

***CHAPTER IV:
Optimization of Conditions for Removal of
Nickel(II) using Sugarcane Bagasse as an
Adsorbent***

IV.1 Abstract

The chapter presents the work on the use of sugarcane bagasse as an adsorbent for the removal of Ni (II) from aqueous solution. Different variables of the biosorbent experiment have been optimised which include pH, initial metal ion concentration, adsorbent dose, contact time and temperature. The biosorbent has been characterised using SEM, FT-IR and BET analysis. Langmuir and Freundlich adsorption isotherms have been used to analyse the biosorption process of the Ni(II) on the sugarcane biosorbent. Langmuir model is best fit to the experimental values with R^2 value more than 0.98. The kinetics of the biosorption was evaluated and it was found that biosorption of the Ni(II) on the sugarcane bagasse biosorbent shows second order kinetics. Thus the chapter describes the efficient use of the sugarcane bagasse biosorbent for the removal of the Ni(II) from synthetic waste water.

IV.2 Introduction

Due to rise in industrial activities [1] as well as natural phenomenon [2], the release of heavy metals in the environment have increased many folds. These heavy metals cause severe toxicity to the biological system i.e. fauna and flora [3-5]. Minimata disease due to toxicity of mercury and Itai-itai disease due to toxicity of cadmium [6] are well documented. Various Agencies of different countries have prescribed the limit of the heavy metals concentration to be released in industrial effluent in the environment. These metals are with density greater than 5 mg/cm^2 [7]. Particularly exposure to nickel which is used in making stainless steel, electronic components, jewellery, coins, may lead to high blood pressure, developmental deficiency, neurological disorder, cardiovascular disease, lung cancer [8]. Oxidative damage due to formation of free radicals by

exposure of nickel is also reported [9]. Breast cancer, infertility, miscarriage are also found to be caused by exposure to the nickel [10-12]. In drinking water maximum permissible limit of Ni (II) is 0.02 mg/L (BIS, 1994).

Owing to the toxic effects of the nickel it is important to minimize the content of nickel in the waste water either by removal or by remediation.

Various methods are available to remove and recover nickel. Important technologies are precipitation, solvent extraction, adsorption, ion exchange, reverse osmosis and electrodialysis [13-20]. These methods involve high cost or technical constraints. Hence there is a need to develop cost effective methods for nickel removal from waste water. Use of ion exchange method by utilization of biomass obtained as industrial /agricultural waste or from microbial biomass has gain momentum. As these biomass possess functional groups such as carboxyl (-COOH), Amide (-NH₂), Thiol (-SH), Phosphate(PO₄⁻³) and Hydroxyl (-OH) [21] which are found to be involved in biosorption of heavy metals. Use of bacterial strains *Bacillus subtilis* WD 90, *Bacillus subtilis* SM 29 [22], *Nostoc calcicola* [23], *Rhizobium leguminosarum* [24] fungal derived biosorbents [25-27] is reported in literature for the removal of nickel from waste water.

Present work is based on the use of Sugarcane bagasse as biosorbent for the removal of heavy metal nickel from synthetic waste water sugar cane bagasse is a solid waste generated by sugar industries.

IV.3 Materials and methods

Chemicals used were of analytical grade and were supplied by Sigma Aldrich.

IV.3.1 Preparation of sugarcane bagasse adsorbent

Adsorbent was prepared as described in chapter 2

IV.3.2 Preparation of nickel solution

To prepare synthetic stock solution (1000mg/L) of Ni(II), calculated quantity of NiSO₄.6H₂O was added double distilled water. The standard solutions were made by diluting the stock solution. All other chemical used, were analytical grade.

IV.3.3 Batch mode adsorption studies

Flasks of 100 ml capacity were used to carry out the batch adsorption experiments. The effect of contact time (30-180 min), temperature (20-50⁰C), pH(2.0-10), adsorbent dose(0.25-5gm/L) and initial metal ion concentration (10-200 mg/L) was investigated. The adsorption of heavy metals on sugarcane bagasse adsorbent was obtained by shaking the 50 ml solutions of heavy metals of known concentrations with prescribed adsorbent dose in an orbital shaker for a known period of time. After equilibration, the suspension of the adsorbent was separated from solution by filtration using Whatman No. 1 filter paper .The concentration of heavy metal ions remaining in solution was measured spectrophotomertrically. The pH of the adsorptive solutions was adjusted using hydrochloric acid and sodium hydroxide. The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution. The percentage removal of heavy metal and amount adsorbed per unit mass was calculated using Equations (1) & (2) respectively [28].

$$\% \text{ Removal of metal ions} = \frac{(C_o - C_e)V}{C_o} \times 100 \quad \dots (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad \dots (2)$$

Where: C_0 is the initial metal ion concentration of test solution in mg/L, C_e is the final equilibrium concentration of test solution in mg/L and V is the amount of the metal ion solution in L.

