of all molecules decreases linearly with the coverage of adsorbent surface. Moreover the assumption of uniform distribution of binding energies up to some maximum binding energy is also considered in this model [38]. Tempkin isotherm is given as:

$$q_e = \left(\frac{RT}{b}\right) \ln(A_T C_e) \quad (7)$$

It can be expressed in the linear form as:

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (8)$$

where  $B_T = (RT)/b$  and  $A_T$  ( $\text{L g}^{-1}$ ) are the Tempkin constant and can be determined by a plot of  $q_e$  versus  $\ln C_e$ . Also,  $T$  is the absolute temperature in Kelvin and  $R$  is the universal gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . The constant  $B_T$  is related to the heat of adsorption and  $A_T$  is the equilibrium binding constant corresponding to the maximum binding energy [32, 39]. Isotherm constants are given in Table 1. According to the data which are presented in table; the Langmuir correlation coefficient values are higher for both of metal ions than those of Freundlich and Tempkin models, and therefore, the Langmuir model gives a better fit to the experimental data. This indicates that a monolayer adsorption process and constant heat of adsorption for all sites has been taken place.

**Table 1:** Isotherm parameters for the removal of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  on to adsorbent.

Metal ions	Langmuir			Freundlich			Tempkin		
	$q_{\text{max}}(\text{mg g}^{-1})$	$K_L(\text{L g}^{-1})$	$R^2$	$n$	$K_f(\text{mg}^{1-n} \text{L}^n \text{g}^{-1})$	$R^2$	$B_T$	$A_T$	$R^2$
$\text{Cd}^{2+}$	58.83	0.243	0.9917	15.456	40.710	0.8331	2.881	$1.805 \times 10^6$	0.8443
$\text{Ni}^{2+}$	56.50	0.582	0.9989	17.452	42.355	0.9188	2.517	$2.980 \times 10^7$	0.9499

#### 4.7. Kinetic study:

In order to achieve the proper designing and modelling of the adsorption operation, the adsorption equilibrium needs to be supplemented with kinetic models. Several kinetic models, namely Lagergren pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion have been used to determine the rate-controlling mechanism of the adsorption process. All kinetic equations are recorded in Table 2, where  $q_e$  and  $q_t$  can be regarded as the amounts of metals adsorbed on the adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively,  $k$  is the rate constant,  $h$  is the initial sorption rate in pseudo-second order model,  $\alpha$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{ min}^{-2}$ ),  $\beta$  is the desorption constant ( $\text{g mg}^{-1} \text{ min}^{-1}$ ),  $k_{\text{intra}}$  is the intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{ min}^{-1/2}$ ) and  $C$  is defined as a constant related with the thickness of boundary layer ( $\text{mg g}^{-1}$ ) [31, 39, 40].

From the kinetic parameters which have been calculated at different times and listed in Table 3, it is confirmed that the adsorption process is in agreement with the pseudo-second order model (Figure 9) due to the high correlation coefficient ( $R^2 > 0.99$ ).

#### 4.8. Thermodynamic studies:

The thermodynamic behaviour of a solution has significant influences on the rate of adsorption and obtained from experiments at various temperatures. In any adsorption procedure, both energy and entropy considerations should be considered in order to determine which process will take place spontaneously. Values of thermodynamic parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) have great significance for practical application of a process. The apparent equilibrium constant ( $K_c$ ) of the adsorption is given by Equation (13):

$$K_c = \frac{C_{ad,eq}}{C_{eq}} \quad (13)$$

Where  $C_{ad,eq}$  is the concentration of metal ion on the adsorbent at equilibrium and  $C_{eq}$  is the equilibrium concentration of metals in solution ( $\text{mg L}^{-1}$ ). The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated by using the following equations:

$$\Delta G^\circ = -RT \ln K_c \quad (14)$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (15)$$

Where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (K) [41, 42]. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined from the slope and intercept of the plot of  $\ln K_c$  vs.  $1/T$  (Figure 10) [31]. The results are reported in Table 4. The negative values of  $\Delta G^\circ$  revealed that the removal was spontaneous, and the decreasing of  $\Delta G^\circ$  is resulted as temperature increased also the value of  $\Delta H^\circ$  shows the endothermic nature of the adsorption. The positive values of  $\Delta S^\circ$  indicate that the freedom of Ni(II) and Cd (II) is not too restricted in the adsorbent and corresponds to increase in the degree of freedom of the adsorbed species [32].

