Research Article

Studies on the Adsorption Mechanism of Nickel Ions by a Cross-Linked Polymer

K. Karthik Kumar*, G.N. Kousalya
PG and Research Department of Chemistry, G.T.N. Arts College, Dindigul - 624005, Tamil Nadu, India.
***Corresponding author's E-mail:** drkkarthikkumar@gmail.com

Received: 16-05-2020; **Revised:** 22-07-2020; **Accepted:** 29-07-2020.

ABSTRACT

The most important problem for many developed countries is the successful removal of heavy metals from aqueous solution. The present investigation describes the adsorption of nickel ions onto cross-linked polymer from its aqueous solution. Contact time, dosage and pH in which medication was found to be most efficient have been examined. The adsorption data were analyzed mathematically using adsorption isotherm such as Freundlich and Langmuir isotherm to study the mechanism of adsorption of Ni(II) ions to this cross-linked polymer. Freundlich isotherm was found to be most applicable. FTIR interpreted before and after adsorption by nickel ions for the study of various functional groups present in cross-linking polymer.

Keywords: Nickel ions, Cross-Linked Polymer, Freundlich isotherm, Langmuir isotherm, FTIR.

INTRODUCTION

Water is life, it is nature's spirit, and it is future hope[1]. For human and other life forms clean drinking water is essential. Heavy metal contamination in water has always been a significant environmental concern, as heavy metals are not biodegradable and can be stored in living tissues[2]. Rapid industrialization has significantly led to the introduction of harmful heavy metals to water sources. Many metals such as Fe, Cu, Zn & Ni can be dangerous beyond certain limits and Other metals such as Hg, Pb & Cd are poisonous and very hazardous to living beings. To address environmental heavy metal pollution it is important to have appropriate solutions. Many techniques have been focused on heavy metal removal and, due to their local availability, technical feasibility and cost effectiveness, adsorption processes are preferred[3].

In the present investigation, the efficiency of the Cross-Linked Polymer (CLP) for the removal of Ni(II) ions from its aqueous solution has been studied and the applicability of the kinetic and equilibrium models for the Ni(II)-CLP system has also been discussed.

MATERIALS AND METHODS

Preparation of Cross-Linked Polymer

The Chitosan-Chem (M) Sdn. Bhd. had kindly supplied chitosan flakes used in the analysis. First, in 100 mL of 1% Sebacic acid (SA) solution, 1g of chitosan flakes were dissolved. The SA solution was heated for 5 min at a temperature between 60 and 70°C, and was continuously stirred at 200 rpm using a magnetic stirrer. This chitosan solution was left overnight to ensure dissolving of all the chitosan flakes. Magnetic stirrer was used to constantly stir the aqueous solution at 200 rpm to prevent the chitosan from sticking to one another or sticking to the surface of the glassware. For making a chitosan-SA film, the chitosan-SA solution was dried on the surface of the OMR sheet[4].

Experimental details

Effect of contact time was studied by treatment Nickel solutions with Cross-Linked Polymer at shaking speed of 250 rpm at different time of 5 to 60 min. To determine the effect of different dosage, the Nickel solution was treated with CLP at different weight of 0.5, 1, 1.5, 2, 2.5 g. pH studied was conducted by treating Nickel was treated with CLP at range of pH values from 3 to 11 at shaking speed of 250 rpm. The pH of the solutions was adjusted with 1 N HCl or NaOH solution by using a pH meter. The concentration of the Nickel was measured by a spectrophotometer at λ_{max} = 420 nm and percentage of removal and quantity of Nickel adsorbed, q_e (mol/g) was calculated using the following formula:

$$\% \text{ Removal} = (C_o - C_e) \times 100 / C_o$$

$$q_e = (C_o - C_e) \times V / W$$

Where, C_o and C_e are initial and equilibrium concentration of Nickel respectively, V is the volume of the solution and W the weight of the CLP used.

