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# Adsorption studies on *Citrus reticulata* (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater

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## Abstract

The ability of fruit peel of orange to remove Zn, Ni, Cu, Pb and Cr from aqueous solution by adsorption was studied. The adsorption was in the order of Ni(II) > Cu(II) > Pb(II) > Zn(II) > Cr(II). The extent of removal of Ni(II) was found to be dependent on sorbent dose, initial concentration, pH and temperature. The adsorption follows first-order kinetics. The process is endothermic showing monolayer adsorption of Ni(II), with a maximum adsorption of 96% at 50°C for an initial concentration of 50 mg l<sup>-1</sup> at pH 6. Thermodynamic parameters were also evaluated. Desorption was possible with 0.05 M HCl and was found to be 95.83% in column and 76% in batch process, respectively. The spent adsorbent was regenerated and recycled thrice. The removal and recovery was also done in wastewater and was found to be 89% and 93.33%, respectively. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Endothermic; Adsorption; Isotherm; Desorption; Regeneration

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## 1. Introduction

Industrial, agricultural and domestic waste pollute water bodies with heavy metals, which reach tissues through the food chain. The toxicity of heavy metals to aquatic organisms has been a subject of interest to biologist for many years. Adsorption of trace

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metals onto natural particulate matter can play an important role in determining trace metal speciation in many aquatic systems [1–4]. Among different types of pollution, the industrial waste constitutes the major source of various kinds of metal pollution in natural water [5]. The important toxic metals, i.e. Cd, Zn, Cr, Pb and Cu finds its way to the water bodies through wastewater from such industries as metal-plating industries of cadmium, nickel batteries, pigment, stabilizers, alloys [6].

Nickel is used in plating plants and is present in their wastewater [7]. About 40% of the nickel produced are used in steel factories, Ni batteries and in the production of some alloys [8]. Manifestation of dermatitis in some workers engaged in electroplating, polishing, paints and pigments may be attributed to nickel poisoning.

The conventional methods for heavy metal removal from wastewater includes reduction, precipitation, ion exchange, reaction with silica, electrochemical reduction, evaporation, reverse osmosis and direct precipitation. Most of these methods involve high capital cost with recurring expenses, which are not suitable for small-scale industries. Studies on treatment of effluents bearing heavy metals have revealed adsorption to be a highly effective, cheap and easy method among the physicochemical treatment processes.

Owing to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low-cost materials. Polymerized onion skin with formaldehyde [9], waste wool [10–12], peanut skin [13,14], modified barks [15,16], barks [17], barley straw [18] have been studied. Removal of nickel by adsorption using solid residue from olive mill products [19], *Mangifera indica* seed shell [20], humic acid type purifying agents [21], coal-based adsorbents [22], burned clay and root [23], furnace gas cleaning sludge [24], hydrous oxides of iron(II) [25] have been reported.

The authors of this study believe that it is possible to process the solid residue of orange fruit peel and convert it to an adsorbent that has a large surface area and thus great potential to adsorb harmful contaminants, such as heavy metals from aqueous solutions and industrial waste at relatively low cost compared with other available adsorbents.

## 2. Material and methods

### 2.1. Adsorbent

Sieved fruit peel of *Citrus reticulata* (orange fruit) was used for the removal of Ni(II) from aqueous solution. The fruit peels were dried, crushed and washed thoroughly with double distilled water to remove the adhering dirt and finally dried in an air oven at 100–105°C for 24 h. After drying the adsorbent was sieved through 150-mesh size and used as such.

### 2.2. Adsorbate solution

Stock solution of Ni(II) was prepared ( $1000 \text{ mg l}^{-1}$ ) by dissolving the desired quantity of nickel nitrate (AR grade) in distilled water. Solutions of other metal ions were prepared ( $1000 \text{ mg l}^{-1}$ ) by dissolving their chlorides or nitrates.

### 2.3. Adsorption studies

Adsorption studies were carried out by batch process. A 0.5-g sample of adsorbent was placed in a conical flask in which 50-ml solution of metal ion of desired concentration was added and the mixture was shaken in a shaker. The mixture was then filtered and final concentration of metal ion was determined in the filtrate by atomic absorption spectrophotometer (model GBC 902). The amount of metal ions adsorbed was calculated by subtracting final concentration from initial concentration.

