

Synthesis and Characterization of Novel β -CD-Xanthate and Its Application in the Treatment of Heavy Metal Containing Wastewater and Lignin Enriched Paper Industry Wastewater

Arbind Chaurasiya

Madan Mohan Malaviya University of Technology

Poom Prakash Pande

pppches@mmmut.ac.in

Madan Mohan Malaviya University of Technology

Kajal Kumar Dey

Veer Bahadur Singh Purvanchal University

Narendra Pratap Tripathi

Indian Institute of Science Education and Research (IISER) Mohali (140306)

Ravi Kumar

Madan Mohan Malaviya University of Technology

Bablu Kumar Singh

Madan Mohan Malaviya University of Technology

Tripathi Shivam Saroj Kumar

Madan Mohan Malaviya University of Technology

Research Article

Keywords: Xanthate, heavy metal, adsorption, paper wastewater, COD removal

Posted Date: March 25th, 2024

DOI: <https://doi.org/10.21203/rs.3.rs-3787149/v2>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: The authors declare no competing interests.

Version of Record: A version of this preprint was published at International Journal of Environmental Analytical Chemistry on April 14th, 2024. See the published version at <https://doi.org/10.1080/03067319.2024.2338278>.

Synthesis and Characterization of Novel β -CD-Xanthate and Its Application in the Treatment of Heavy Metal Containing Wastewater and Lignin Enriched Paper Industry Wastewater

Arbind Chaurasiya¹, Poorn Prakash Pande^{1*}, Kajal Kumar Dey², Narendra Pratap Tripathi³, Ravi Kumar¹,
Bablu Kumar Singh¹, Tripathi Shivam Saroj Kumar¹

¹Department of Chemistry and Environmental Science, Madan Mohan Malaviya University of
Technology, Gorakhpur (273010), Uttar Pradesh, India

²Centre for Nanoscience & Technology, Prof. Rajendra Singh (Rajju Bhaiya) Institute of Physical
Sciences for study and Research, Veer Bahadur Singh Purvanchal University, Jaunpur (222003), Uttar
Pradesh, India

³Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali
(140306), Punjab, India.

(*Corresponding authors: pppande@gmail.com)

Abstract

The β -cyclodextrin xanthates (β -CDXs) have been synthesized by the reaction of β -cyclodextrin (β -CD) with CS₂ in the presence of alkaline medium (NaOH), through xanthation process resulting the reaction mixture was turn to turbid orange color as a desired product. The desired product was extracted in diethyl ether and dehydrated in hot air oven at 50°C. The synthesized β -CDXs has been characterized by UV, FTIR, ¹HNMR, DSC, Δ pH_{PZC} and SEM analysis. Further, β -CDXs and raw β -CD has been used for the heavy metals removal (Cu²⁺ and Ni²⁺) and also used for treatment of lignin enriched paper industry wastewater (LEPIW). The maximum % removal of β -CD, β -CDX1, β -CDX2 and β -CDX3 for Cu²⁺ ion at optimum dosage of 2 g/L, optimum pH of 6.5, temperature of 45°C, initial concentration of 1000 mg/L and at contact time of 80 min was 73.6, 91.9, 93.4 & 95.8% and for Ni²⁺ ion at optimum dosage of 2.5g/L, optimum pH of 5.8, initial concentration of 1000 mg/L, temperature of 55 °C and contact time of 100 min was 65.8, 88.6, 91.3 & 94.1% respectively. While LEPIW treatment efficacy of 54, 77, 83 and 86 % has been noticed (initial COD: 2.0 g/L, pH: 7, optimum temperature: 40 °C at 80 min operating time) for β -CD, β -CDX1, β -CDX2 and β -CDX3 respectively. The calculated data were well fitted in Langmuir isotherm model confirmed the adsorption of Cu²⁺ & Ni²⁺ ions onto the β -CDXs adsorbent is monolayer. The rate of adsorption of heavy metals (Cu²⁺ and Ni²⁺) on the β -CDXs adsorbent has been controlled by kinetic model of Pseudo second order indicating the chemisorption. The optimal adsorption capacities of β -CD, β -CDX1, β -CDX2 and β -CDX3 has been found to be 357.14, 473.93, 510.20 & 534.75 mg/g for Cu²⁺ and 294.11, 384.61, 408.16 & 423.72 mg/g and for Ni²⁺ ions, respectively.

Keyword: xanthate; heavy metal; adsorption; paper wastewater; COD removal

1. Introduction

Water is still essential for human survival, but in modern industrialized countries, the risk of water contamination brought on by exposure to hazardous metals like copper and nickel has grown significantly [1]. Major ecological issues arise when untreated wastewater is released into habitats as a result of operations like mining, galvanoplastic processes, and pipe corrosion. Even though these metals are only minimally required for human health, but excessive levels permissible limit of these metal ions are very dangerous for human, plants, and others living organism [2]. The permissible limit of copper for human health has been found to be 0.25mg/L. The human bodies associate with copper metal in excess concentration of permissible limit (PCL) contribute to serious diseases including liver, kidney damage, and insomnia, Wilson's disease Alzheimer's disease etc. Similarly, the permissible limit of nickel for human health has been also found to be 0.20mg/L. The excess PCL levels of nickel can create toxicity for human bodies including Dermatitis, nausea, chronic asthma, coughing and potentially carcinogenic [3], [4]. Therefore, it is necessary for us to remove this copper and nickel metal from contaminated wastewater. Recently, a various type of conventional methods has been developed for the elimination of hazardous metals from wastewater, such as, membrane filtration, chemical precipitation, ion-exchange, reverse osmosis, electrochemical treatment technique, and flocculation-coagulation etc. [5]. However, these procedures have significant limitations, including being confined to a narrow range of metal ion concentrations, producing a considerable volume of hazardous sludge, and being highly expensive. Hence, the heavy metal removal can be done by *ADSORPTION* method using low-cost adsorbents is found to be more eco-friendly [6], [7]. The advantage of adsorption technique is high selectively to eliminate heavy metal ion as of wastewater because of adsorbent have high surface area, high adsorption capacities, cost effectiveness, high abundance in nature and easy handling and much more active sites than bulk [8], [9]. These are important parameters which explain why the adsorbent is economical. The high cost of commercially available adsorbents limits their use. Hence, there is a growing need of indigenously developed, low-cost adsorbents [10]. However, there are some biological adsorbents that may be of concern for being less specific and having low adsorption capacity when it used directly. Therefore, it should be noted that the appropriate modification of biological adsorbent that is chelating ligand containing groups like carboxylic, alcohol, amine, sulphides, thiols, dithiocarbamates, dithiophosphates and xanthates groups have been exclusively study for this purpose and can eliminate the drawback and improve their specificity and adsorption capacity significantly because of their binding affinity of chelating ligand is much more than that of non-chelating ligand in aqueous solution and form a very stable complex [11]. This is due to predominantly entropy change in case of chelating ligand in comparison to the non-chelating ligand [12]. One of them xanthate groups containing compound is an important class of chelating ligand which have high binding affinity to coordinated with heavy metals resulting in the formation of metal xanthate complex.