**Table 2:** Mathematical equations in  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  removal kinetics.

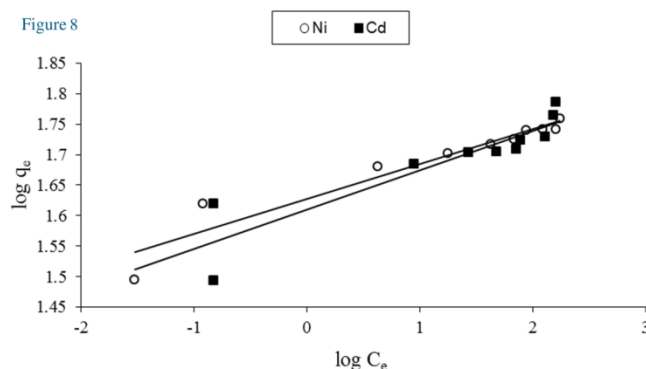
Kinetic models	Linear equations	Plot	Calculated coefficients
Lagergren	$\ln(q_e - q_t) = \ln q_e - k_1 t$	pseudo-first order	order
		(9) $\ln(q_e - q_t)$ vs. $t$	$k_1 = -\text{slope}$ , $q_e = e^{\text{intercept}}$
Pseudo-second	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$		order
		(10) $\frac{t}{q_t}$ vs. $t$	$k_2 = \text{slope}^2 / \text{intercept}$ , $q_e = 1 / \text{slope}$
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$		
		(11) $q_t$ vs. $\ln(t)$	$\alpha = e^{(\text{intercept}/\text{slope} - \ln(\beta))}$ , $\beta = 1/\text{slope}$
Intra-particle diffusion	$q_t = k_{\text{intra}}(t)^{1/2} + C$		(12) $q_t$ vs. $t^{1/2}$
			$k_{\text{intra}} = \text{slope}$ , $C$

**Table 3:** Kinetic parameters for the removal of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  on to adsorbent.

Metal ions	Lagergren pseudo-first order			pseudo-second order			Elovich			Intra-particle diffusion		
	$q_e(\text{mg g}^{-1})$	$K_1$	$R^2$	$q_e(\text{mg g}^{-1})$	$K_2$	$R^2$	$\beta$	$\alpha$	$R^2$	$K_{\text{diff}}$	$C$	$R^2$
$\text{Cd}^{2+}$	21.14	0.0170	0.9416	49.51	$3.598 \times 10^{-3}$	0.9992	0.172	21.970	0.9849	1.9251	29.634	0.9393
$\text{Ni}^{2+}$	29.98	0.0189	0.9567	52.08	$2.468 \times 10^{-3}$	0.9987	0.131	49.827	0.9816	2.5429	25.658	0.9372

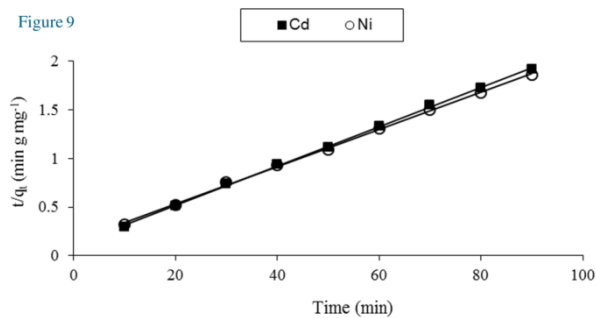
**Table 4:** Thermodynamic parameters for the removal of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  on to adsorbent.

Metal ions	$\Delta S^\circ(\text{kJ mol}^{-1} \text{ K}^{-1})$	$\Delta H^\circ(\text{kJ mol}^{-1})$	$\Delta G^\circ(\text{kJ mol}^{-1})$				
			283(K)	293(K)	303(K)	313(K)	323(K)
$\text{Cd}^{2+}$	0.111283	29.41659	-2.17571	-3.10594	-4.2518	-5.33259	-6.65003
$\text{Ni}^{2+}$	0.183565	50.68214	-1.29067	-3.03423	-5.0224	-6.69948	-8.63883

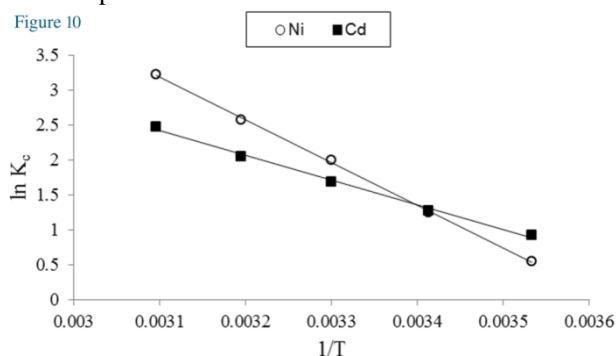


**Fig. 8:** Freundlich plots for the removal of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  on to adsorbent; adsorbent dose 2.4 g/L, temp. 25 °C, pH 4.





**Fig. 9:** Pseudo-second-order kinetic plots for the removal of Ni<sup>2+</sup> and Cd<sup>2+</sup> on to adsorbent.



**Fig. 10:** Thermodynamic plots for the removal of Ni<sup>2+</sup> and Cd<sup>2+</sup> on to adsorbent.

### 5. Conclusion:

The present study indicates that the waste tire rubber ash is an effective and cheap adsorbent for the removal of Ni (II) and Cd (II) from aqueous solutions. Maximum removal occurs at a contact time of 100 min, pH 4.0 and at 2.4 gL<sup>-1</sup> of adsorbent. It was found that the adsorption behaviour of metal ions is according to the Langmuir isotherm and pseudo- second- order kinetic model describes the equilibrium adsorption data perfectly.

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