### 2.4. Effect of pH

The effect of pH on the adsorption of Ni(II) was studied as follows.

One hundred milliliters Ni(II) solution was taken in a beaker. The pH of solution was adjusted by adding dilute solution of HCl or NaOH. The concentration of Ni(II) in this solution was then determined (initial concentration). Fifty milliliters of this solution was taken in a conical flask and treated with 0.5 g of adsorbent and after equilibrium the final concentration of Ni(II) was determined.

### 2.5. Desorption of Ni(II)

The desorption studies were carried out by batch as well as by column process under similar conditions. Fifty milliliters of the sample containing  $10 \text{ mg l}^{-1}$  Ni(II) was treated with 1 g of adsorbent. The pH of the solution was adjusted to 6 and was left in contact with adsorbent for 24 h. The solution was then filtered and filtrate was analyzed for Ni(II). The adsorbent was then transferred to another conical flask and treated with 50 ml of 0.05 HCl solution. It was again filtered and desorbed Ni(II) was determined in the filtrate. The column studies were conducted using 1 g of orange fruit peel in a glass column (0.6 cm in diameter) with a glass wool support. The adsorbent was washed with distilled water and 50 ml solution containing 0.5 mg of Ni(II) (pH 6) was passed through the column. The Ni(II) adsorbed was then eluted with 0.05 M HCl solution with a flow rate of  $1 \text{ ml min}^{-1}$ . Ni(II) eluted was collected in 10-ml fractions and then determined by atomic absorption spectrophotometer.

### 2.6. Regeneration studies

A 0.5-g amount of adsorbent was treated with 50 ml Ni(II) solution ( $50 \text{ mg l}^{-1}$ ) in a conical flask and after equilibrium time it was filtered. The adsorbent was then treated with 50 ml HCl solution (0.05 M) for 24 h. It was filtered and filtrate was analysed for Ni(II) desorbed. The adsorbent was washed several times with distilled water in order to remove excess acid. It was again treated with 50 ml Ni(II) solution and the above procedure was repeated a number of times (five times or cycle).

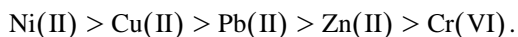
### 2.7. Recovery of Ni(II) from electroplating wastewater

The removal and recovery of Ni(II) from electroplating wastewater was carried out by batch as well as by column operations. 50 ml of the waste containing  $10 \text{ mg l}^{-1}$

Ni(II) was taken in a conical flask and its pH was adjusted to 6 and then treated with 1 g of adsorbent. The removal and recovery of Ni(II) was carried out as described above. In another experiment, 50 ml of the waste was taken in a beaker and its pH was adjusted to 6. It was then passed through the column containing 1 g of adsorbent and the removal and recovery of Ni(II) was carried out as described above.

### 3. Result and discussion

The percent adsorption behaviour of different metal ions on orange fruit peel shows that the adsorption of Ni(II) is maximum (97.5%) while Cr(VI) adsorbed least (30%) Fig. 2. The percent adsorption follows the order



#### 3.1. Effect of contact time

The adsorption increases with increasing contact time. The Ni(II) uptake vs. time curve at different temperatures (Fig. 1) shows that initially (at 15 min contact time) the adsorption of Ni(II) is low at 30°C and increases as the temperature is increased to 50°C. However, when contact time is increased at 30°C, the adsorption also increases and equilibrium is attained after 2 h. Maximum uptake of Ni(II) occurs at 50°C but equilibrium time remains the same (2 h). The metal uptake vs. time curves at different temperatures are single, smooth and continuous leading to saturation, suggesting possible monolayer coverage of metal ions on the surface of the adsorbent.

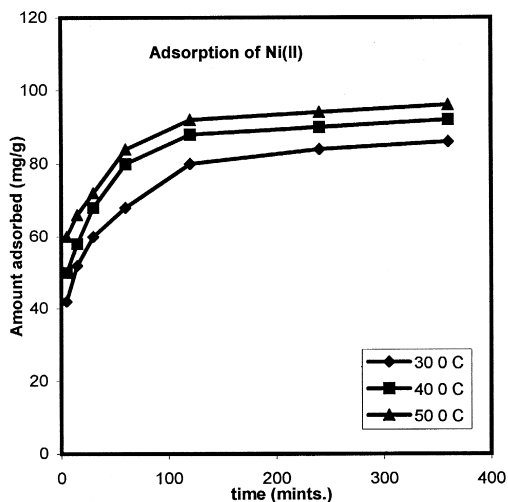
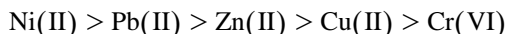


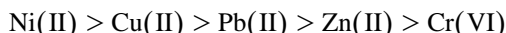
Fig. 1. Effect of contact time.