Depending upon its coordination behavior, xanthates show a diverse application as in industries [13], [14]. Metal xanthate adduct caught the interest of many researchers for the separation of metals ions from the wastewater [15]. The utilization of xanthates, which may be generated via the xanthation process by reaction of alcoholic hydroxide and carbon disulfide (CS₂) in an alkaline medium, is proposed as one of the advanced procedures for the elimination of heavy metal from wastewater [16]. Xanthates can make coordination compounds with number of transition metals due to their complex forming ability. Researchers have developed an insoluble natural poly-saccharide biopolymer-based xanthate that is an inexpensive method for removing heavy metals from wastewater. Many researchers have reported polysaccharides-based xanthate for elimination of heavy metals few of them has used only for extraction of Cu²⁺ and Ni²⁺ ions like, in 2016 a altered adsorbent hydroxypropyl cellulose has been developed for Cu²⁺ and Ni²⁺ ions removal from contaminated water whose adsorption capacity was observed as 126.58 and 114.29 mg/g at pH 5-6 and temperature 30 °C for copper and nickel ions respectively [17]. Another researcher synthesized an adsorbent in 2010 which was orange peel xanthate and their adsorption capacity has been observed as 77.60 and 15.45 mg/g at pH 5.0-5.5 and temperature 25 °C for copper and nickel ions respectively [18]. In 2014, a modified sawdust xanthate has been also synthesized whose adsorption capacity was observed to be 64.58 and 40.86 mg/g at pH 6 and temperature 25 °C for copper and nickel ions respectively [19]. All these above reported data the adsorption is quite low. So, we have to synthesized a beta-cyclodextrin-Xanthates (β-CDX) from beta-cyclodextrin (β-CD) which shows the adsorption capacity is higher in comparison with the above-mentioned reported data because of β-CD has contain large number of -OH functional groups and their cyclic structure encapsulated to transition metal and its xanthate contain large number of xanthate groups (-C(=S) S⁻) which is capable to coordinate large number of copper and nickel ion. Therefore, the adsorption capacity of β-CDX were quite higher than above reported data.

Beta-cyclodextrins (β-CD) is the most abundant and inexpensive naturally occurring cyclical oligosaccharides capable of forming solid inclusion complexes with an extensive range of hydrophobic guest molecules. β-CD is soluble in aqueous solution, but the xanthate of β-CD is insoluble in aqueous phase of metal ions solution. Therefore, the synthesized insoluble beta-cyclodextrin xanthate (β-CDX) can be efficiently utilized in the treatment heavy metal ion form waste water for batch adsorption experiments. The β-CDX has not been outlined in any literature for the elimination of copper and nickel ions.

In this article, we have to the synthesized β-CDX using Wing's procedure of xanthation process. The synthesized β-CDX has been characterized by employing techniques such as UV-visible spectroscopy, FTIR spectroscopy, ¹HNMR spectroscopy, differential scanning calorimetry (DSC) analysis, scanning electron microscopy (SEM) analysis and point of zero charge (ΔpHpzc) analysis. The application of

synthesized hydrogel utilized in the procedure of contaminated water including heavy high density metal ions. The study of the impact of numerous single parameters like the effectiveness of the dosage, pH, operating time, temperature and concentration at initial point has been performed in batch experiment. And also study the adsorption isotherm like Langmuir, Freundlich and Temkin model, and also study the adsorption kinetics such as Pseudo first order, Pseudo second order and Intraparticle diffusion model. To check the feasibility of adsorption process we have also studied the thermodynamic criterion viz change in Gibb's free energy, the change in enthalpy and change in entropy.

2. Material and methods

2.1. Materials

All chemicals *viz.* beta-cyclodextrin (β -CD) powder as raw material (Figure 1), Carbon disulfides (CS_2), NaOH, pentahydrate of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and hexahydrate of nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) of analytical grade were purchased from S.D. Fine Chemical, (Mumbai, India). The stock solution of Cu^{2+} and Ni^{2+} were made by dissolving required amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in double distilled (DD) water, respectively. In the laboratory, PIW was created by immersing 1 kg of wood chips with a size range of 1-10 mm in a 10-liter solution of 1 N NaOH. The digestion process took place over 2-3 months at temperatures between 30-40°C.

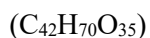
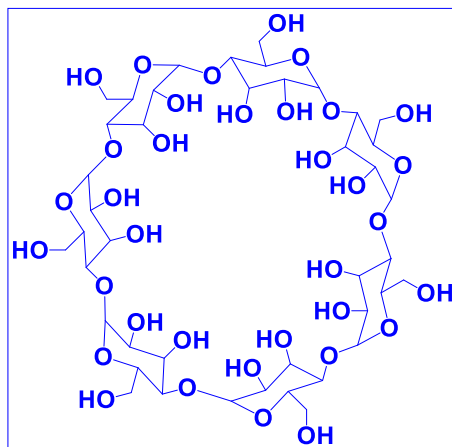


Figure 1. Molecular structure of β -CD.

