

Synthesis and Characterisation of Pentaerythritol Xanthate Co-Polymeric Hydrogel and its Application for Toxic Metal Removal

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Abstract:- There are three new grades biodegradable Pentaerythritol Xanthate (PEX) based co-polymeric Hydrogels (PEXHs), were synthesized for the effective removal of toxic metal ions from wastewater. Such novel eco-friendly PEXHs were prepared from the synthesised PEX and the resulting hydrogels were have been confirmed by FTIR, UV-Visible spectroscopy. The synthesized hydrogels were utilized for the removal of toxic metal ions from wastewater such as Co²⁺ and Ni²⁺ ions that quantitatively determined with the help of UV-1900i spectrometer (Shimadzu Corporation Japan). It was found that PEXH1, PEXH2, and PEXH3 remove 83.75%, 89.37%, 93.75% and 91.11%, 92.77%, 95% of Co²⁺ and Ni²⁺ respectively. These results show that synthesized hydrogels act as excellent adsorbents for the removal of metal ions in comparison to many other adsorbents reported earlier in the literature.

Keyword:- Pentaerythritol Xanthate-Based Hydrogel; Adsorption Isotherm; Wastewater; Toxic Metal; Kinetic Models.

I. INTRODUCTION

Water contamination by toxic metals is one of the major challenges in India. In the many regions of India freshwater reservoir is contaminated with different types of toxic metals like, Co, Ni, Cu etc [1]. In addition, India is a developing country and the industrial activities have increased significantly in last 10-20 years. Fresh water utilization and the disposal of contaminated water generated via industrial activities create problems for environment and ecology. The presence of toxic metals in the water results in harmful effects on natural ecosystem and human health such as central nervous system, kidney, skin and teeth problem, liver, or lung problem and so on, and intake of large amount of such metals can lead to death [2-3]. These metals even in small concentration, can exhibit toxic effects and pose human and environmental health risk. So, the removal of such toxic metals from wastewater is a very importance issue.

The various physical, biological, and chemical process technologies are used for the detoxification of the water. Basically, biological treatment is recommended for high organic containing wastewater and chemical treatment methods is recommended for all types of pollutants like, organic/inorganic, TS/TDS/TSS. For toxic metals removal many physical/chemical methods like chemical precipitation[4], ion exchange[5], membrane filtration[6], flocculation-coagulation[7], reverse osmosis[8] etc have been reported in literature. The selection of any treatment methods depends upon the efficacy and treatment cost. In this regard adsorption-based treatment option is widely recommended for the toxic metal removal. Adsorption method is simple and effective treatment technique for the toxic metal ions removal at low cost. In addition, adsorption treatment methods depend upon the types of pollutants and the types of adsorbents used for the toxic metal removal. The other favorable properties like, high surface area, adsorption capacity and easy to handle and have more active sites rather than bulk are considered during the selection of adsorbent[9]. The dominance of adsorption technique is very selectively to eliminate the toxic metals from wastewater.

Available adsorbents can be classified in to physical and chemical adsorbents. Generally physical adsorbents performance depends upon the available active sites. The number of these active sites can be increased by various physical and chemical methods. While chemical adsorbents work based on the available active sites and the structure and bonding of the adsorbents. In the available literature various physical/chemical adsorbents like clay, activated carbon, TiO₂, etc [10-14] have been reported for wastewater treatment. The biggest disadvantage of hydrogel is the disposal of used adsorbent which may be generated in bulk after industrial application. In this regard biodegradable chemical adsorbent may play an important role for industrial application. Over the last few years, hydrogels a class of adsorbent materials (biodegradable) having hydrophilic properties and have high adsorbing capacity can be recommended for cleaning of toxic water. Generally, polymer hydrogel is composed of functional groups like OH, COOH, and NH₂ etc. Other advantageous properties

like excellent swelling capacity, porous nature, good adsorption capacity, attracts their uses as adsorbents. Hydrogels have a 3D network structure that is efficient to absorb water in their network structure. The hydrophilic groups in the polymeric network enable the construction of a flexible structure that facilitates facile solute transport into the three-dimensional gel network and forms stable complexes with the functional groups on a long polymeric chains [15-17]. Hydrogels play an important role for capturing toxic metal ions from wastewater and can eject these dangerous pollutants upon changes in the external environment (change in pH, temperature, time, dosage, etc.). Pentaerythritol xanthate-based hydrogel has a three-dimensional network with pentaerythritol-modified pentaerythritol xanthate hydrogel entrapped within the polymeric networks which helps in the trapping of metal ions by the mechanism of physical and chemical adsorption. In previous studies, broad research has been done, mainly focusing on characterization of adsorbent materials, maximum adsorption capacity, adsorption kinetics, etc. But preparation, characterization application of pentaerythritol xanthate-based hydrogel is almost rare in the literature.

Present studies cover the preparation of chemical hydrogel based adsorbent and their application to removal of toxic metal ions, turbidity, swelling and water retention capacity and also study the adsorption kinetics of metal ions of hydrogels. In addition, overall comparable studies in terms of execution and low-cost adsorbent with the other treatment options have been reported in this work.

II. MATERIAL AND METHODS

A. Materials

All the chemicals/reagent required during experimental investigation of AR (analytical reagent) grade were purchased from SD Fine Chemical Pvt. Ltd. Mumbai & Himedia Laboratories Pvt. Ltd, Mumbai, India. The double distillation column based distilled water with conductivity 0.5 to 3 $\mu\text{mhos/cm}$ was used to prepare all the solutions. Tap water with conductivity 50-800 $\mu\text{S/cm}$ was used to study the swelling capacity of the hydrogels. The stock solution of Co & Ni was prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ & $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.

➤ Synthesis of Pentaerythritol Xanthate (PEX) and Xanthate-Based Polymeric Hydrogel (PEXH)

• Synthesis of Pentaerythritol Xanthate (PEX)

PEXs were synthesized by the reported methods [18]. In a two-neck 250 mL round bottom flask, pentaerythritol (5.36 g) dissolved in distilled water (25 mL) and stirred for 5 minutes. After that NaOH (2.0 g) dissolved in distilled water (25 mL) was added into it with continuous stirring (350 rpm) for 120 minutes at 45°C. After completion of reaction, flask was cooled to 20°C, then carbon disulphide (2.50 g) was added into the solution and stirring was continued for another 24 h at 22°C under inert atmosphere. After completion of the reaction an orange coloured turbid solution was obtained [18]. The orange colour product was extracted with the help of diethyl ether and methanol. The product was dried at 40°C in hot air oven and purified by recrystallization from methanol (yellow colour) as mechanism is shown in Fig 1.

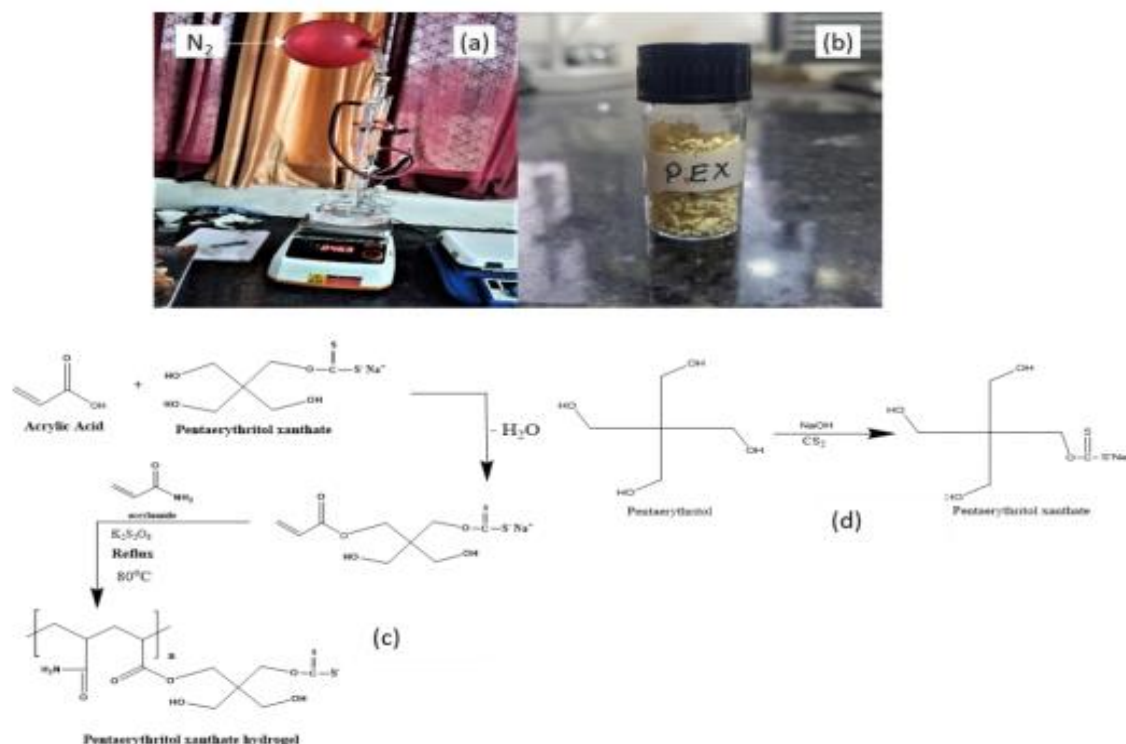


Fig 1 Synthesis of Pentaerythritol Xanthate (a) Experimental Set-Up of Hydrogel (b) PEX (c) Reaction Mechanism for PEXH (d) Reaction Mechanism of PEX