### 3.2. Effect of concentration

The effect of concentration on the adsorption behaviour of metal ions is shown in Fig. 2. It can be concluded that maximum adsorption of Ni(II), Cu(II), Zn(II) and Pb(II) occurs at 40 mg l<sup>-1</sup> initial concentration whereas the adsorption of Cr(VI) remains minimum over a wide range of concentration (20–100 mg l<sup>-1</sup>). However, at lower concentration (20 mg l<sup>-1</sup>) the adsorption follows the order



and at higher concentration (100 mg l<sup>-1</sup>), the adsorption behaviour follows the order



showing that percent adsorption of Ni(II) remains maximum over a wide range of initial concentration while adsorption of Cr(VI) is least under similar conditions.

### 3.3. Effect of temperature on metal adsorption

The temperature range used in this study was from 30°C to 50°C. Adsorption increases with increase in temperature. Thermodynamic parameters such as standard free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were calculated using the following equations [26–28].

$$K_C = \frac{C_{AC}}{C_e}$$

where  $K_C$  is the equilibrium constant.

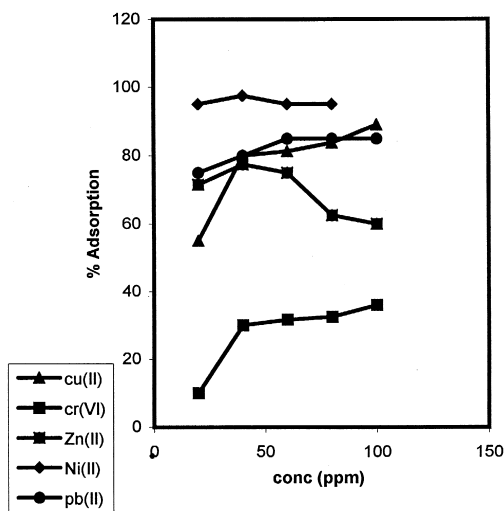
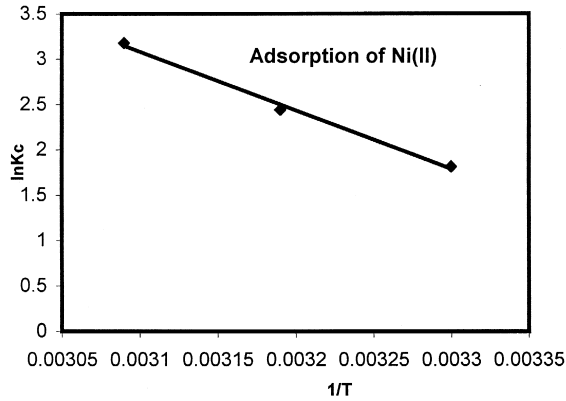


Fig. 2. Effect of concentration.

Fig. 3.  $\ln K_C$  vs.  $1/T$ .

$C_{AC}$  and  $C_e$  are the equilibrium concentrations ( $\text{mg l}^{-1}$ ) of the metal ion on the adsorbent and in the solution respectively.  $\Delta G^0$  was calculated from the relation

$$\Delta G^0 = -RT \ln K_C$$

where  $T$  is temperature in kelvin and  $R$  is gas constant.  $\Delta H^0$  was calculated from the following equation

$$\log K_C = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}$$

$\Delta H^0$  and  $\Delta S^0$  were obtained from the slope and intercept of Van't Hoff plots of  $\log K_C$  vs.  $1/T$  (Fig. 3). Positive values of  $\Delta H^0$  (Table 1) suggest the endothermic nature of adsorption. The negative values of  $\Delta G^0$  indicate spontaneous nature of adsorption of Ni(II) on the adsorbent. The positive value of  $\Delta S^0$  shows the increased randomness at the solid/solution interface during the adsorption of metal ion on fruit peel of orange. The increase in adsorption capacity of fruit peel of orange at higher temperature may be attributed to the enlargement of pore size or activation of the adsorbent surface [29]. The values of  $K_C$  are also high at all temperatures and increase with rise in temperature (Table 1) showing endothermic process.