Adsorption isotherm

The analysis and design of adsorption separation processes requires the relevant adsorption equilibria, which is the most important piece of information in understanding an adsorption process. It is also important for designing an adsorption system. The adsorption equilibrium indicates how the adsorbate molecules distribute between the liquid phase (solution) and the solid phase (adsorbent) when the adsorption process reaches an equilibrium state. To describe the adsorption equilibrium data of Nickel on adsorbent, polmer composites, Langmuir and Freundlich isotherm models were used. The Freundlich isotherm can be efficient on multilayer and also, heterogeneous surface and is expressed by the following equation.

$$q_e = KFC_e^{1/n} \quad \text{(or)} \quad \log q_e = \log KF + 1/n \log C_e$$

Where, q_e and C_e is the amount of adsorbed adsorbate per unit weight of adsorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively and KF and 1/n are Freundlich constant characteristics of the system, which are determined from the log q_e vs. log C_e. Also, Langmuir adsorption is very useful for predicting adsorption capacities and also interpreting into mass transfer relationship. The isotherm can be written as follows:

$$q_e = q_m Q_0C_e / (1 + bC_e) \quad \text{(or)} \quad (C_e/q_e) = (1/Q_0) + (b/K_L)\, C_e$$

Where, Q_o and b were the Langmuir constants, which measures of monolayer (maximum) adsorption capacity (in mg/g) and energy of adsorption (in g/L) respectively. The Langmuir parameters were obtained from the linear correlations between the values of Ce/qe and Ce.

FT-IR Spectra

FT-IR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The adsorbent was taken carefully, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

RESULTS AND DISCUSSION

Contact Time

The sorption capacity (SC) of the sorbent was determined by varying contact time in the period of 5-60 min. About 1g of the sorbent was mixed with 50ml of the solution having an initial concentration of 10mg/l. The contents were shaken thoroughly by using a mechanical shaker. The contents were filtered and analysed for Ni^{2+} ion. As is evident from Figure-1, the SC of the sorbent reached saturation at 40min. Hence, 40 min is fixed as the contact time for the further studies. The SC at the period of 40 min of CLP was found as 910mg/kg. The Sorption capacity is calculated by

$$SC = C_i\text{-}C_e \times V/M = (C_i\text{-}C_e)/1/50 \times 1000 \text{ mg/g} = x \text{ mg/g}.$$

Where C_i is the initial concentration of Nickel solution

C_e is the equivalent concentration of Nickel solution

V is the volume of Nickel solution

M is the weight of Nickel solution

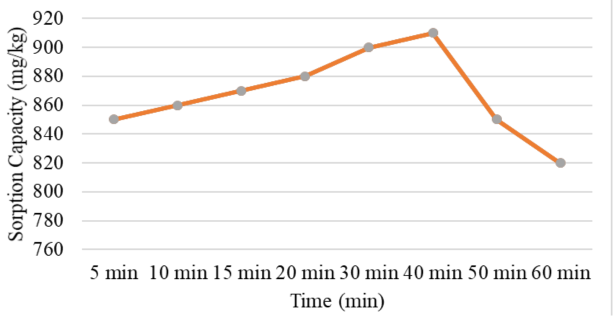

Figure 1: Contact Time vs Sorption Capacity

Dosage

The adsorption data for the variation of dose of adsorbent is presented in Figure-2. The percentage removal of heavy metal ion by CLP as an adsorbent is found to increase with increase in dose of adsorbent. This is mainly due to the increase in availability of active adsorption studies. The SC of the sorbents was determined by varying dosage level in the range of 0.5g to 2.5g. The different dosage level of adsorbent was added with 50ml of the stock nickel solution having an initial concentration of 10mg/l. The contents were shaken thoroughly by using a mechanical shaker. The contents were filtered and analysed for Ni^{2+} ion. As is evident from the effect of contact time 40 min is fixed as the contact time for the sorbent for this study. The percentage removal of SC was determined by varying different dosage such as 0.5g, 1g, 1.5g, 2g, 2.5g. It was observed that the percentage of removal was high in 2.5g. Hence, the further studies were carried at fixed dosage of 2.5g as such.