2.2. Methods

2.2.1. Synthesis of beta-cyclodextrin xanthate

The beta-cyclodextrin xanthate was synthesized following Wing's method [20] with slight modifications. In a two-neck round bottom flask, 2.0 g of beta-cyclodextrin was dissolved in DD water (25 ml), and alkaline solution (1.24N NaOH) was placed in reaction mixture. The whole mixture (homogeneous) was stirred for 30 min at 60°C. Subsequently, reaction mixture was cooled to 30 °C, 0.53 ml of CS₂ was added, and stirred for 6 hrs at room temperature, yielding a yellow-colored liquid as a desired product. The desired product was washed with water, acetone, and ether to removed excess alkali and impurities from that product resulting dried solid was stored in a sealed jar at 6-8°C after overnight drying in an oven at 30°C. The molar ratio of beta-cyclodextrin/NaOH/CS₂ for the synthesis of beta-cyclodextrin xanthate was maintained at 1:7:5. While the molar ratio of beta-cyclodextrin/NaOH for xanthation remained constant at 1:7, the concentration of CS₂ was varied. The defined molar mass of one mole of beta-cyclodextrin was 1135.0 g. Three grades of beta-cyclodextrin xanthates were synthesized using the similar procedure by varying the amount of CS₂. The detailed description for the molar ratio of beta-cyclodextrin, NaOH and CS₂ and also their percentage yield, is shown in Table 1.

Table 1. Details of molar ratio of beta-cyclodextrin, NaOH and CS₂ for the synthesis β-cyclodextrin-xanthates (β-CDXs)

S.N.	Xanthates	β-CD (mmol)	NaOH(mmol)	CS ₂ (mmol)	%Yields
1.	β-CDX1	1.78	12.46	8.90	91.22
2.	β-CDX2	1.78	12.46	10.68	94.95
3.	β-CDX3	1.78	12.46	12.46	97.76

The yield of the β-CDXs was calculated as represented in Equation 1.

$$\% \text{ Yield} = \frac{W_{\beta\text{-CDX}}}{W_M} \times 100 \quad (1)$$

Where; $W_{\beta\text{-CDX}}$ is the weight of dry β-CDX, and W_M is the weight of β-CD and weight of CS₂.

2.2.2. Characterization

The properties and heavy metal concentration of β-CDXs were assessed utilizing the UV-1900i spectrophotometer from Shimadzu Corporation, Japan. The identification of functional moieties in the synthesized beta-cyclodextrin xanthates was conducted through Fourier Transform Infrared Spectroscopy

(FTIR) using the Spirit QATR-S instrument from SHIMADZU, Japan. ^1H NMR spectra were traced on a Bruker Biospin Avance III FT-NMR 400 MHz spectrometer at room temperature, with trimethyl silane (TMS) serving as the primary reference. Differential Scanning Calorimetry (DSC) experiments were performed in the range of temperature 25 to 600°C (heating rate: 10 °C/min) in a nitrogen atmosphere using a Shimadzu DSC 60 TSW 60 instrument from Japan. The surface morphology of β -CDXs before and after the adsorption of heavy metals has been carried out scanning electron microscope JEOL (JSM 6490 LV, USA)

2.2.3. Heavy metal ion removal and LEPIW treatment using β -CDXs xanthate

Adsorption experiments for toxic metal ions involved for the preparation of 1000 mg/L stock solution of Cu^{2+} and Ni^{2+} ions. The solution pH was set using 0.1 M HCl and NaOH solutions. The solution consisting of heavy metal ions was brought into contact with precisely measured quantities of β -CD, β -CDX1, β -CDX2, and β -CDX3 samples in a conical flask. Stirring was facilitated by a magnetic stirrer operating at 300 rpm. Following a suitable duration, the mixture underwent centrifugation, and the remaining concentration of toxic metals in the aqueous solution were evaluated using a UV-visible spectrophotometer through the calibration curve method. The removal % (R) and adsorption capacity (q_e) were computed using Equations (2) and (3) respectively.

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

$$q_e = \frac{(C_i - C_f)}{m} \times V \quad (3)$$

Where, C_f & C_i represents the final and initial concentrations of metal ions (mg/L), respectively, V indicates volume of metal ion solution in litre, m denotes the mass of adsorbent in grams.

The possible mechanism for the synthesis of β -CDXs and the Cu^{2+} and Ni^{2+} removal by β -CDXs from aqueous solutions is demonstrated in Figure 2 (a) and (b).