Table 1  
Thermodynamic parameters for adsorption Ni(II)

Temperature ( $^{\circ}\text{C}$ )	$K_C$	$\Delta G^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta H^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^0$ ( $\text{kJ mol}^{-1}$ )
30	6.14	-4.7226		
40	11.5	-6.5586	53.89	0.1923
50	24	-8.7984		

### 3.4. Adsorption isotherms

The adsorption data has been analysed in the light of Langmuir and Freundlich adsorption models. The Langmuir equation may be described as

$$\frac{1}{x/m} = \frac{1}{\theta^0 b} \frac{1}{C} + \frac{1}{\theta^0}$$

where  $x/m$  is metal uptake per unit weight of adsorbent,  $C$  is the equilibrium concentration of metal ( $\text{mg l}^{-1}$ ),  $\theta^0$  and  $b$  are Langmuir constants relating to adsorption capacity and adsorption energy respectively. The Langmuir isotherm is valid for monolayer adsorption onto the surface of the adsorbent containing a finite number of identical sites. The plot of  $1/(x/m)$  against  $1/C$  gives a straight line (Fig. 4) at each temperature showing the applicability of Langmuir isotherm. The adsorption capacity ( $\theta^0$ ) for the uptake of Ni(II) increases from 80 to 158  $\text{mg g}^{-1}$  by increasing the temperature from 30°C to 50°C showing the process to be endothermic. The values of Langmuir constant  $K(\theta^0 b)$  vary linearly with the temperature (Fig. 5) and hence Van't Hoff type equation has been applied to carry out the computation of the thermodynamic parameters [20]. The values are summarized in Table 3. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter ( $R_L$ ) which is defined by the following relation:

$$R_L = \frac{1}{1 + bC_0}$$

where  $C_0$  is the initial metal ion concentration ( $\text{mg l}^{-1}$ ) and  $b$  is the Langmuir constant. The  $R_L$  values at 30, 40 and 50°C are found to be 0.057, 0.0542 and 0.0848, respectively, showing favourable adsorption of Ni(II) [30,31].

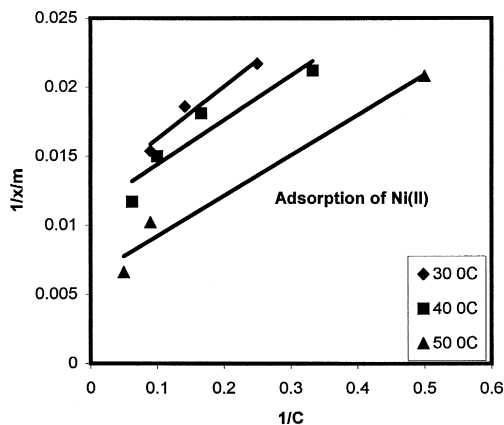


Fig. 4. Langmuir isotherm.

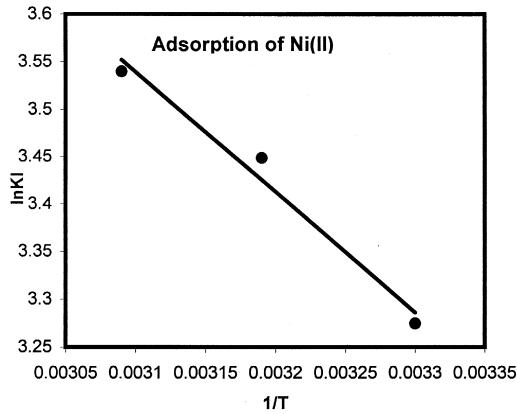


Fig. 5.  $\ln K_1$  vs.  $1/T$ .