IV.4 Results and discussion

IV.4.1 Characterizations of adsorbent

The biosorbent prepared was characterized using SEM and BET and FTIR techniques as described in chapter 2.

IV.4.2 Analysis of the metal

Samples of solutions were filtered through filter paper and then the filtrates were collected and analyzed for metal concentration using UV-Visible spectrophotometer (systronic 2203). The amount of metal adsorbed during the contact time with activated sugar cane bagasse was estimated using the calibration curve (Abs vs Concentration).

IV.4.3 Effect of contact time

To investigate the effect of varying contact time (30-180 min) on the percentage removal of Ni(II), the biosorbent dose used was 2g/L, initial metal ion concentration was 50mg/L at pH 6.0 at 30⁰C. Figure 1 shows that metal removal efficiency of the biosorbent increases rapidly with increasing contact time upto 100 min followed by slight increase in metal removal efficiency. The optimum time to study metal removal efficiency using sugarcane biosorbent is 120 minutes and the same contact time is used in further experiments.

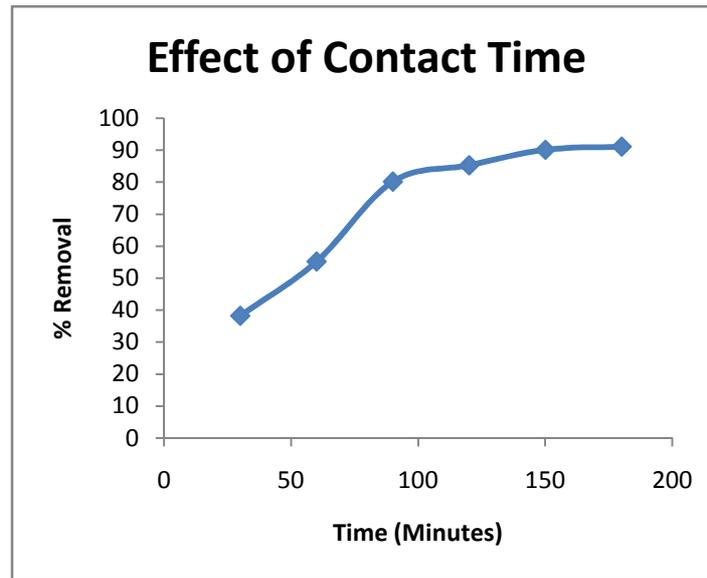


Figure IV.1 Effect of Contact time on percentage removal of Ni(II) by sugarcane baggase adsorbent

IV.4.4 Effect of operating temperature

To investigate the effect of the temperature on the percentage removal of the Ni(II) by sugarcane biosorbent the experiments were performed at different temperatures 20, 30, 40 and 50 °C using 2g/L biosorbent dose, 50 mg/L initial metal ion concentration and contact time 120 minutes. Figure 2 shows that increasing the temperature from 20 to 50 °C increases the metal uptake by the biosorbent. Increase in metal removal is attributed to the better interaction between metal ions and the biosorbent. 30°C is found to be the optimum temperature.

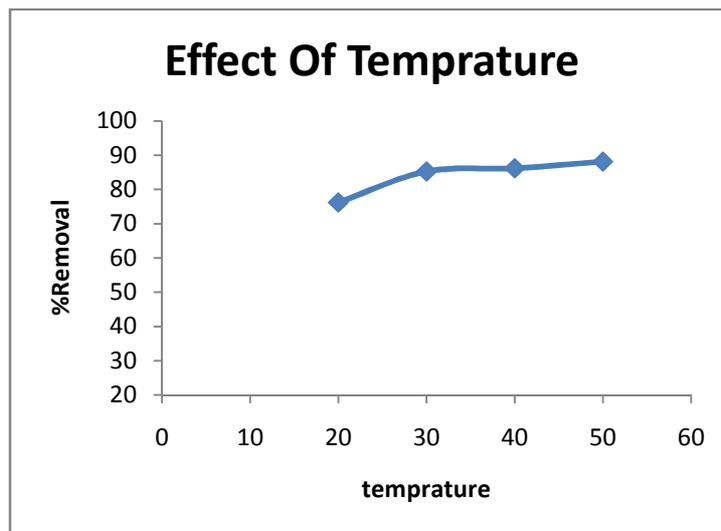


Figure IV.2 Effect of Temperature on percentage removal of Ni(II) by sugarcane bagasse adsorbent.