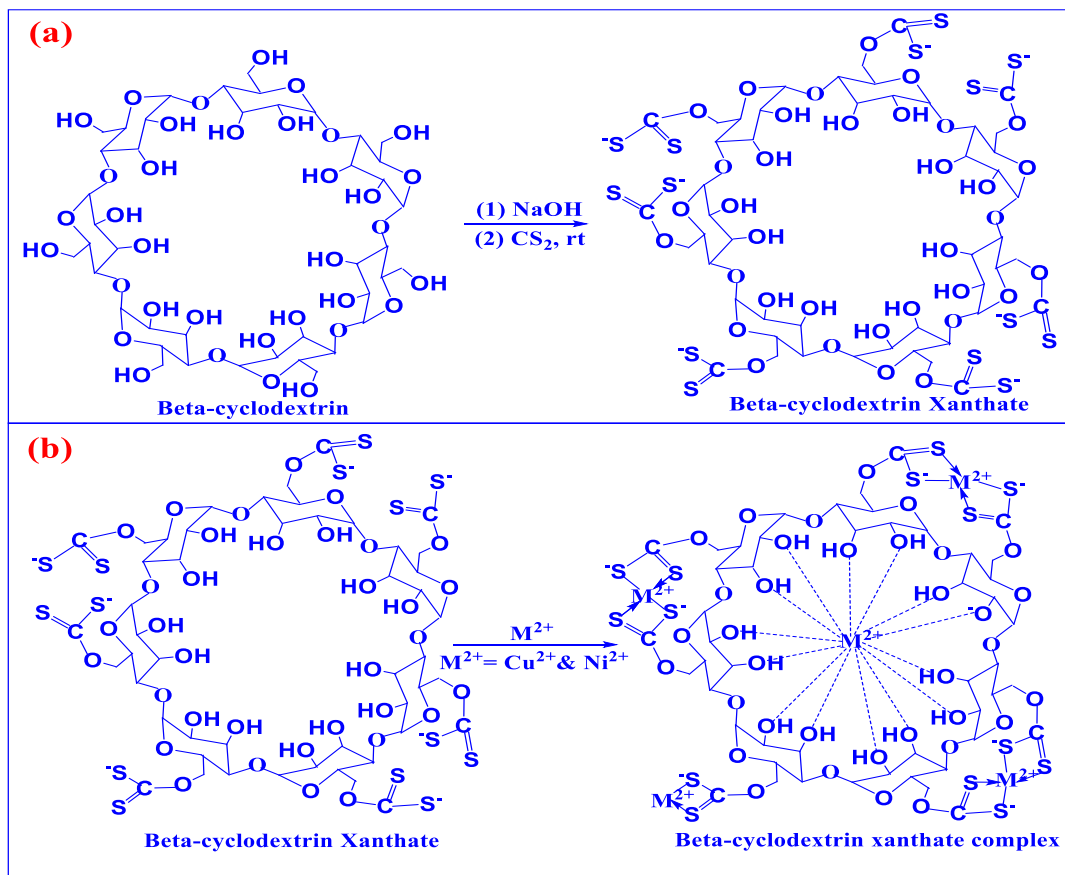


Figure 2. General mechanism of (a) synthesis of β -CDXs and (b) elimination of Cu^{2+} and Ni^{2+} ions by β -CDXs from wastewater.

LEPIW [21] containing initial chemical oxygen demand (COD) of 1000 mg/L was treated at optimized adsorbent dose, neutral pH and environmental temperature of 40 °C.

2.2.4. Calibration curve for copper and nickel ion

Calibration curve basically, a plot between absorbance and known concentration of Cu^{2+} and Ni^{2+} metal ions solution by using UV-visible spectrophotometer. The significance of the calibration curve is to be determined the equilibrium concentration of unknown solutions by using the value of molar absorptivity (ϵ). The calibration curve performed in Cu^{2+} and Ni^{2+} ions concentration range 100- 1000 mg/L, which demonstrated in Figure 3 (a) & (b) respectively.

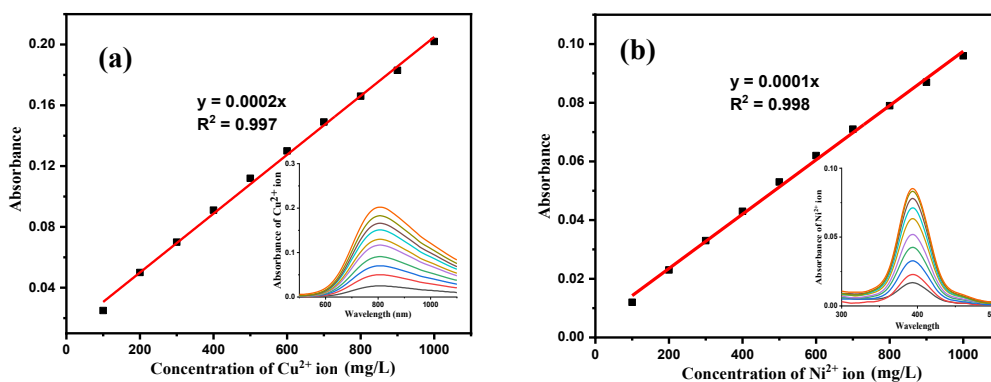


Figure 3. Calibration curve for (a) Cu^{2+} (b) Ni^{2+} metal ion.

Figure 3 (a) & (b) shows that the maximum wavelength has been found to be 806 nm & 393 nm for Cu^{2+} and Ni^{2+} metal ions respectively [22], [23]. At fixed maximum wavelength, the absorbance of different known concentration of Cu^{2+} & Ni^{2+} metal ions were noted. Finally, a linear graph was plotted between absorbance and known concentration. After that the molar absorptivity (ϵ) value were found to 0.0002 & 0.0001 for Cu^{2+} & Ni^{2+} metal ions respectively. By using the value of molar absorptivity (ϵ), the equilibrium concentration of unknown Cu^{2+} and Ni^{2+} ions solutions were determined.

The details description of adsorption isotherm, kinetic & thermodynamic parameters were included in the supplementary file [24].

3. Result and discussion

3.1. Characterization

3.1.1. UV-visible spectroscopy

The formation of β -CDXs from starch has been confirmed by UV-visible spectroscopy which demonstrated in Figure 4 (a). From figure 4 (a) it is clearly show that in β -CD there is only one absorption band appeared at 282 nm due to $n - \sigma^*$ transition of -OH functional groups but in case of all three grades β -CDXs, two absorption bands appeared due to the xanthate groups which is presented in the β -CDXs. Because xanthate groups behaves like chromophore group and contribute to the $n - \pi^*$ and $\pi - \pi^*$ transition at 315 nm and 397 nm respectively [25]. Hence xanthate groups are present in starch confirmed by UV- visible spectroscopy.