The Freundlich adsorption isotherm was also applied for the adsorption of Ni(II)

$$\ln \frac{x}{m} = \ln K_f + \frac{1}{n} \ln C$$

where  $C$  is the equilibrium concentration ( $\text{mg l}^{-1}$ ),  $x/m$  is the amount adsorbed per unit weight of adsorbent ( $\text{mg l}^{-1}$ ),  $K_f$  and  $n$  are Freundlich constants. The linear plot of  $\ln(x/m)$  vs.  $\ln C$  at each temperature indicates that adsorption of Ni(II) also follows Freundlich isotherm (Fig. 6). The Freundlich constant  $K_f$  also show linear variation with temperature (Fig. 7) and hence used to calculate thermodynamic parameters as described earlier [20].

The values of Langmuir and Freundlich constants at different temperatures are shown in Table 2. The thermodynamic parameters for the two isotherms are shown in Table 3.

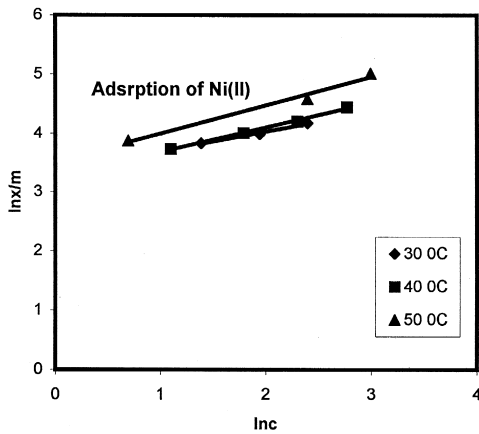
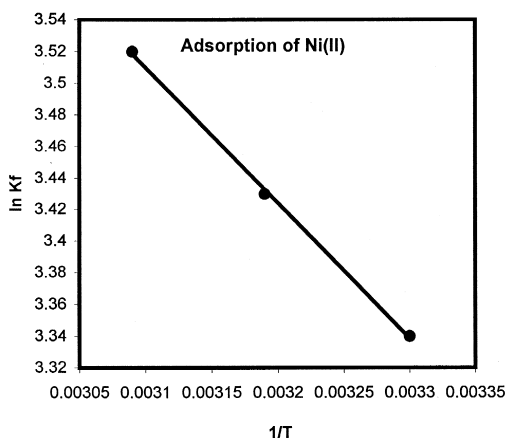


Fig. 6. Freundlich isotherm.



Fig. 7.  $\ln K_f$  vs.  $1/T$ .

The positive value of  $\Delta H$  indicates that the process is endothermic. The values of Langmuir and Freundlich constants are very high ( $K \gg 1$ ) at each temperature indicating that Ni(II) ions are strongly adsorbed. The increase in  $K$  values with rise in temperature also confirms that the process is endothermic (Table 2). The free energy of the process at all temperatures is negative and decreases with increase in temperature which indicates that the process is spontaneous and spontaneity increases with increase in temperature. The entropy of the overall system is negative and almost constant showing the favourable adsorption [20].

Table 2

Langmuir and Freundlich constant at different temperature for adsorption of Ni(II)

Temperature (°C)	Langmuir isotherm				Freundlich isotherm		
	$K_L$	$\ln K_L$	$b$	$\theta^0$	$K_f$	$\ln K_f$	$1/n$
30	26.3852	3.2728	0.3298	80	28.4344	3.3476	0.3395
40	31.1526	3.4388	0.3489	89.2857	30.8272	3.4284	0.3499
50	34.2465	3.5335	0.2157	158.7301	33.7371	3.5186	0.4775

Table 3

Langmuir and Freundlich isotherm at different temperature for adsorption of Ni(II)

Temperature (°C)	Langmuir isotherm			Freundlich isotherm		
	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJ K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )	$-\Delta S$ (kJ K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )
30	-8.2446	-0.06139		-8.4330	-0.0501	
40	-8.9487	-0.06168	10.3684	-8.9216	-0.05009	6.7589
50	-9.4889	-0.06144		-9.4489	-0.0501	

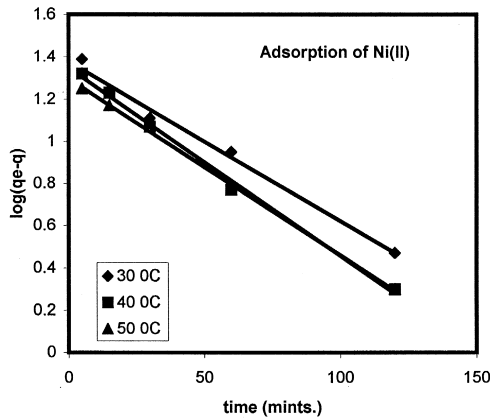


Fig. 8. Lagergren plot.