• *Synthesis of PEX Based Co-Polymeric Hydrogel (PEXHs)*

Xanthate based polymeric hydrogels (PEXHs) was synthesized by using the method reported in literature [19] for the preparation PEXHs. These co-polymeric hydrogels have been synthesized by reacting PEX with acrylamide and acrylic acid in two neck 250 mL round bottom flask equipped with a magnetic stirring bar and a condenser with the cooling system at 45°C for 90 minutes. The three-grade hydrogel was prepared and the ratio of PEX, acrylamide, acrylic acid along with PEXH yield was reported in Table 1. The yield of the PEXH was calculated as,

$$\% \text{ yield} = \frac{\text{Weight of product}}{\text{Weight of reactant}} \times 100$$

Table 1 Composition of Initial PEX, Acrylic Acid, Acrylamide & NaOH for PEXH Preparation

Hydrogel	Xanthate, PEX (mg)	Acrylic Acid Monomer (mg)	Acrylamide Monomer (mg)	NaOH (mg)	Yields
PEXH G-1	10	3603	3554	2000	77.78%
PEXH G-2	20	3603	3554	2000	87.52%
PEXH G-3	30	3603	3554	2000	93.71%

➤ *Toxic Metal Ions Removal*

Removal mechanism of toxic metals (Co & Ni) with the help of synthesised adsorbent PEXHs and the adsorption mechanism of toxic metal ions with PEXHs. Different adsorption parameters like adsorbent dose, solution pH, adsorption time, pollutants dose, & operating temperature were optimized via experimental study. Stock solution of 4000 ppm of both Co & Ni ions was used for the experimental study. The solution metal concentration was studied in the range of 200-4000 ppm. The desired (lower) concentration solution from stock solution was prepared as per equation 1.

$$C_1 \cdot V_1 = C_2 \cdot V_2 \quad (1)$$

Where, C1, C2 are the initial & final concentrations of solution and V1 & V2 are the initial and final volume of the solution. All the experiments were performed in 100 ml conical flask with working volume of 40 ml. Experiments was performed in incubator cum shaker at 350 rpm speed. pH study of the solution was performed in the range of 1.5-9.0 for Co & 2.5- 7.5 for Ni & 0.1 M solution of HCl and NaOH solution was used to maintain the solution pH. Adsorbent dose in the range of 1-7.5 g/L was used in the experimental investigation. The adsorbent dose was study in the range 1-7.5 g/L to optimize the dose for Co and Ni metal removal. Temperature study was performed in the range of 20-65 °C for both Co & Ni ions. After, completion each experiments adsorbent was filtered with the help of filter paper (Whatman's paper No. 42). The % removal of toxic metal was calculated by the equation (2),

$$\% \text{ removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Before mixing all reagents, acrylic acid monomer was passed through aluminium oxide to make inhibitor free. The reaction was executed in an inert (N₂) atmosphere. After completion the reaction mixture the addition of (1 mL) potassium persulphate solution (10% of w/v) was added in solution and heated at 80°C for 30 minutes. The reaction mixture was placed in a water bath and stirred continuously. After that reaction was stopped and cooled naturally till the normal temperature. After cooling, obtained PEX-PAA+PAM gel was dried at (80-85°C) for 24 h in a hot air oven [20]. The polymerization mechanisms acrylic acid and acrylamide of monomers with PEX shown in the Fig.1.

Where (C_o) is the initial concentration of metal ion and (C_e) is the equilibrium concentration of metal ions.

➤ *Adsorption Isotherm Study*

Isotherm studies such as Langmuir, Freundlich and Temkin were used to understand the mechanism of PEXH adsorbent for the Co and Ni removal. The absorption capacity (q_e) was determined for PEXH was determined as per the equation 3.

$$q_e = \frac{C_o - C_e}{W} \times V \quad (3)$$

Where V is the volume of metal ions solution, C_o is the initial metal concentration of solution, C_e is the equilibrium concentration of metal solution, and W is the mass of adsorbent (PEXH), and q_e is the adsorption capacity (mg/L).

Langmuir-isotherm [18] model is recommended for monolayer adsorption on the surface of limited number of common sites, without lateral interaction. It can be represented as equation 4.

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b q_{\max} \cdot c_e} \quad (4)$$

Where q_{max} is the maximum adsorption constant (mmol⁻¹g) and b is the Langmuir equilibrium constant (L mmol⁻¹) [21].

Freundlich isotherm models applicable on multi-layered adsorption which describing non-ideal and reversible adsorption. It is restricted to the formation of monolayer adsorption. The linear form of Freundlich isotherm model can be presented as equation 5.

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (5)$$

Where k_f and n are the Freundlich isotherm coefficient the values of n and k_f are obtained from the slope ($1/n$) and intercept ($\log k_f$) by plotting the graph between $\log q_e$ vs $\log C_e$ [21–24].

Temkin isotherm model presumes linear decrease of heat of adsorption. In Temkin isotherm model due to the adsorbate-adsorbent isotherm interaction it is uniformly distributed od binding energy to some maximum energy. Temkin isotherm model can be expressed as equation 6,

$$q_e = B \log A + B \log C_e \quad (6)$$

Where, B is the heat of adsorption and A is the equilibrium binding constant [21].

➤ Adsorption Kinetic Study

To understand the adsorption mechanism, several kinetic models' pseudo first-order, second-order and intraparticle diffusion were considered in current study.

The pseudo 1st order kinetic model was studied using Lagergren equation which can be represented as equation 7 [25], [26].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

Where q_t & q_e are adsorbed metal ions quantity (mg g^{-1}) at time (t) (min^{-1}) & at equilibrium; k_1 -pseudo 1st order kinetic model rate constant. By plotting the graph between $\ln(q_e - q_t)$ vs (t) value k_1 and q_e can be calculated by considering straight line.

The lined form of pseudo 2nd order model can be represented as equation 8.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Intercept and slope of the graph plotted between t/q_t vs t gives a straight line which is used to determine the constant parameters [21-27].

Intraparticle diffusion rate model is recommended to find out the diffusion rate constant (K_p) which can be presented as equation 9 [21-29].

$$q_t = k_p t^{0.5} + C \quad (9)$$

Where (k_p) is the intraparticle diffusion rate diffusion constant (mg g^{-1} and $\text{min}^{0.5}$) and attained from the slope of the plot of (q_t vs $t^{0.5}$).

➤ Thermodynamic Study

The thermodynamic parameters involving change in Gibbs free energy ΔG° , entropy ΔS° , and enthalpy ΔH° to be determined with the help of following equations 10,11, and 12 [22-23], [30-32].

$$K_c = \frac{q_e}{C_e} \quad (10)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (12)$$

Where, K_c is the equilibrium constant, R is the Gas constant, and T is the temperature (Kelvin). Plot the graph $\ln K_c$ vs $1/T$ according to equation number (11) to obtain the values of ΔH° and ΔS° respectively. ΔG° can be calculated with the help of equation number (12).