3.1.2. Fourier-Transform Infrared (FTIR) Spectroscopy

A qualitative study to investigate the functional groups of β -CD, β -CDX1 β -CDX2 and β -CDX3 by using FT-IR spectroscopy as demonstrated in Figure 4 (b). From Figure 4 (b) indicate that the absorption band of β -CD, β -CDX1 β -CDX2 and β -CDX3 are identical in between the range of the wavenumber 3500 to 2800 cm^{-1} because of stretching vibration O-H and C-H bond [26]. The absorption band exhibit at 1,155 and 1026 cm^{-1} were due to stretching vibration of C–O–C and alcoholic O-H bond of β -CD, β -CDX1 β -CDX2 and β -CDX3 [27]. However, after xanthation of β -CD some distinct changes occurred. Also, a adsorption band appeared at 997 cm^{-1} when the β -CD is treated with CS_2 , which is corresponding to the vibration of C=S of $-\text{C}(=\text{S})\text{S}^-$ group [28]. The existence of this band is due to the presence of sulfur groups in the β -CDXs. And finally, the absorption band occurred at 1650 and 1367 cm^{-1} is due to the C-O stretching vibration of cyclic alcohol and C-O-C bond of xanthate groups which confirms the β -CDXs has been successfully synthesized from β -CD [29].

3.1.3. Differential Scanning Calorimetry (DSC) analysis

DSC is a one important analytical tool that measure the stability (melting point) of the materials. The stability of pure β -CD and β -CDX3 has been determined by using a differential scanning calorimetric analysis. The DSC curve for β -CD and β -CDX3 were demonstrated in Figure 4 (c). Figure 4 (c) states that the endothermic peak of β -CD observed at around 93°C its melting point [30] that means β -CD is heat absorbed, but in case of β -CDX3 the multiple exothermic peaks observed at 55, 236, 260 & 399 °C. The major exothermic peak of β -CDX3 were occurred at around 236 °C its melting point that means β -CDX3 is heat released. From above observation it is clear that the β -CDX3 is quite stable than that of β -CD.

3.1.4. Point of zero charge ($\Delta\text{pH}_{\text{PZC}}$) analysis

The point of zero charge ($\Delta\text{pH}_{\text{PZC}}$) analysis has been performed to analyze of charge onto the surface of β -CD, β -CDX1 β -CDX2 and β -CDX3 adsorbent. $\Delta\text{pH}_{\text{PZC}}$ is the pH for which the total surface charge of the adsorbent is equal to zero. Generally, for pH of the solution $< \Delta\text{pH}_{\text{PZC}}$, adsorbent surface will contain mainly positive charge, while at pH values $> \Delta\text{pH}_{\text{PZC}}$, the total surface charge will contain negative charge [31]. From experimental results $\Delta\text{pH}_{\text{PZC}}$ values were found to be 5.7, 4.5, 4.1 and 3.8 for β -CD, β -CDX1 β -CDX2 and β -CDX3 which is less than operating pH 6.5 as demonstrated in Figure 4 (d). This indicates, surface charge of β -CD, β -CDX1 β -CDX2 and β -CDX3 is primarily negative and interaction of metal ions (Cu^{2+} and Ni^{2+}) with β -CD, β -CDX1 β -CDX2 and β -CDX3 adsorbent is favorable.

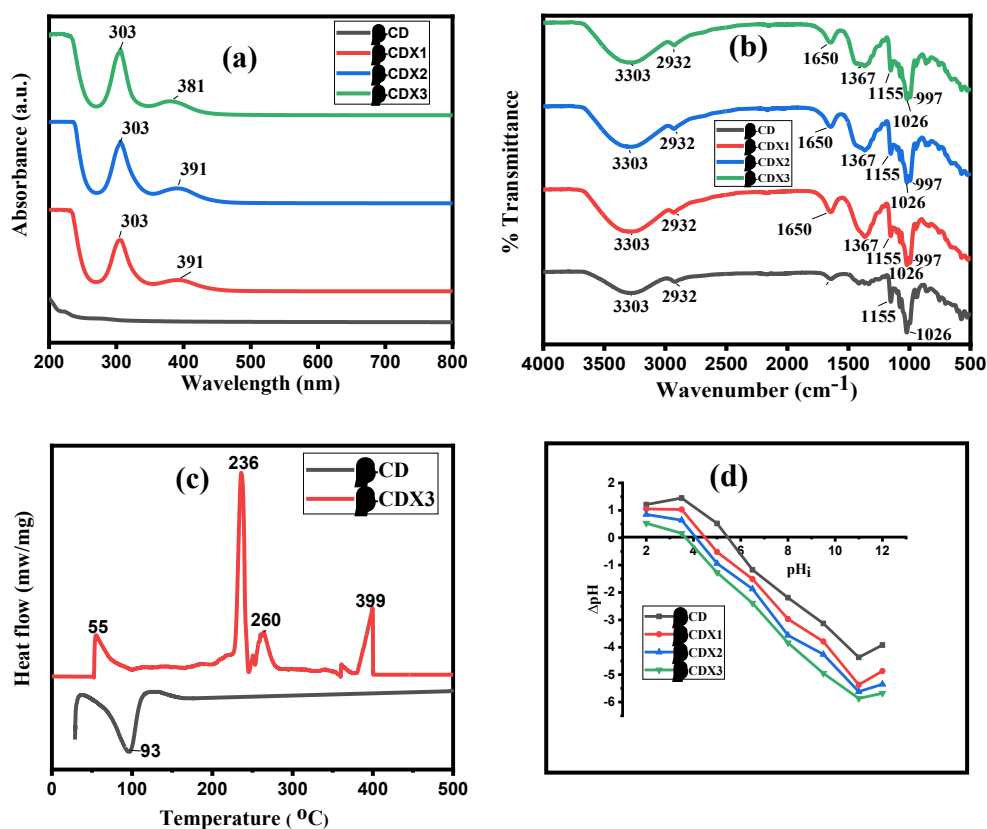


Figure 4 (a) UV-visible spectra of β -CD, β -CDX1, β -CDX2 and β -CDX3, (b) FTIR spectra of β -CD, β -CDX1, β -CDX2 and β -CDX3, (c) DSC curve of β -CD and β -CDX3, (d) PZC curve of β -CD, β -CDX1, β -CDX2 and β -CDX3.