### 3.5. Adsorption dynamics

The rate constant of adsorption is determined from the following first-order rate expression given by the equation [32]

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t$$

where  $q$  and  $q_e$  are amounts of metal adsorbed ( $\text{mg g}^{-1}$ ) at time  $t$  (min) and at equilibrium, respectively, and  $K_{ad}$  is the rate constant for adsorption ( $\text{l min}^{-1}$ ). The straight-line plots of  $\log(q_e - q)$  vs.  $t$  at different temperatures (Fig. 8) indicate the applicability of the above equation. Values of  $K_{ad}$  were calculated from the slope of the linear plots. Table 4 shows the adsorption rate constant is not affected with increase in temperature.

### 3.6. Intraparticle diffusion

The rate constant for intraparticle diffusion ( $K'$ ) is calculated by the equation [33]

$$q = K_{ad} t^{1/2}$$

where  $q$  is the amount adsorbed ( $\text{mg g}^{-1}$ ) at time  $t$  (min). Plots of  $q$  vs.  $t^{1/2}$  are shown in Fig. 9 for different temperatures.  $K_{ad}$  values were obtained from the slope of the

Table 4  
Rate constant at different temperature for adsorption of Ni(II)

Temperature (°C)	Lagergren rate constant $K_{ad}$ ( $\text{l min}^{-1}$ )	Intraparticle rate constant $K_{ad}$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )
30	$1.750 \times 10^{-2}$	1.1238
40	$2.049 \times 10^{-2}$	2.2432
50	$1.934 \times 10^{-2}$	3.8063

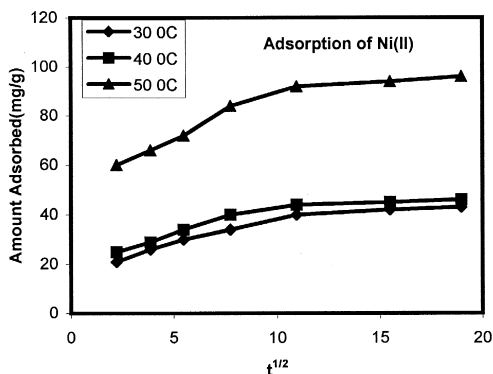


Fig. 9. Intraparticle diffusion.

linear portion of the curves for each temperature (Table 4).  $K_{ad}$  values increase when temperature is increased from 30° to 50°C.

### 3.7. Effect of pH

The effect of pH on the adsorption of Ni(II) by orange fruit peel is presented in (Fig. 10). The pH of the aqueous solution is an important controlling parameter in the adsorption process [34]. At lower pH value, the  $H^+$  ions compete with metal cation for the exchange sites in the system thereby partially releasing the latter. The heavy metal cations are completely released under circumstances of extreme acidic conditions [35–37]. The percent adsorption is minimum (40%) at pH 2 and increases as the pH is increased. The maximum adsorption occurs at pH 6 (97.5%) but adsorption decreases when pH is increased further. The minimum adsorption at low pH (pH 2) may be due to the fact that high concentration and high mobility of  $H^+$  ions, the hydrogen ions are preferentially adsorbed compared to Ni(II) ions.

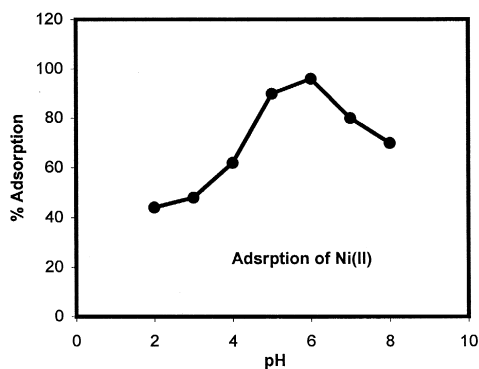


Fig. 10. Effect of pH.