IV.4.5 Effect of pH

Figure IV.3 shows the effect of pH on the percentage removal of the nickel. Experiments were performed using biosorbent dose 2gm/L, initial metal ion concentration 50mg/L, contact time 120 minutes, operating temperature 30⁰C. Experiments were performed at various pH values viz; 2, 4, 6, 8 and 10. The percentage removal of the metal increases with increase in pH and reaches the maximum value at pH 6.0 further increase in pH has negative effect and percentage removal of nickel decreases. It is documented that at lower pH protonation of the adsorbent sites occur hence availability of the binding sites to the metal decreases. At higher pH metal hydroxides are precipitated out.

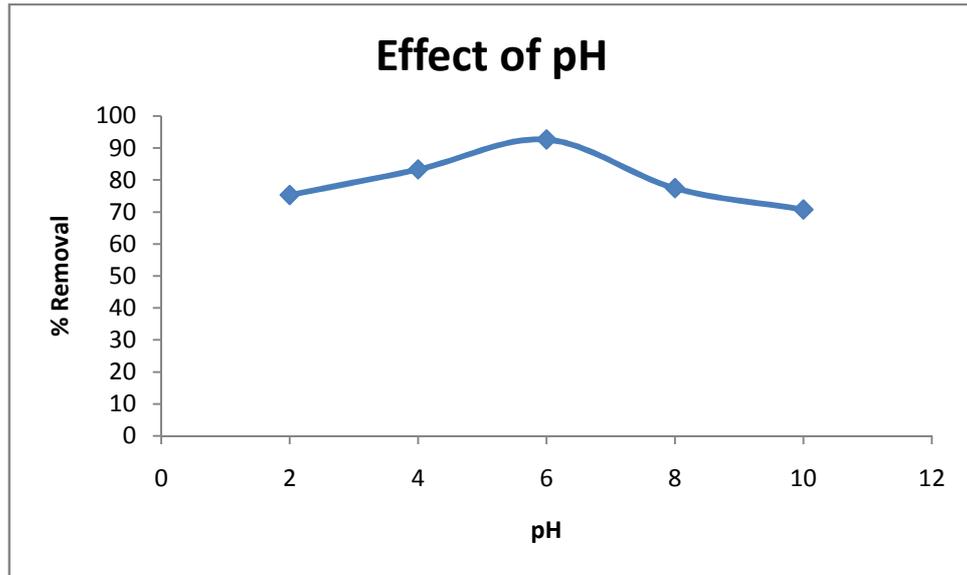


Figure IV.3 Effect of pH on % removal of Nickel ion by sugarcane bagasse adsorbent.

IV.4.6 Effect of adsorbent dose

To study the effect of biosorbent dose experiments were performed with varying biosorbent dose i.e. 0.25, 0.5, 1.0, 2.0, 3.0, 5.0 g/L. Initial metal ion concentration was 50 mg/L, contact time 120 minutes, pH 6.0 and operation temperature 30⁰C. A sharp increase in the percentage removal of the metal was observed with increase in dose and reaches optimum value using biosorbent dose 2gm/L as is evident from the figure 4. Increase in biosorbent dose increases the availability of the binding sites to the metal.