3.1.5. Nuclear Magnetic Resonance (NMR) Spectroscopy

The ^1H NMR spectroscopy is most powerful technique to assigned any chemical structure of any compound. The ^1H NMR spectra of β -CD and β -CDX3 are demonstrated in Figure 5 (a) and (b). For β -CD, proton

chemical shift at 4.49 ppm was assigned to external -OH¹, at 5.69 ppm to internal -OH², at 5.74 ppm to also internal -OH³, at 4.82 ppm to H¹, at 3.63 ppm to H³ and H⁶, at 3.57 ppm to H⁴ & H⁵ and at 3.32 ppm to H² [32]. After xanthation, all characteristic peaks were similar to native β -CD. But two characteristics ¹HNMR peak at 4.49 and 574 ppm of -OH functional groups are missing due to the formation of xanthate. These observations confirm the β -CDX3 successfully synthesized from β -CD.

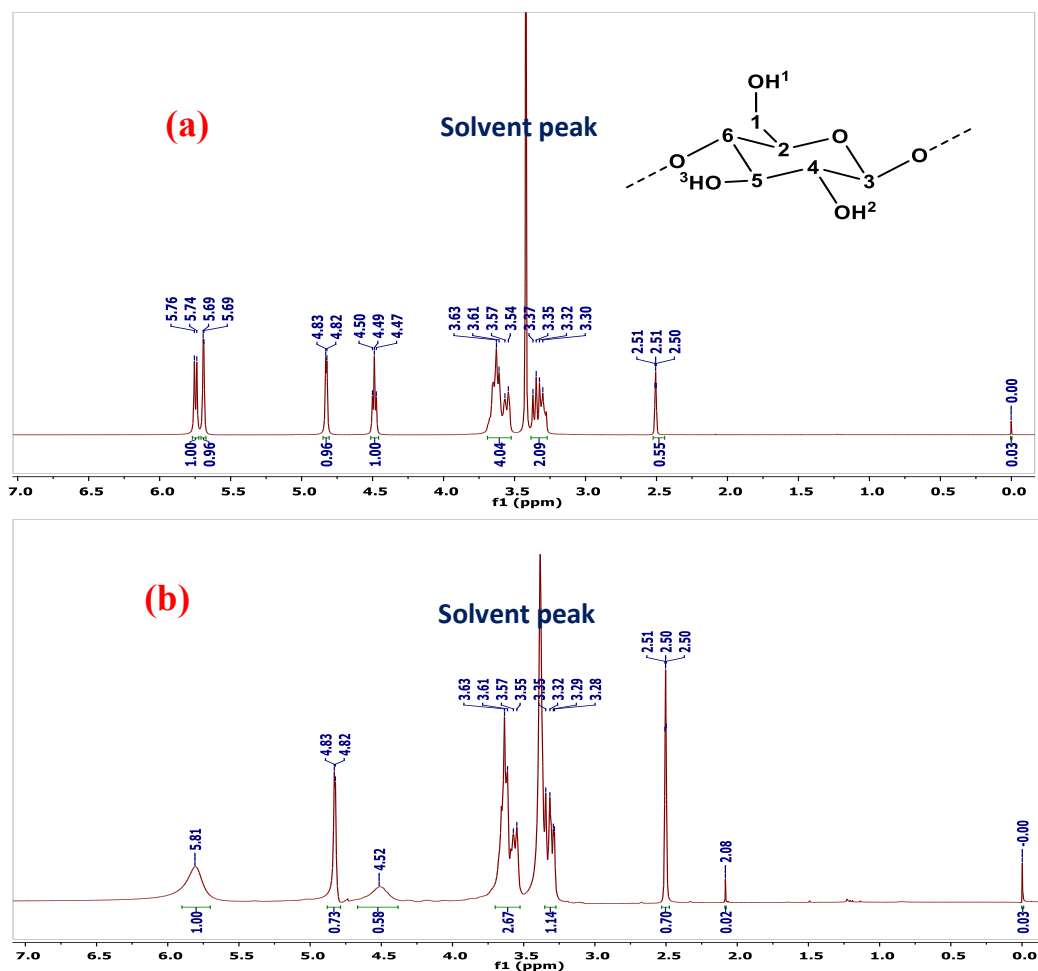


Figure 5. ¹H NMR spectrum of (a) β -CD & (b) β -CDX3

3.1.6. Scanning electron microscopy (SEM) analysis

The SEM analysis was used to identify microscopic morphology of the β -CDX3 adsorbent as demonstrated in Figures 6 (a), (b) and (c) respectively. In Figure 6 (a), irregular pores can be distinctly seen on the β -CDX3's surface. This can be the result of the evaporation during the drying process of the composite. The porous nature of the hydrogel may offer a crucial requirement for the adsorption of Cu^{2+} & Ni^{2+} metal ions and facilitate their collectability on the adsorbent. Furthermore, Figure 6 (b) and (c) clearly show that following adsorption of Cu^{2+} & Ni^{2+} metal ions, the surface of β -CDX3 becomes more uneven and rough. Their surface is covered with particles of varying sizes, showing that Cu^{2+} & Ni^{2+} metal ions were successfully absorbed.