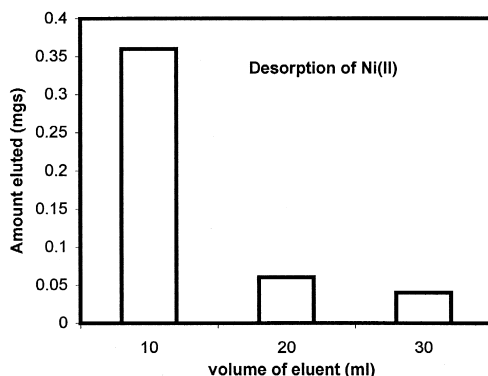


Fig. 11. Desorption of Ni(II).

### 3.8. Desorption studies

The adsorption of Ni(II) on fruit peel of orange is highly pH dependent hence its desorption is possible by controlling the pH. Fig. 11 shows the desorption trend of Ni(II) by column operation. Ni(II) is retained in the column as long as pH of the solution is maintained at 6. Desorption starts when a solution of 0.05 M HCl is passed through the column. It is important to note that desorption of Ni(II) is rapid and 95.83% Ni(II) could be eluted in 30 ml of effluent from the column. However, the desorption is slow and incomplete by batch process. The desorption of Ni(II) from a solution containing 50 mg l<sup>-1</sup> Ni(II) by batch process was 76% (Table 5).

### 3.9. Regeneration studies

In order to make the process of adsorption and recovery of Ni(II) more economical, it is necessary to regenerate the spent adsorbent. The adsorption and desorption of Ni(II) on fruit peel of orange by column operation after each regeneration cycle (by 0.05 M HCl) is shown in Table 5. It is interesting to note that adsorption remains maximum (98%) up to the 3rd regeneration cycle and then goes down to 95% in the 4th cycle. The recovery or desorption of Ni(II) also remains maximum (90%) up to the 3rd cycle and decreases to 70% in the 4th cycle of regeneration. This behaviour indicates that the

Table 5  
Effect of regeneration on the adsorption and desorption of Ni(II) by fruit peel of orange

Sample No.	No. of cycles	Amount of Ni(II) before adsorption (mg l <sup>-1</sup> )	Amount of Ni(II) after adsorption (mg l <sup>-1</sup> )	Adsorption (%)	Amount Ni(II) desorbed with 0.05 M HCl (mg l <sup>-1</sup> )	% Recovery
1	1	10	0.1	99	9.9	99
2	2	10	0.2	98	9.6	97
3	3	10.2	0.2	98	8.82	90
4	4	11.18	0.5	95	7.43	70

Table 6  
Analysis of electroplating wastewater

Metal ions/pH	Concentration (mg l <sup>-1</sup> )
Cr(VI)	30
Cu(II)	7.9
Ni(II)	14.5
Zn(II)	12.9
Pb(II)	2.1
pH	3.2

Table 7  
Removal and recovery of Ni(II) from electroplating wastewater. Amount of adsorbent = 1 g

Volume of electroplating waste water (ml)	Amount of Ni(II) before adsorption (mg l <sup>-1</sup> )	Amount of Ni(II) after adsorption (mg l <sup>-1</sup> )	% Removal	Amount Ni(II) desorbed with 0.05 M HCl (mg l <sup>-1</sup> )	% Recovery
50	14.5	1.5	89	12.62	93.3

adsorbent can be used successfully four times after regeneration for the removal and recovery of Ni(II) from wastewater.

### 3.10. Recovery of Ni(II) from electroplating wastewater

Fruit peel of orange as an adsorbent was utilized for the removal and recovery of Ni(II) from electroplating wastewater by column operation. The electroplating wastewater collected from one of the electroplating industries in Aligarh (India) was analyzed in our laboratory and the results are shown in Table 6. The adsorbed Ni(II) was recovered (93.33%) with 0.05M HCl. These results are shown in Table 7.

## 4. Conclusion

The fruit peel of orange (*Citrus reticulata*) is a low-cost adsorbent which is abundantly available in India as waste material. It can be used as an effective adsorbent for the removal and recovery of Ni(II) from waste water. The adsorption of Ni(II) is pH dependent and maximum removal occurs at pH 6. The adsorption follows first-order kinetics. The process is endothermic and follows Langmuir and Freundlich isotherm. The adsorbed Ni(II) can be recovered using 0.05 M HCl solution. However, the recovery of Ni(II) by column operation is higher (95.8%) as compared to batch process (76%). The spent adsorbent can be regenerated and reused making the adsorption process more economical.

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