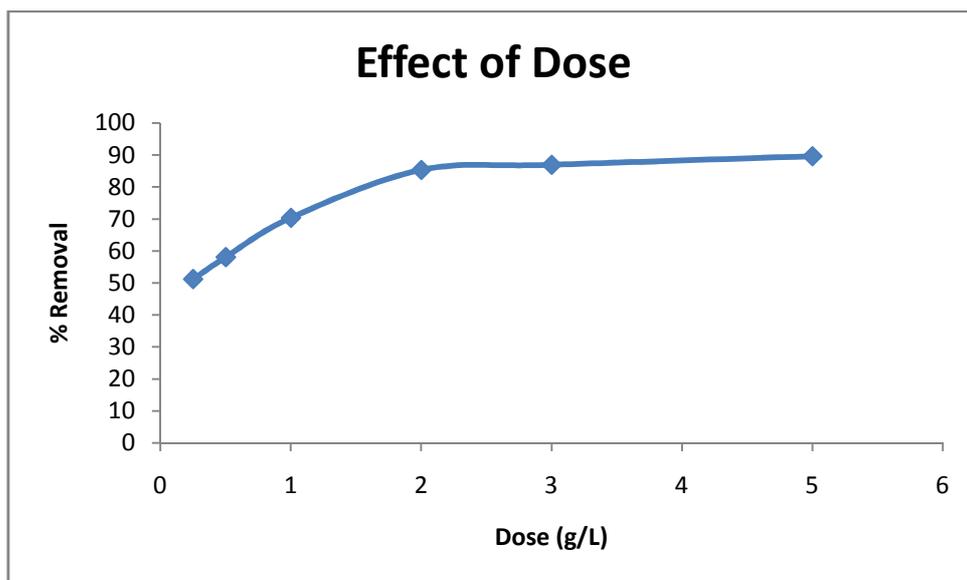


Figure IV. 4 Effect of adsorbent dose on percentage removal of nickel.

IV.4.7 Effect of initial metal ion concentration

Figure 5 shows the effect of initial ion metal ion concentration (10-200 mg/L) on the nickel removal from synthetic waste water. The effect was investigated using 2 gm/L adsorbent dose, 6.0 pH, contact time 120 min. percentage removal of Ni(II) is maximum when initial ion metal ion concentration is 10 mg/L. increasing metal ion concentration above 10 mg/L decrease. At lower concentration the available sites are higher. At higher concentration no of metal ion increases compare to available binding sites. Thus removal of metal ions depends on initial ion metal ion concentration.

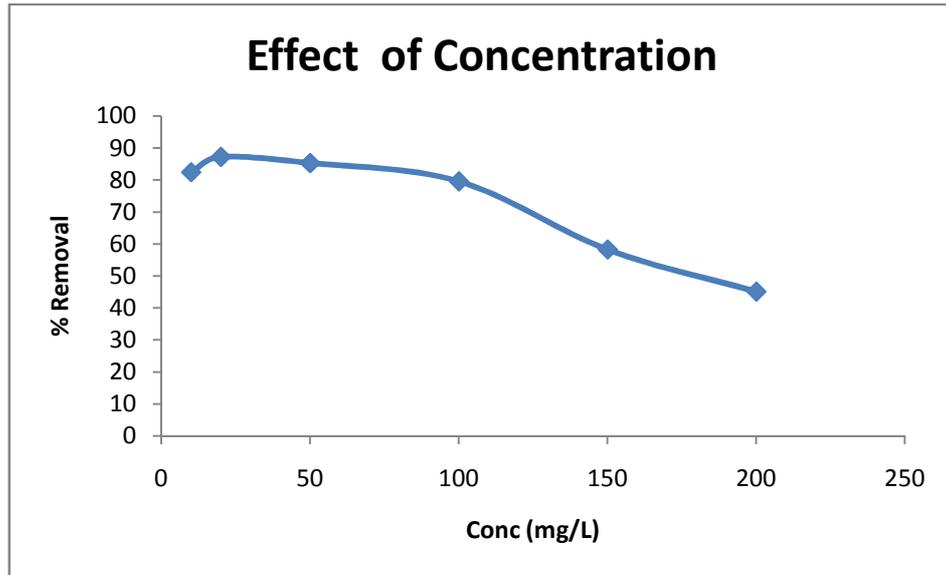


Figure IV.5 Effect of initial metal ion concentration on percentage removal of Nickel ion by sugarcane baggase adsorbent

IV.4.8 Adsorption isotherm models

Adsorption isotherms are used to represent the equilibrium relationship between the mass of the solute adsorbed per unit mass of the adsorbent and the equilibrium concentration of the solute. In this study, Langmuir and Freundlich models Equations (4) and (5) respectively were employed to study the experimental data. Langmuir considered adsorption of an ideal gas on ideal surface. Langmuir isotherm is based on the assumption that the adsorption takes place at specific homogeneous sites on the adsorbent. Freundlich isotherm is based on the assumption of heterogeneous adsorption surface and the active sites with different energy (Equations 4 and 5)

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

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad \dots (5)$$

Where q_{\max} (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant related to the free energy of adsorption, K_f (mg/g) is the Freundlich constant which is an estimate of relative adsorption capacity of adsorbent and $\frac{1}{n}$ is the adsorption intensity. The experimental data were applied to the equation above and a plot of $\frac{C_e}{q_e}$ vs C_e was drawn to verify the applicability of Langmuir isotherm and was shown in Figure 6. A linear plot of q_e vs c_e was tried to verify the suitability of Freundlich isotherm, as shown in Figure 7. The constants in the isotherm equations were evaluated and reported in Table 1. From the table, it was observed that Langmuir isotherm represented the equilibrium adsorption of nickel and the value of regression coefficient (R^2) was comparatively higher for Langmuir isotherm (0.98) than Freundlich isotherm (0.86). This result suggests monolayer coverage of the surface of activated sugarcane bagasse by nickel ions since the Langmuir isotherm assumes that the surface is homogeneous. As expected for an endothermic process, the values of q_{\max} and K_L increased with increase in temperature.