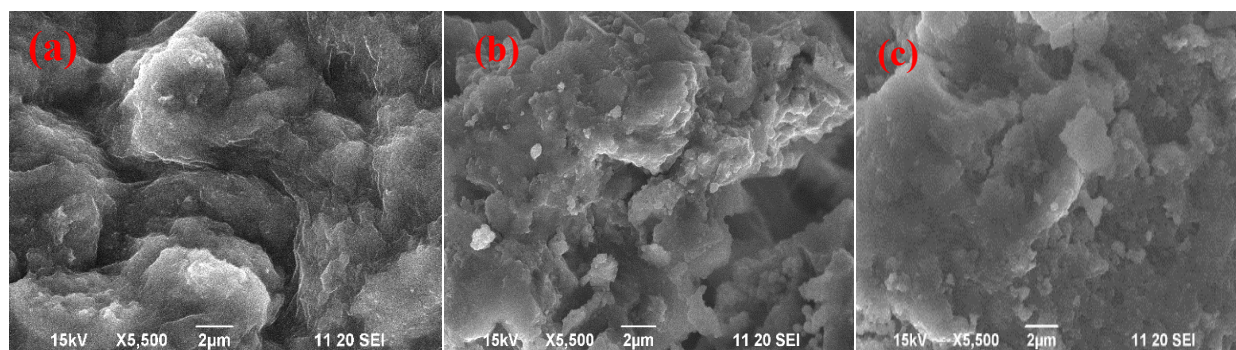


Figure 6. SEM image of (a) β -CDX3 (b) β -CDX3-Cu & (c) β -CDX3-Ni

3.2. Removal of Cu^{2+} and Ni^{2+} ions from wastewater

The treatment of wastewater containing Cu^{2+} and Ni^{2+} ions for the adsorption onto the β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent has been studied via single parameter of batch experiment process. In batch experiment, all parameter like, effect adsorbent dosage, pH, solution temperature, initial concentration and contact time has been optimized by using single parameter studies.

3.2.1. Effect of adsorbent dosage

The adsorbent dosage is an essential factor that affects the Cu^{2+} and Ni^{2+} ions removal by the β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent in aqueous phase at range of 0.5 g to 3.5 g as displayed in Figure 7 (a) and (b) respectively.

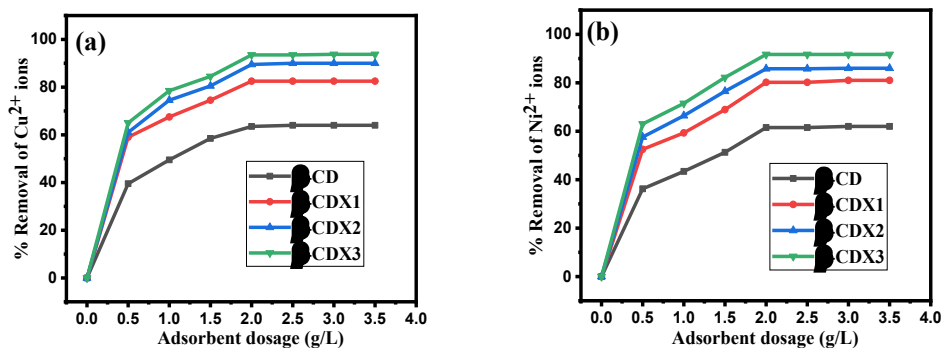


Figure 7. Effect of adsorbent dosages on % removal of (a) Cu^{2+} (b) Ni^{2+} ion at optimum pH: 6.5, temperature: 45°C for Cu^{2+} and 55°C for Ni^{2+} , initial concentration: 1000 mg/L and contact time: 80 min for Cu^{2+} and 100 min for Co^{2+} ion.

Figure 7 (a) and (b) demonstrated, that upto the adsorbent dosage 2.0 g for both metal ions, the removal % of metal ions increased with the increase in amount of adsorbent dosage. This may be concern that the large number active site are available to deposited the heavy metal ion on the adsorbent surface [33]. But, further increase the amount of adsorbent dosages in the metal ions solution, the % removal of that metal ion remains constant because the accessibility of all adsorption sites are almost occupied on the interface of the adsorbent [34]. After the inspection of the effect of dosage, the maximum % removal has been found to be 63.5, 82.5, 89.5 and 93.5 % for Cu^{2+} ions and 61.5, 80.2, 85.8 and 91.7 % for Ni^{2+} ions at 2.0 g of adsorbent dosage of $\beta\text{-CD}$, $\beta\text{-CDX1}$, $\beta\text{-CDX2}$ and $\beta\text{-CDX3}$ adsorbent respectively.

3.2.2. Effect of solution pH

The influence of pH is essential for the % removal of heavy metal ion form wastewater. The impact of pH for the elimination of Cu^{2+} and Ni^{2+} ions in the pH range from 2 to 12 as illustrated in Figure 8(a) and (b) respectively.

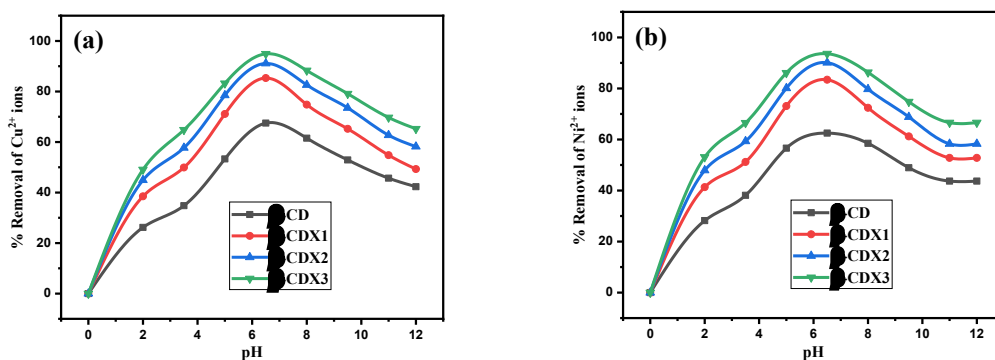


Figure 8. Effect of solution pH on % removal of (a) Cu^{2+} (b) Ni^{2+} ion at optimum adsorbent dosage: 2.0 g/L, temperature: 45°C for Cu^{2+} and 55°C for Ni^{2+} , initial concentration: 1000 mg/L and contact time: 80 min for Cu^{2+} and 100 min for Co^{2+} ion.