III. RESULT AND DISCUSSION

➤ Characterization

• Fourier-Transform Infrared (Ftir) Spectroscopy:

The FTIR spectra of PEX and PEX based polymeric hydrogel are shown in the Fig.2(a), (b), (c) and (d) respectively. The broad adsorption band of wave number range 3309-3343 cm^{-1} in PEXH shows -OH stretching vibration, and the range of adsorption band 2923-2954 cm^{-1} corresponds to C-H stretching, and the Sharpe peak of range 1500-1700 cm^{-1} are due to the presence of C-H, C=O, -OH, -C-H and also stretching vibration of C=O in -CONH₂ confirms the amide group in polymeric hydrogel[33]. The absorption peak of 1552 corresponds to -CH₂. The adsorption peak 1315 cm^{-1} shows the presence of C-N bond, and the peak 1177 cm^{-1} shows alcoholic C-O & peaks 1125 and 580 cm^{-1} this corresponds that the -(C=S) and C-S group of PEX present in synthesized polymeric hydrogel and the presence of -C-O-C confirmed wavenumber 1039 cm^{-1} . The FTIR spectra of Pentaerythritol Xanthate shown in fig.2 (a) the adsorption peak 3309 cm^{-1} and 1640 cm^{-1} confirms the O-H stretching & bending which indicated the presence of hydroxyl group which means the pentaerythritol xanthate was not replaced by carbondisulphide. The adsorption peak of 1125 cm^{-1} shows the presence of xanthate group -(C=S) and the adsorption peak of 990 cm^{-1} shows the presence of -(C-O-C) group. The 2954 cm^{-1} corresponds to -(C-H) stretching[34]. The absorption peak 1000-600 cm^{-1} corresponds to -(C-H) out of plane, and 536 cm^{-1} corresponds -(C-S) stretching vibration. The absorption peak 1381 cm^{-1} corresponds to -(C-OH) group [35].

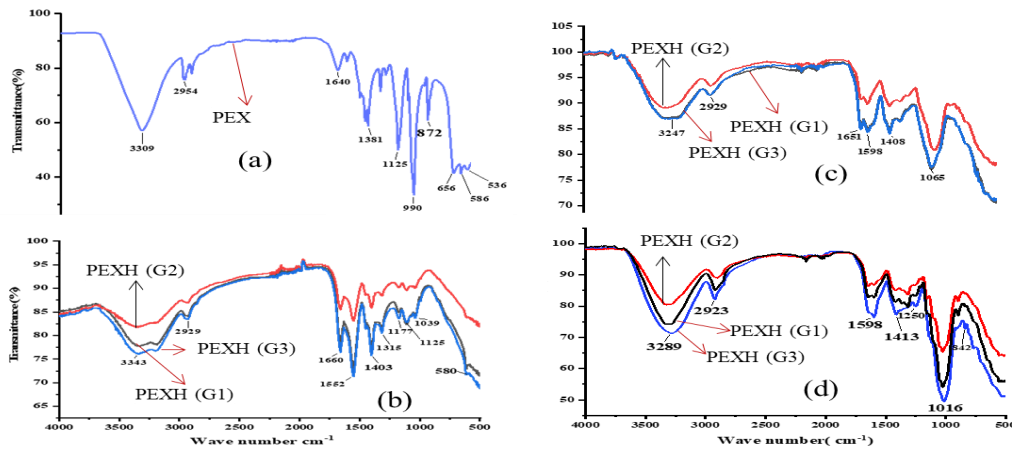


Fig 2 FT-IR Spectra of (a) Pentaerythritol Xanthate (PEX) (b) PEX Polymeric Hydrogel (c) Ni Adsorbed PEX Polymeric Hydrogel (d) Co Adsorbed PEX Polymeric Hydrogel.

• *Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy of PEX-PAA-PAM Polymeric Hydrogel (PEXH):* -

SEM enables the viewing of the material porosity, topology, and physical properties of the synthesised PEXH as seen in fig.3 Co (II) and Ni (II) metal ions are shown to be adsorbed before and after, respectively, in fig 3. The findings of the study showed 3D porous structures with distinct, interconnected micropores. Water and hazardous metal compounds will be able to travel throughout the structure thanks to the hydrogel's accessible pores. Before the adsorption of Co (II) and Ni (II) metal ions, these holes had distinct, very thin walls. After the adsorption of metal ions (Co (II) and Ni (II) in Fig 3., the PEXH polymeric hydrogel maintained its structural resilience. It was clear

from this that the Co (II) and Ni (II). This demonstrated a close binding between the metal ions and the adsorbent, which filled the pore with Co (II) and Ni (II) through an intramolecular interaction. The percentage of Co (II) and Ni (II) element on the PEX-PAM co-AA hydrogel was calculated using the EDX spectrum of the PEX-PAM co-AA G-3 hydrogel. The PEX-PAM co-AA G-3 hydrogel's EDX findings are displayed in Fig 4. S, Co (II), and Ni (II) are three common constituents on the PEX-PAM co-AA G-3 hydrogel surface. The whole element distribution was visible in the EDX spectrum, which showed that the PEX-PAM co-AA G-3 structure included S with a frequency of 2% wt. Additionally, Co (II) and Ni (II), which are components of PEX-PAM co-AA G-3 hydrogel, were seen in the EDX spectrum with 7 and 6 % weight, respectively.

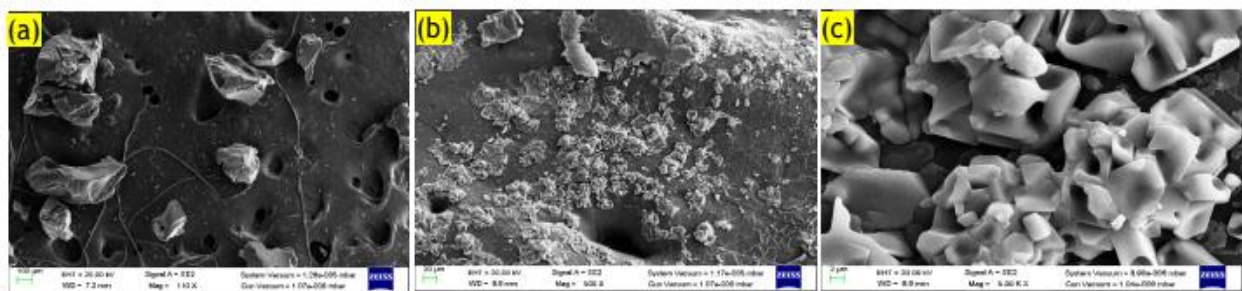


Fig 3 SEM Image of (a) PEX-PAM Co-AAG-3 Hydrogel, (b) PEX-PAM Co-AAG-3 Hydrogel Co (II) & (c) PEX-PAM Co-AAG-3 Hydrogel Ni (II)

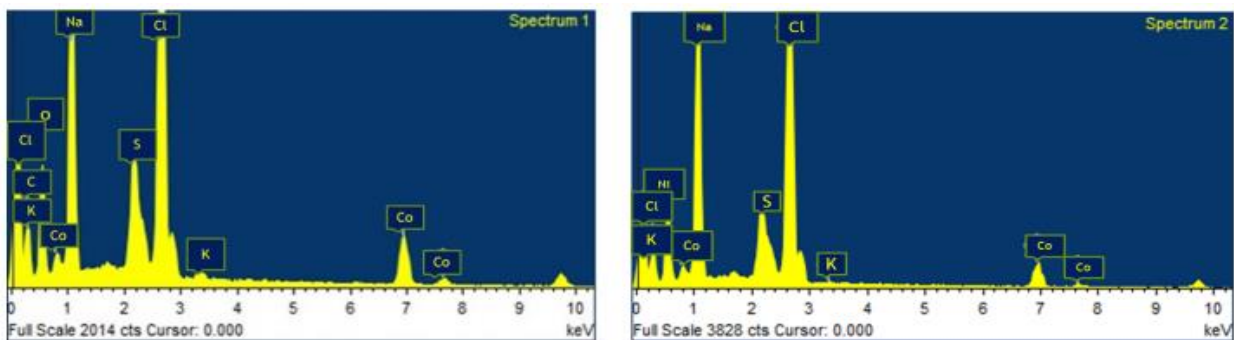


Fig 4 EDAX Image of (a) PEX-PAM Co-AAG-3 Hydrogel -Co (II) and EDAX Image of (b) PEX-PAM Co-AAG-3 Hydrogel -Ni (II).

• *Using Gel Permeable Chromatography for Analysis (GPC): -*

We characterise synthetic copolymeric hydrogel and ascertain its molecular weight and polydispersity using the Gel Permeation Chromatography (GPC) analytical method. The molecular weight properties of PEX-PAM-co-AA G-3, such as number average mol weight (M_n), weight average mol weight (M_w), size average mol weight (M_z), and polydispersity index (PDI), were quantified. The analysis of the GPC data for the synthesised hydrogel PEX-PAM-co-AA G-3 produced the result shown in Fig. 5). Fig.5 also shows a visual depiction of the GPC analysis. The narrow PDI- M_w/M_n (1.8) of the synthesised PEX-PAM-co-AA G-3 hydrogel demonstrates the suitability of the approved procedure utilised to create the hydrogel, which is produced from Pentaerythritol xanthate (PEX). The GPC data of the synthesised PEX-PAM co-AA G-3 are given in the table 2.