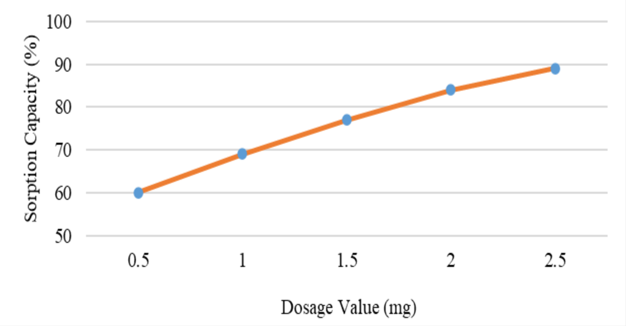

Figure 2: Dosage vs Sorption Capacity

pH

The removal of nickel from aqueous solution was highly dependent on the solution pH in many cases as it attached the surface charge on the sorbent. The pH of the working solution was control by using HCL/NaOH. SC of the sorbent was determined at five different pH levels viz., 3, 5, 7, 9 and 11 and the results are shown in Figure-3 A maximum SC was observed at pH level between 3-11 and the maximum adsorption was observed at pH 5. Adsorption increases with the increase in pH.

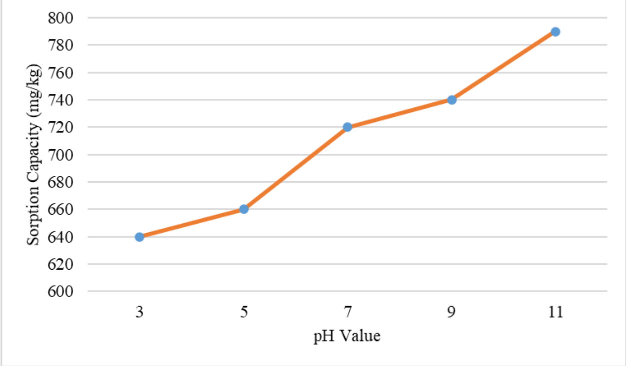

Figure 3: pH vs Sorption Capacity

There is an adsorption at lower pH of CLP could be ascribed for the hydrogen ions competing with Ni(II) ions for adsorption site. At higher H^+ concentration, the adsorbent surfaces become more positively charged, thus reducing the attraction between adsorbent and metal ions. At higher pH, the adsorbent surface takes more negative charges, thus attracting more Ni(II) ions.

However, it was also observed that the adsorption capacity of Ni(II) ions decreased with further increase in pH due to the formation of anionic hydroxide which reduced the concentration of free Ni(II) ions.

Isotherm data analysis

Freundlich Adsorption Isotherm

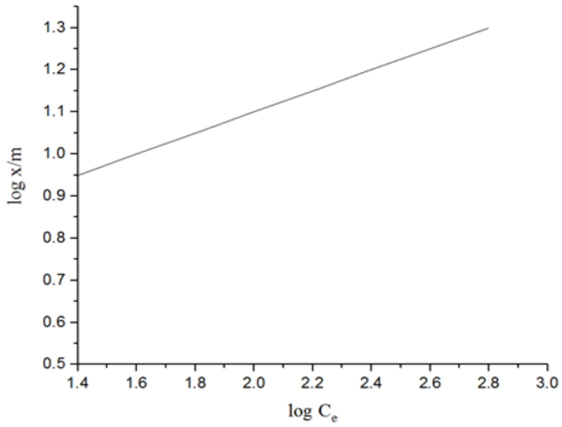

Figure 4: Freundlich Adsorption Isotherm of CLP

In general, as k value increases the adsorption capacity of adsorbent is also increases. The value of n is greater than one is favorable for adsorption condition.

Langmuir Adsorption Isotherm

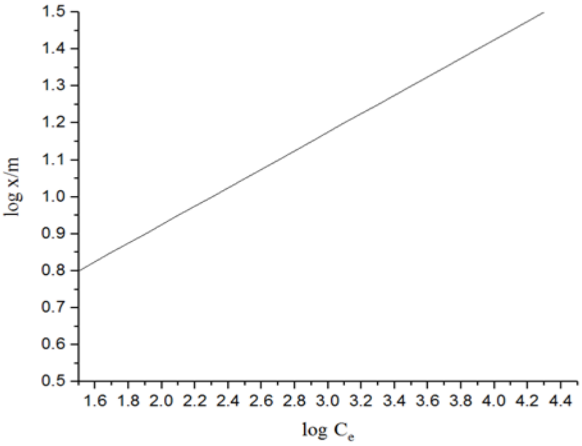

Figure 5: Langmuir Adsorption Isotherm of CLP

The Langmuir constants b and RL were determined from slope and intercept on the plot. The value of RL in the present investigation is found to be 0.71 which shows the adsorption of nickel on Flax seed is favorable. RL value is less than one if shows that the sorption behaviour follows the R.E. Treybal et. al.