Table IV.1 Adsorption isotherms studies

Langmuir Isotherm			Freundlich Isotherm		
q_{\max} (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)	R^2
52.0204	0.2394	0.98	1.8328	1.9943	0.86

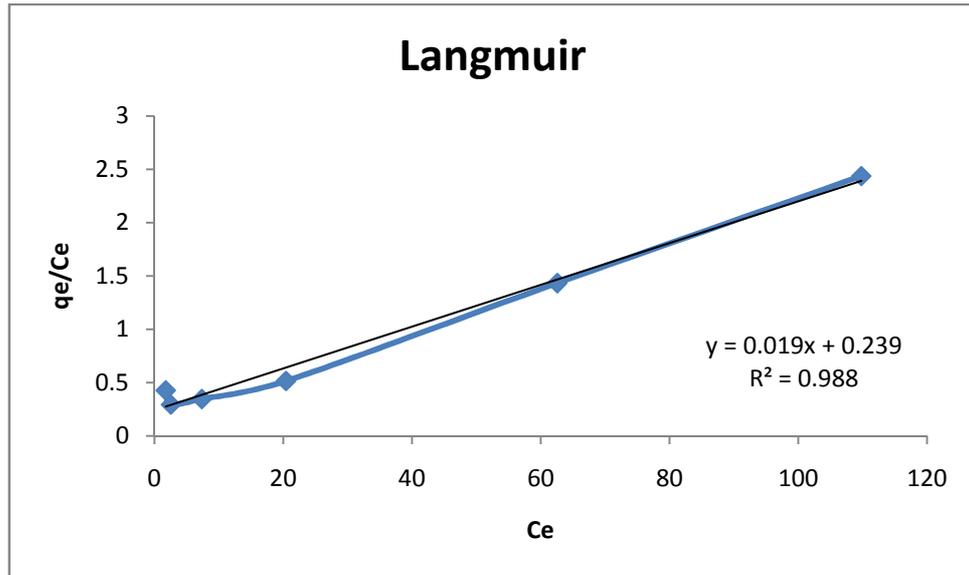


Figure IV.6 Langmuir adsorption isotherm

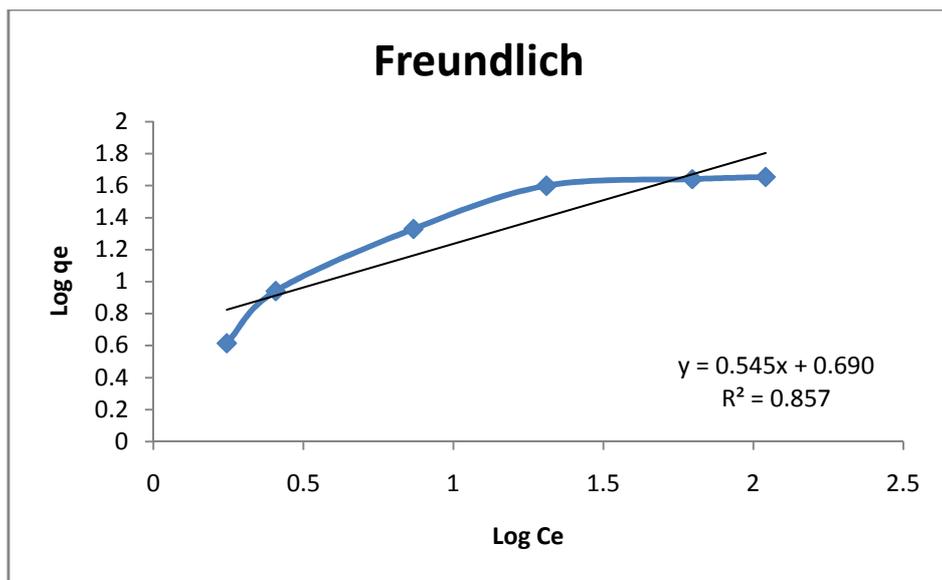


Figure IV.7 Freundlich adsorption isotherm

IV.4.9. Kinetic studies

The studies on the rate of removal are essential for the proper design of waste water treatment facilities. In this study, the pseudo-second-order equation (Equation 6) and intraparticle diffusion model (Equations 7) have been applied to the experimental data to analyze the adsorption kinetics of Nickel ions:

$$\frac{t}{q_t} = \frac{1}{k_2 q_1^2} + \frac{1}{q_1} t \quad \dots (6)$$

Where q_1 (mg g/1) is the maximum adsorption capacity and q_t (mg g/1) is the amount of nickel adsorbed at time, t , and k_2 (g (mg min)/1) is the equilibrium rate constant for pseudo-second order adsorption. The intraparticle diffusion model can be represented as

$$q_t = k_t t^{1/2} + I \quad \dots (7)$$

Where q_t (mg/g) is the amount of metal adsorbed at time, t , and k_t (mg/ (g min^{1/2})) is the intraparticle diffusion rate constant and I (mg/g) is a constant that is related to boundary layer thickness. Results of the kinetic data modelling indicated that the pseudo-second order model (Fig. 8) describes the adsorption of nickel better than the other model. The pseudo second order model assumes that two surface sites will be occupied by one adsorbate ion. The pseudo-second order model could not identify the diffusion mechanism. Due to this, intra-particle diffusion model was employed and was presented in Figure 8 as q vs $t^{1/2}$. If the plot passes through the origin, then intraparticle diffusion is the rate controlling step. But, a larger intercept was observed in this experiment which confirmed that the boundary layer effect is greater. The correlation coefficients of pseudo-second order model is greater than that of intra particle diffusion model. The constants in the kinetic models were presented in Table 2.

Table IV.2 Kinetic studies of Ni(II) adsorption by sugarcane bagasse biosorbent.

Pseudo First Order		Pseudo Second Order	
k_1 (min^{-1})	R^2	k_2 ($\text{g/mg}\cdot\text{min}$)	R^2
0.0131	0.95	2.42×10^{-6}	0.98

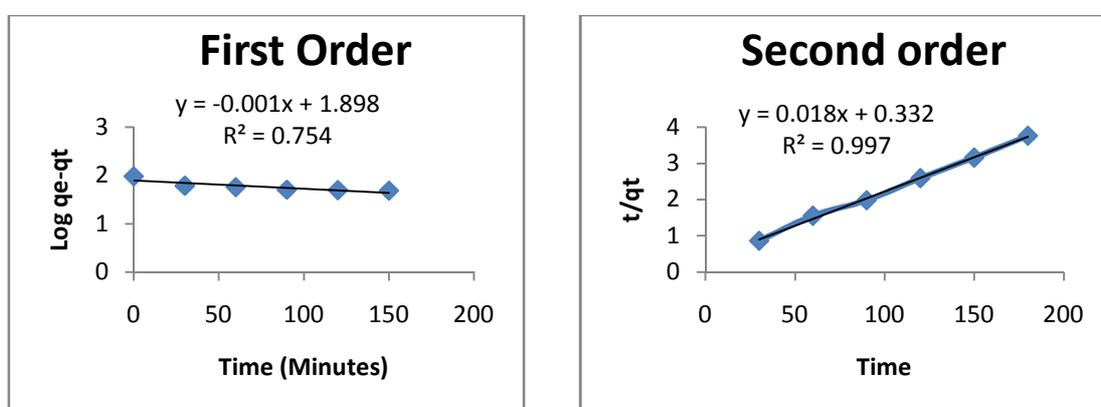


Figure IV.8 kinetic studies of the Ni(II) on the sugarcane biosorbent

IV.5 Conclusion

The study successfully demonstrated the application of sugarcane baggase powder as an adsorbent for the removal of Ni (II) ions from the synthetic waste water. pH 6.0 is found to be the optimum pH for maximum removal of the Ni(II) by the sugarcane bagasse biosorbent. Removal efficiencies increased with increase in adsorbent dose while metal removal capacities decreased. Endothermic nature of the adsorption process is evident from the increased removal at higher temperature. The Langmuir isotherm was demonstrated to provide the best fit for the equilibrium sorption data confirming a monolayer adsorption pattern. The pseudo-second order model fitted well (with $R^2 > 0.99$) for the kinetic data. From this study, we conclude that activated sugar can baggase

powder merits further exploration in large-scale continuous systems to evaluate the practical applicability of its use in effluent treatment plants.

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