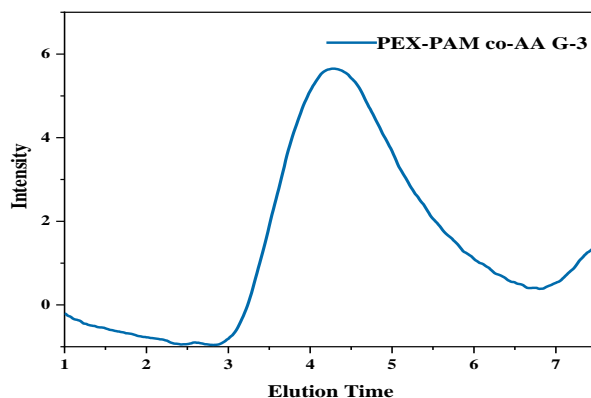


Fig 5 Gel permeable Chromatography of PEX-PAM Co-AA G-3 Hydrogel

Table 2 Gel Permeable Chromatography Data of PEX-PAM Co-AA G-3 Hydrogel

Parameters	Obtained values
M_w	16702150
M_n	154499
$PDI = M_w/M_n$	1.08

• *Studies of Swelling and Retention of Polymeric PEXHs Swelling and retention capacity of PEXHs in Tap and Distilled Water*

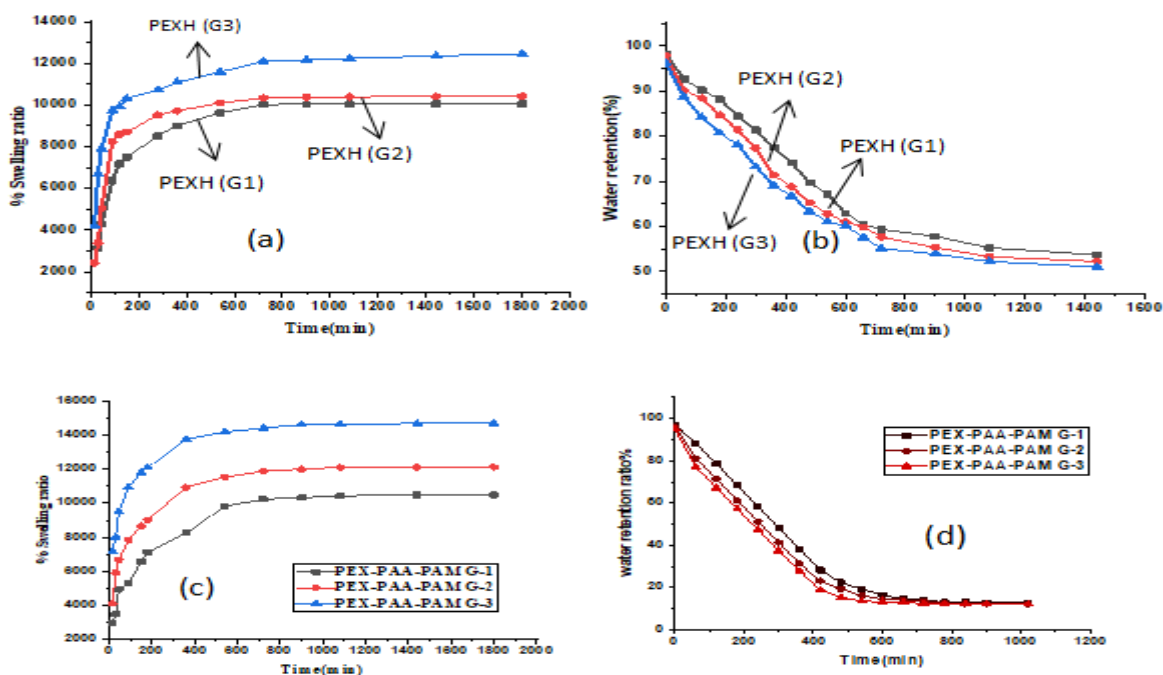


Fig 6 PEXHs Properties (a) Swelling in Tap Water (b) Retention in Tap Water (c) Swelling in Distilled Water (b) Retention in Distilled Water.

The swelling and retention properties of three grade PEXH (as PEXH1, PEXH2, PEXH3) has been tested in tap and distilled water. The Fig 6 (a) & (b) represent the swelling and retention capacity in tap water while Fig 6 (c) & (d) represents the swelling and retention capacity in distilled water. The fig indicates PEXi shows higher swelling capacity in distilled water in comparison with tap water. Also, the PEXi shows lower retention time in distilled water in comparison with tap water. It is obvious tap water contains higher TDS in comparison with the distilled water [36]. On the other hand, greater the surface areas of the synthesized polymeric hydrogel assist adsorptive site for the contaminants with swelling capacity. So, the swelling capacity of hydrogel have greater adsorption potential towards pollutants like organic, inorganic, and dyes. From the fig. 6(a) indicates the percentage swelling ratio (SR) of PEXH 1, PEXH 2, and PEXH3 move up to the 10048, 10423 & 12458% respectively in tap water and 10499, 12129 & 14712% respectively in distilled water with respect to original dried hydrogel weight at room temperature. The

Fig. 6(b) and (d) indicates swelled hydrogel lose their absorb water by 53.69, 52.22, & 51.01% in case of tap water and 12.72, 12.21, and 12.16 % in case of distilled water in 24 h at 298K temperature. Overall, it is clear that as the time increases the water retention ratio decreases at constant temperature 298K. This leading the capability of WRR of polymeric hydrogel makes good removal of contaminants from wastewater.

➤ Removal of Turbidity by the use of Synthesised Polymeric Hydrogel Pexhs.

The turbidity removal with the help of synthesised hydrogel PEXH was shown in the form of graph in Fig 7. From this graph it is clear that on increasing the time the removal of turbidity increases. On varying the amount of hydrogel, the surface area of the hydrogel increases. After sometime at specific dosage the removal was not affected because the synthesised gel has been mugged the available turbidity.

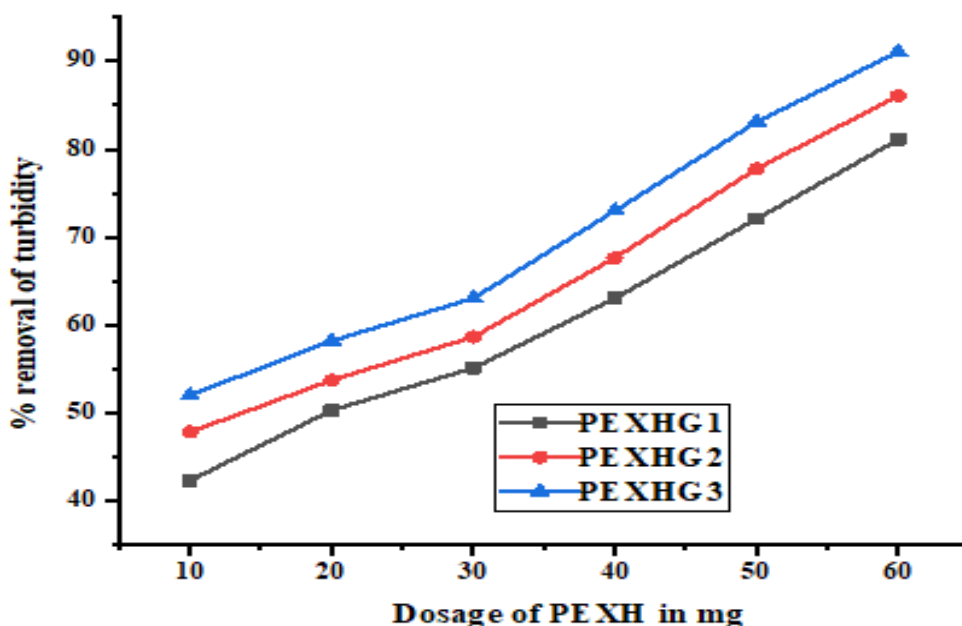


Fig 7 % Removal of Turbidity with PEXHs

➤ Toxic Metal Removal Co and Ni by Pexhs

There are several adsorption effects for the removal of Co and Ni metal ions has been studied with the help of adsorbent PEXHs. The effect of process parameters such as, effect of Dosages, effect of pH, effect of initial Concentration, effect of Temperature and effect of Time has been optimized.