FTIR analysis

FTIR spectra of CLP before and after adsorption of Ni ions is shown in Figure 6a and 6b respectively.

In fig 6a, the –OH stretching frequency appeared at 3324 cm^{-1} and -NH bending frequency at 1759 cm^{-1}. The –CO stretching frequency appeared at 1172 cm^{-1}.

In fig 6b, the OH stretching frequency shifted from 3324 cm^{-1} to 3367 cm^{-1} and –NH bending frequency shifted from 1759 cm^{-1} to 1763 cm^{-1}. The –CO stretching frequency shifted from 1172 cm^{-1} to 1168 cm^{-1}.

There is no disturbance in fundamental groups. A very small shift is occurred due to adsorption of Ni metal. The intensity of transmittance of peaks were relatively more at 622 cm^{-1} in the case of nickel loaded sorbent compared with unloaded sorbent. This may be attributed due to the interaction between fundamental groups and nickel during the adsorption process. Hence the presence of FTIR band at 622 cm^{-1} in the nickel sorbed composite suggests the bonding between the nickel and the sorbent.

The formation of NiO shows that the Nickel adsorbed on the CLP.

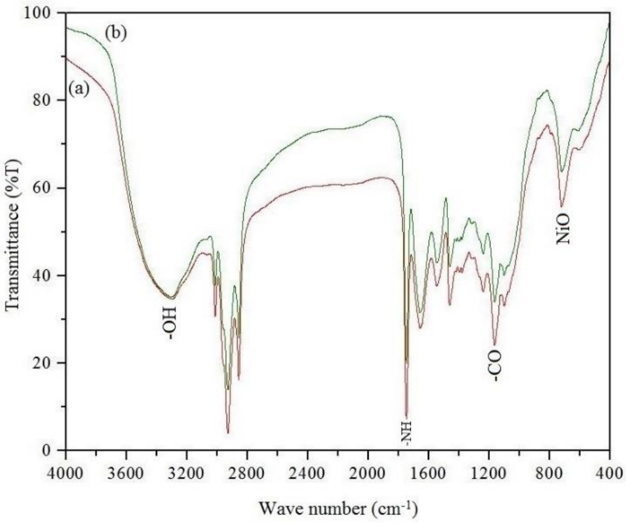

Figure 6: FTIR spectra of

a) CLP before adsorption of Ni ions

b) CLP after adsorption of Ni ions

CONCLUSION

- ✓ A significant adsorption of Nickel onto CLP was found using different variables like contact time, pH and adsorbent dosage, in which dosage was found to be most effective.
- ✓ The maximum removal of Nickel is found to be 89% at dosage of 2.5g maintaining parameters like pH and contact time, which were 30 min respectively.
- ✓ The isotherm models were analyzed using the Langmuir and Freundlich for equilibrium data.
- ✓ CLP could be used as low cost adsorbents in effective effluent treatment, especially for the removal of metal ions.
- ✓ The results will be highly useful in the design of waste water treatment plants for the removal of nickel.

REFERENCES

1 Modoi, O. C., Roba, C., Török, Z., & Ozunu, A. (2014). Environmental risks due to heavy metal pollution of water resulted from mining wastes in NW Romania. *Environmental Engineering and Management Journal*, *13*(9), 2325–2336. https://doi.org/10.30638/eemj.2014.260

2 Kulshreshtha, S. N. (1998). A global outlook for water resources to the year 2025. *Water Resources Management*, *12*(3), 167–184. https://doi.org/10.1023/A:1007957229865

3 Jonathan Febrianto, Aline Natasia Kosasih, Jaka Sunarso, Yi-Hsu Ju, Nani Indraswati, Suryadi Ismadji. (2009). Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *Journal of Hazardous Materials*, 162(2-3), 616-645. https://doi.org/10.1016/j.jhazmat.2008.06.042.

4 Karthik Kumar K. & Kousalya G.N. (2020). Cross-linking of Chitosan with Sebacic acid and its Characterisation. *Alochana Chakra Journal*, *IX*(2231), 2107–2112.

Source of Support: None declared.

Conflict of Interest: None declared.