➤ Effect of PEXHs Dose

• Effect Of PEX Based Polymeric Hydrogel Dosages on Adsorption and Percentage Removal of Metal Ions Co and Ni in their Solutions

The %removal of metals Cobalt and Nickel were examined by varying dosages (1-7.5 g/L) grades PEXH1, PEXH2, PEXH3 with preparing metal solution

concentration of 4000 mg/L as shown in the fig.8 for Cobalt & Nickel metal for percentage removal of metal ions respectively. Here in this process, 40 ml of stock solution from both metal ion concentration and varying dosages of PEXHs and this experiment will be performed at 25°C temperature. From the fig.8 the percentage removal of Co (II) and Ni (II) metal ions increases with an increase in PEXHs dosages for all grades, but decreases the absorbance and at certain point it becomes constant at 5 g/L this is called optimum dosage of PEXH 1, PEXH 2, PEXH 3 for Co and Ni metal ion and the % removal were observed for Co(II) is 83.75, 89.37, & 93.125% and for Ni(II) is 90.55, 92.22, & 95.0% respectively. Slower adsorption rates the number of active sites increases due to the lack of adsorbate in the solution and therefore further increasing the dosage it shows no effect towards adsorption[21].

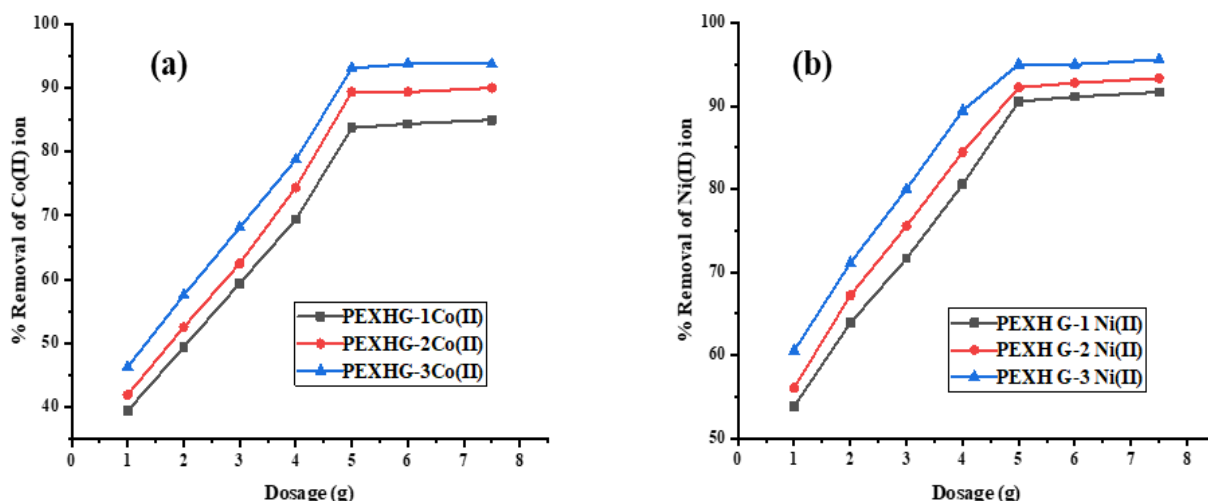


Fig 8 (a) % Removal of Co and (b) Ni Metal Ions at Different Dosages

➤ Effect of pH

• Effect of pH on Adsorption of Co and Ni Metal Ions on PEXHs

The study of pH can also be performed for the percentage elimination of Co (II) and Ni (II) metal ions using the concentration 4000 mg/L as shown in the fig9. In this process varying pH from (1.5-9) for Co and for Ni from (2.5-7.5) then the maximum percentage removal for Co (II) Co is 84.375, 90.0, & 93.75% was obtained at pH 6 called optimum pH of Co (II) and for Ni (II) are 91.11, 92.22, & 95.55% was obtained at 5.5 called optimum pH of Nickel for all the three grades of PEXH 1, PEXH 2, and PEXH 3 respectively. For greater pH the percentage removal of Co and Ni instantly fall to minimum value because the metal ions combine with the hydroxyl group to form metal hydroxides that precipitate out. When the pH is low (less

than 5), H⁺ incite the generation COOH by protonation reaction and gives COO⁻ which reduces the electrostatic attraction towards metal ions and amino group can also easily protonated and form ammonium cation which have strong electrostatic repulsion force with toxic metal ions for lower pH value[37-39]. In addition of amino group protonation decreases with increase in ph. Xanthate group of synthesised hydrogels also plays an important role for retarding the removal of Co (II) and Ni (II) metal ions from wastewater. On the hydrolysis of metal ions and the precipitated out of xanthates reactions should be observed at the time of consideration of chemical reaction 13. [40].



Where, M²⁺= toxic metal ions and X= xanthate.

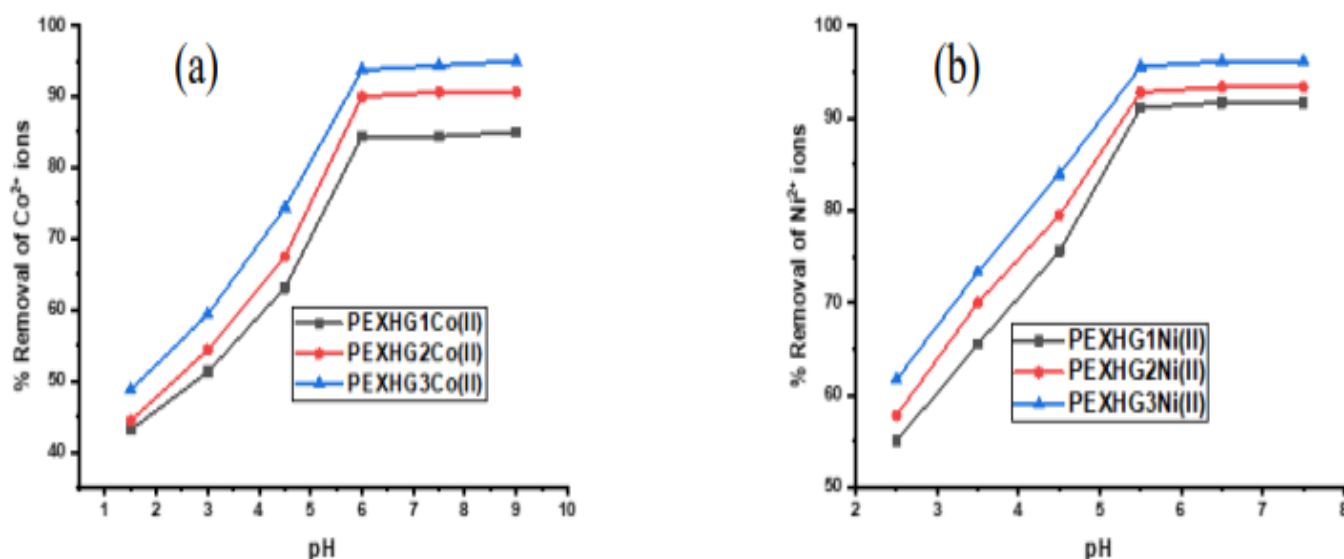


Fig 9 (a) % Removal of Co (II) and (b) Ni (II) Metal Ions at Different pH with Optimum Dosage (5 g/L) for Co (II) and Ni (II)

- *Effect of Temperature and Study of Thermodynamic Parameters: -*
- *Effect of Temperature on Adsorption of Co and Ni Metal Ions on PEXH: -*

The effect of temperature was studied when the Co (II) and Ni (II) metal ions adsorbed on PEXH varying with different temperatures of 25-65°C for Co & 20-60 for Ni and the graph achieved are shown in the fig 10(a) and (b) for Co (II) and Ni (II) metal ions. From the graph adsorption of Co and Ni metal ions increases with increase in temperature and the percentage removal of Co (II) and Ni (II) metal ions increases, but after at certain temperature the percentage removal of metal ions starts decreases due to increase in temperature. In the fig.10(a) for Co (II) the percentage removal increases at temperature 55°C and after that it starts decreasing on increasing temperature, and in fig.10(b) for Ni (II) it increases up to 50°C and after that it decreases with increasing temperature. This all process indicates that the adsorption process is endothermic[21].

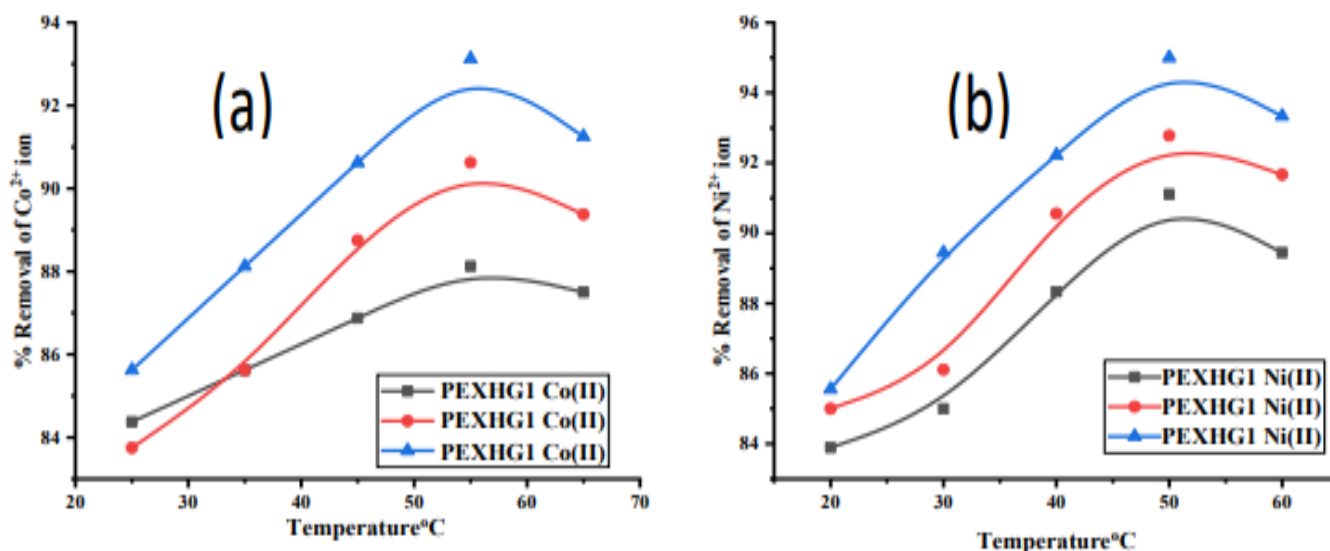


Fig 10 (a) % Removal of Co(II) and (b) Ni(II) Metal Ions at Different Temperature with Optimum Dosage (5 g/L) for Co(II) and Ni(II) and Optimum pH 6 for Co and 5.5 for Ni.

➤ *Effect of Concentration*

The effect of concentration was studied when the Co(II) and Ni(II) metal ions adsorbed on PEXH varying with different concentrations of 200-4000 mg/L for Co(II) and Ni(II) and the graph achieved are shown in the fig.11 for Co(II) and Ni(II) metal ions. From the graph it is clear that the removal efficiency of Co and Ni metal ions decreases with increase in concentrations and the percentage removal of Co(II) and Ni(II) metal ions decreases from 97 to 48% in case of Co and 98 to 54% in Ni with increases in concentrations. In case of low concentrations of Co(II) and Ni(II) metal ions adsorption on PEXH is large, & less adsorption at higher concentration [41-42].

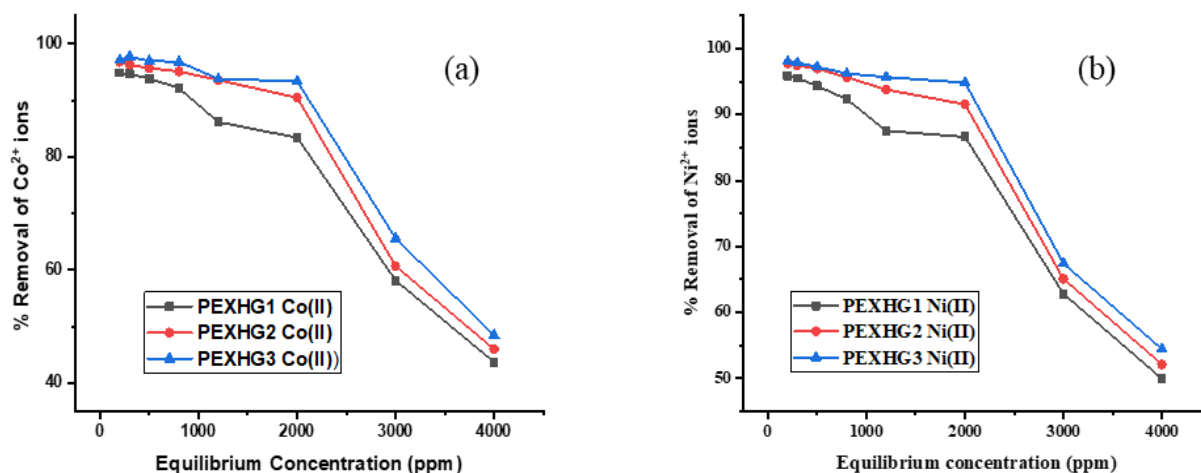


Fig 11 (a) % Removal of Co and (b) Ni Metal Ions at Different Concentration with Optimum Dosage (5 g/L) for Co and Ni and Optimum pH 6 for Co and 5.5 for Ni and with Optimum Temperature 55 °C for Co and 50 °C for Ni.

• *Effect of Time:* -

Time is one of the most important applications in adsorption process. The effect of time was studied when the Co and Ni metal ions adsorbed on PEXH varying with different time intervals of 25-185 minutes for Co and Ni are shown in the fig.12 metal ions. From the graph it is clear that the rate of adsorption of metal ion increases rapidly and then perfect removal efficiency was attained within 125 min for Co and 105 min for Ni and it is called saturation time then after that it becomes constant.[42-43].

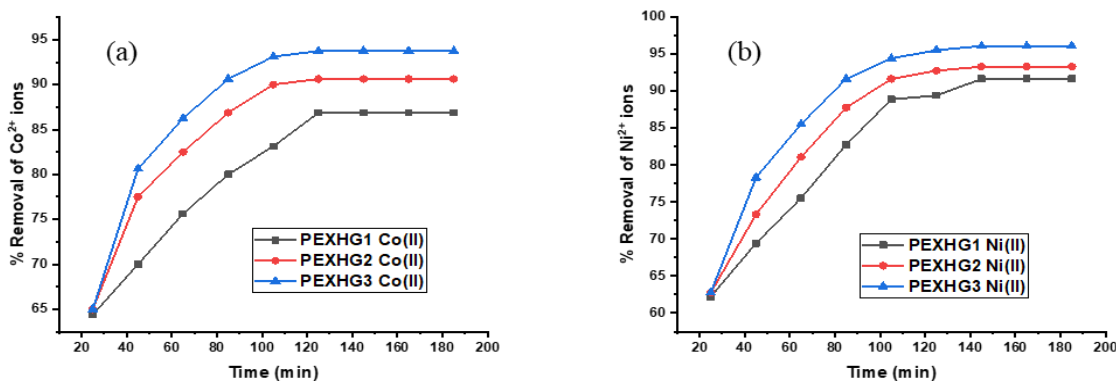


Fig 12 % Removal of Co and Ni Metal Ions at Different Time Interval with Optimum Dosage (5 g/L) for Co and Ni and Optimum pH 6 for Co and 5.5 for Ni and with Optimum Temperature 55 °C for Co and 50 °C for Ni and with Optimum Time 125 Minutes for Co and 105 Minutes for Ni.

➤ *Isotherm Studies Of Adsorption*

Basically, isotherms were written in the form of mathematical representation for describing the aspects leading the retention of substance from, the watery environment to a crystalline phase at constant pH, concentration, temperature. During this study, we used three adsorption isotherm model such as Langmuir (physisorption), Freundlich(multilayer adsorption), & Temkin isotherm (helps to correlate adsorption isotherms of water contaminants) model for the adsorption of metal ions on pentaerythritol xanthate-based hydrogel[29]. Adsorption isotherm study for Co and Ni ion adsorption are conducted at 55 and 50 °C, pH 6 for Co and 5.5 for Ni, time 125 min for Co and 105 min for Ni etc. The initial dose of Co and Ni has been 5 g/L. The adsorption capacity (q_e) of PEXH at equilibrium condition was determined by using equation (3) with the help of Langmuir, Freundlich, Temkin adsorption isotherms model.

Table 2 indicates different isotherm parameters of suggested isotherm like Langmuir, Freundlich, Temkin. Table 2 represent value of R-square of Langmuir for Co ion

adsorption 0.997, 0.993, 0.950 & and for Ni metal adsorption 0.994, 0.994, 0.991 and the value of R-square of Freundlich for Co ion adsorption 0.976, 0.991, 0.959 and for Ni metal adsorption 0.987, 0.994, 0.998 for Pentaerythritol xanthate based polymeric hydrogel's, PEXH1, PEXH2, & PEXH3 adsorbent respectively. Higher value of R2 for Langmuir and Freundlich isotherm indicates twice parameter based are more relevant. In Langmuir isotherm model is a dimensionless factor and can be represented by equation 14.

$$R_L = \frac{1}{1 + C_e K_L} \tag{14}$$

Where, R_L is the dimensionless Langmuir constant which indicates that adsorption possibilities are either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

In case of Co and Ni adsorption by suggested adsorbent is in the range 0-1.

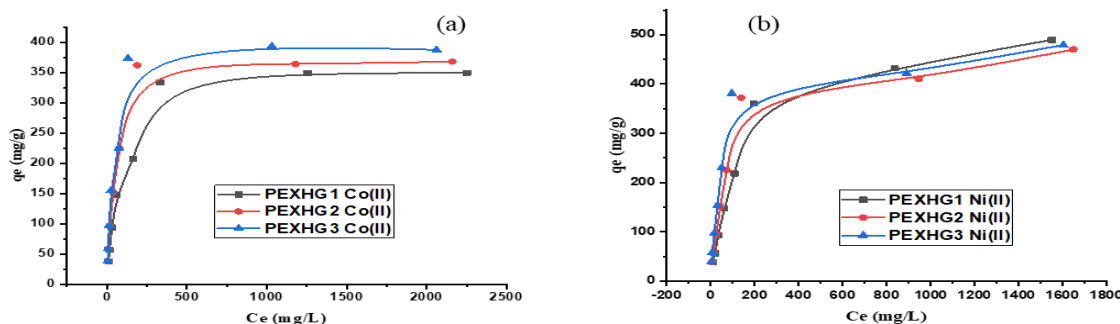


Fig 13 (a) Adsorption Isotherm Studies of Co and (b) for Ni on PEXHs.

Table 3 Adsorption Isotherm Parameters for Co and Ni Adsorption on PEXHs for Different Grades

Tested Metal ions	Langmuir isotherm model (physisorption)			Freundlich isotherm model (Multilayer adsorption)			Temkin isotherm model		
	K_L (L/mg)	q_{max} (mg/g)	R^2	K_f (L/g)	1/n	R^2	B (mg/g)	A (L/g)	R^2
PEXH Co (II) G-1	0.01179	353.35	0.997	10.8238	0.5965	0.976	183.57	0.1228	0.931
PEXH Co (II) G-2	0.01759	374.53	0.993	11.9423	0.6672	0.991	217.67	0.1675	0.935
PEXH Co (II) G-3	0.01668	487.80	0.950	15.2359	0.6565	0.959	219.85	0.2277	0.912
PEXH Ni (II) G-1	1613.066	307.69	0.994	11.6836	0.6007	0.987	186.17	0.1418	0.889
PEXH Ni (II) G-2	3148.699	325.73	0.994	1.08873	0.9017	0.994	198.10	0.2488	0.918
PEXH Ni (II) G-3	3854.523	350.87	0.991	15.8245	0.6802	0.998	223.36	0.2635	0.872

➤ Adsorption Kinetics Studies

To understand the adsorption mechanism, we introduced several kinetic models such as pseudo 1st order, pseudo 2nd order & intra-particle diffusion. These kinetic models used for their applications with the innovative data for metal ions onto adsorbent[44].

• Pseudo First Order Kinetics

The pseudo first order kinetic model was studied using Lagergren equation 15 which is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{15}$$

Where q_e and q_t are the quantity of metal ions adsorbed (mg g^{-1}) at time (t) (min^{-1}) at equilibrium and k_1 is the pseudo first order kinetic model rate constant. The straight line of pseudo first order model shows that metal ion adsorbed on PEXH shown in fig.14. the graph plot between $\ln(q_e - q_t)$ vs (t) slope and intercept gives the value of k_1 and q_e , the value of (R^2) considerably low, appeared poor quality of linearization. [25-26]

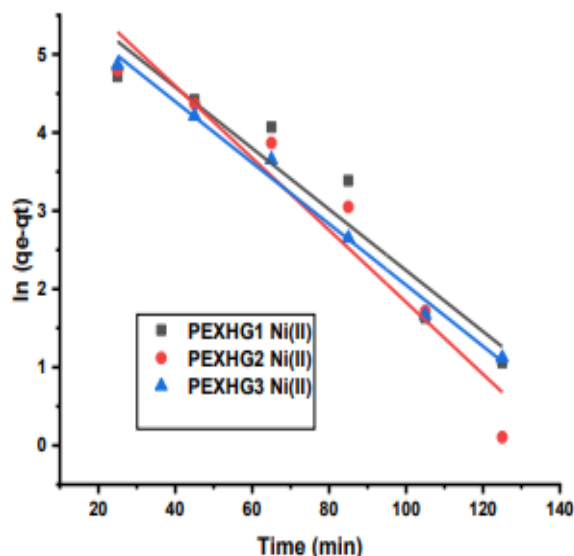
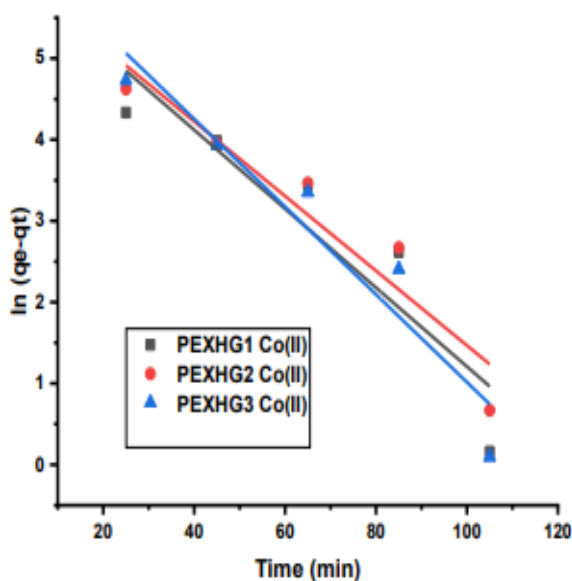


Fig14 Pseudo-First-Order Curves for Co & Ni on PEXH

• Pseudo 2nd Order Kinetics

The adsorption technique was also calculated with the help of 2nd kinetic model through the gamut of time. The linear form of pseudo second order model can be represented by equation 16: -

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{16}$$

Intercept and slope of the graph plot between (t/q_t vs t) gives a linear line data induced in table4. Account of concentrations calculated, the corresponded well experimental data are taken, and the value of (R^2) is nearly equal to 1. This demonstrate that the pseudo 2nd order kinetic model is superior than the pseudo 1st order [21-27].

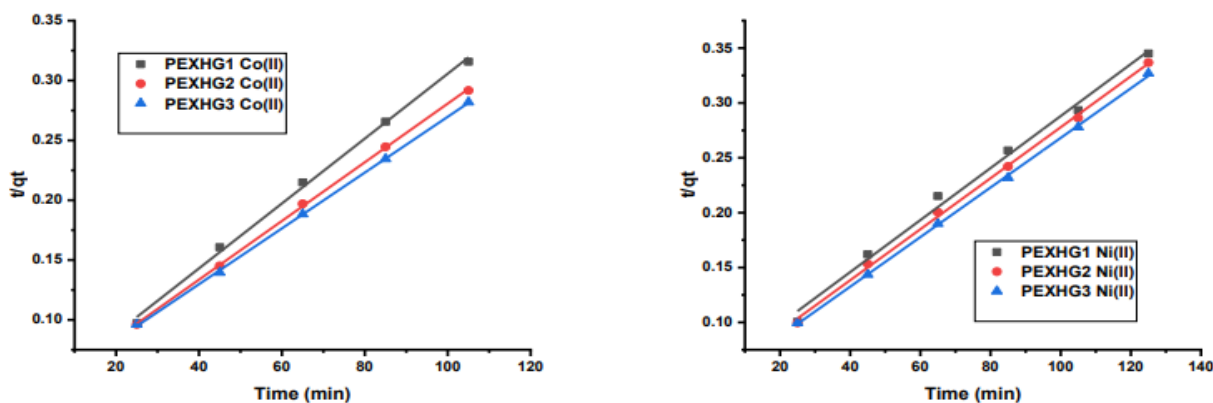


Fig 15 Pseudo 2nd Order Curves for Co & Ni Ions on PEXHs

➤ *Intraparticle Diffusion Model*

For penetrable adsorbent, the dispersal of the adsorbate molecule or ion into the pores into an account being taken applicable on kinetic model for the process the potential of intraparticle diffusion was analysed for metal ions Co and Ni adsorption on PEXH using intraparticle diffusion model, the diffusion rate constant (K_p) which are represented by equation 17.

$$q_t = k_p t^{0.5} + C \tag{17}$$

Where (k_p) is the intraparticle diffusion rate diffusion constant (mg g^{-1} and $\text{min}^{0.5}$) and attained from the slope of (q_t vs $t^{1/2}$). Plot is straight shown in fig.16(a & b) the metal ion concentration did not pass through origin this indicates the intraparticle rate diffusion is not only rate controlling step, although kinetics model may run coincidentally controlling the adsorption rate[28-29].

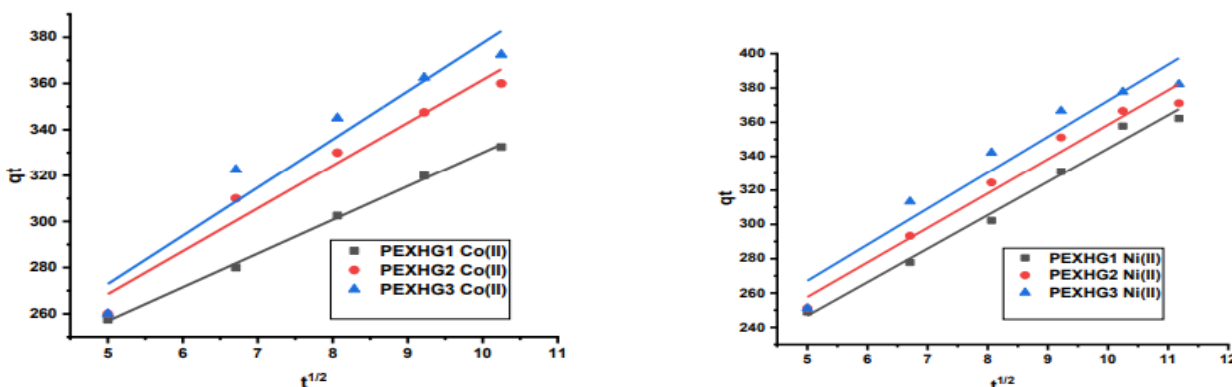


Fig 16 Intra-Particle Diffusion Plots for Co and Ni on PEXHs

Table 4 The adsorption Kinetics Model Parameters of Co and Ni Metal Ions Adsorbed by Synthesised PEXHs

Attested metal ions	Pseudo 1 st order			Pseudo 2 nd order			Intra-particle diffusion		
	K1 (min^{-1})	qe (mg/g)	R ²	K2 ($\text{g}(\text{mg} \cdot \text{min})$)	qe (mg/g)	R ²	K _{diff} ($\text{mg}(\text{gmin}^{1/2})$)	qe (mg/g)	R ²
PEXH Co (II) G-1	0.0485	429.46	0.799	2×10^{-4}	369.00	0.996	14.61	183.82	0.997
PEXH Co (II) G-2	0.0459	429.73	0.881	1×10^{-4}	408.16	0.999	18.61	175.45	0.951
PEXH Co (II) G-3	0.0540	610.90	0.887	1×10^{-4}	429.18	0.999	20.92	168.29	0.912
PEXH Ni (II) G-1	0.0390	464.23	0.898	3.49×10^6	421.94	0.991	19.56	148.90	0.983
PEXH Ni (II) G-2	0.0460	624.64	0.918	4.08×10^6	431.03	0.998	20.17	156.79	0.968
PEXH Ni (II) G-3	0.0391	387.78	0.987	4.64×10^6	442.47	0.999	21.08	161.69	0.918

➤ *Thermodynamic Parameter Studies*

Thermodynamic parameter of the Co and Ni metal ions on PEXH adsorbent, this involves change in available energy ΔG° , enthalpy ΔH° & entropy ΔS° , to be set on. Where, K_c is the equilibrium constant, R is the Gas constant whose value is $8.314 \text{ JK}^{-1}\text{mol}^{-1}$, and T is the temperature (Kelvin). ΔH° (KJ mol^{-1}) and ΔS° ($\text{K}^{-1}\text{J mol}^{-1}$) & ΔG° (KJ

mol^{-1}) are used to obtained the values by plotting the graph $\ln K_c$ vs $1/T$. Obtained data are shown in the table 5. From the table 5 it can be seen that the overall value of Gibbs free energy was negative during the process this reflects process that is thermodynamically advantageous and spontaneous adsorption of Co and Ni metal ions onto PEXH.

Table 5 Thermodynamic Parameter Studies for Co & Ni Adsorption on PEXHs for Different Grades

Adsorbent	Adsorbate	Temperature (k)	Thermodynamic parameter			
			ΔG (kJ mol ⁻¹)	ΔH (kJmol ⁻¹)	ΔS (jmol ⁻¹ K ⁻¹)	R ²
PEXHG-1	Co ²⁺	298	-0.19	8.59	29.41	0.994
		308	-0.44			
		318	-0.74			
		328	-1.07			
PEXHG-2		298	-0.07	17.57	58.96	0.973
		308	-0.44			
		318	-1.20			
		328	-1.79			
PEXHG-3		298	-0.43	22.10	75.33	0.976
		308	-1.01			
		318	-1.74			
		328	-2.71			
PEXHG-1	Ni ²⁺	293	-0.09	18.14	61.68	0.908
		303	-0.31			
		313	-1.07			
		323	-1.92			
PEXHG-2		293	-0.30	22.62	77.59	0.909
		303	-0.54			
		313	-1.69			
		323	-2.53			
PEXHG-3		293	-0.41	30.08	103.81	0.984
		303	-1.32			
		313	-2.24			
		323	-3.58			

As temperature increases more will the negative value of ΔG° . It shows increased equilibrium adsorption, & ΔH° and ΔS° are positive values which indicates that the process has strong affinity and is endothermic of Co and Ni respecting PEXH [23-31].

➤ *Comparison with other Adsorbents*

The Highest adsorption capacities of monolayer adsorption PEXH adsorbent for Toxic metal removal from wastewater was compared with other adsorbents which have been reported in literature are shown in the table 6. Many studies addressed that hydrogels are very effective adsorbent for the removal of toxic metal ions from wastewater. In this study, it is clear that the adsorption capacities of PEXH higher in comparison to earlier mentioned in Literatures. Therefore, the synthesised PEXH adsorbent is very excellent in comparison to other adsorbents. The kinetics study also demonstrates that the pseudo²nd order kinetic can be applied to achieve the greatest outcomes.

Table 6 Adsorption Capacities Comparison of Metals Co & Ni Ions Removal

Adsorbents	Hydrogels Adsorption capacities(mg g ⁻¹)	Metal ions	References
Chitosan-sodium lignosulphonate-acrylic acid Hydrogel	385	Co ²⁺	[45]
Glucan/Chitosan Hydrogel	232	Co ²⁺	[46]
Almond green hull	45.5	Co ²⁺	[47]
Amination graphene oxide	116.35	Co ²⁺	[48]
Cation exchange resins IRN77	86.17	Co ²⁺	[49]
Activated carbon	13.88	Co ²⁺	[50]
Chitosan-based Hydrogel	161.8	Ni ²⁺	[51]
Polyacrylic acid Hydrogel	128.8	Ni ²⁺	[52]
Magnetic-hydroxy apatite/chitosan composite	112.36	Ni ²⁺	[53]
Magnetic anionic hydrogel	93	Ni ²⁺	[54]
Pentaerythritol xanthate-based polymeric Hydrogel	350.87	Ni ²⁺	Present Study
Pentaerythritol xanthate-based polymeric Hydrogel	487.80	Co ²⁺	Present Study

IV. CONCLUSIONS

The current study demonstrates the successful application of the synthesized pentaerythritol xanthate-based hydrogels (PEXH), towards the removal of toxic metal ions viz. Co^{2+} and Ni^{2+} from wastewater. The effect of time on the removal of Co^{2+} and Ni^{2+} ions from wastewater has been studied and it was found that the equilibrium has been reached within 105 min for cobalt and 125 min. for nickel. The kinetic study of adsorption reveals that pseudo-second-order kinetic model better fits the experimental data. The isotherm studies showed maximum adsorption capacities for the removal of metal ions Co^{2+} and Ni^{2+} using PEXH adsorbent were found 353.35, 374.53, and 487.80 mg g^{-1} and 307.69, 325.73, 350.87 mg g^{-1} respectively. On the basis of the experimental results, it may be concluded that the adsorbent PEXH has been found to be very effective for the elimination of toxic metals Co^{2+} and Ni^{2+} from wastewater.

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