The experimental findings demonstrated the % Cu^{2+} and Ni^{2+} ions removal raised with rise in pH upto 6.5 for Cu^{2+} and Ni^{2+} ions. This is because there are a greater number of H^+ ions accessible at lower pH levels, which compete with the heavy metal ions for the adsorption onto the interface of the adsorbent. As a result, heavy metal removal efficiency is reduced [35]. However, the percentage of heavy metal ion elimination boost when the pH rise upto to 6.5. This could be evident that the ionization of xanthogenic acidic group ($-\text{C}(\text{C}=\text{S})\text{SH}$). [36]. After that, the % removal of the metal ion is then reduced when the pH is raised to 6.5 because a higher pH allows for the maximum number of OH^- ions to be present in the solution, which can precipitate with metal and form metal hydroxide [37]. Hence, the maximum % removal has been found to be 67.5, 85.3, 91.1 and 94.9 % for Cu^{2+} ions and 62.5, 83.4, 90.1 and 93.6 % for Ni^{2+} ions at pH 6.5 by β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent respectively.

3.2.3. Effect of concentration

For the calculation of the adsorption capacity for adsorption of Cu^{2+} and Ni^{2+} ions on the β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent at different initial concentration, it is must to evaluate the consequence of concentration for the % removal of Cu^{2+} and Ni^{2+} ions from contaminated water in the range of concentration 100 mg/L to 1500 mg/L which were presented in Figure 9 (a) & (b) respectively.

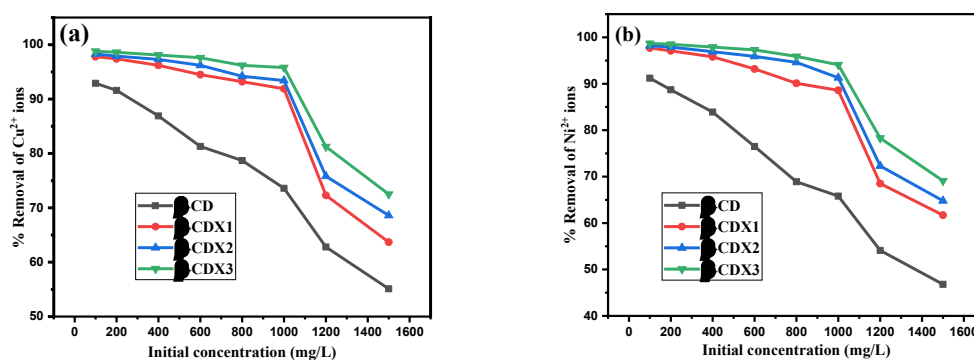


Figure 9. Effect of initial concentration on % removal of (a) Cu^{2+} (b) Ni^{2+} ion at optimum adsorbent dosage: 2.0 g/L, pH: 6.5, temperature: 45°C for Cu^{2+} and 55°C for Ni^{2+} ion, and contact time: 80 min for Cu^{2+} and 100 min for Co^{2+} ion.

The experimental findings from the Figure 9 (a) and (b) indicates that the % removal of Cu^{2+} and Ni^{2+} ions gradually decline with raise in the initial concentration Cu^{2+} and Ni^{2+} ions upto 1000 mg/L. The main reason

for this phenomenon because the available Cu^{2+} and Ni^{2+} ions in their solution is less in comparison to the accessible active sites present at the adsorbent surface at lower concentration Cu^{2+} and Ni^{2+} ions. Further, raise the Cu^{2+} and Ni^{2+} concentration above from 1000mg/L, the % removal of these metal ions sharply decreased because the existing active sites for Cu^{2+} and Ni^{2+} adsorption decreases at maximum concentrations of these metal ions and get quickly saturated when concentration of Cu^{2+} and Ni^{2+} ions was raised above to the 1000 mg/L [38]. Hence, the optimum % removal has been found to be 73.6, 91.9, 93.4 and 95.8 % for Cu^{2+} ions and 65.8, 88.6, 91.3 and 94.1 % for Ni^{2+} ions at initial concentration 1000 mg/L by β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent respectively.

3.2.4. Effect of temperature

The investigation of thermodynamic parameter like ΔG , ΔH & ΔS for the adsorption of Cu^{2+} & Ni^{2+} ions onto β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent must be study the effect of temperature on the removal % of Cu^{2+} & Ni^{2+} ions from wastewater in range of temperature 20 °C to 80 °C as represented in Figure 10 (a) and (b) respectively.

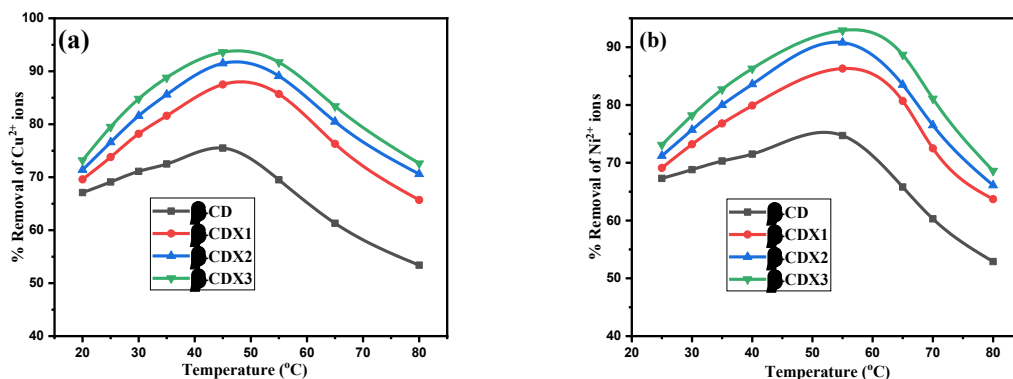


Figure 10. Effect of solution temperature on % removal of (a) Cu^{2+} (b) Ni^{2+} ion at optimum adsorbent dosage: 2.0 g/L, pH: 6.5, initial concentration: 1000 mg/L and contact time: 80 min for Cu^{2+} and 100 min for Co^{2+} ion.

The experimental data from Figure 10 (a) and (b), it has been noted that the % removal of Cu^{2+} and Ni^{2+} ions raise with raise in temperature upto 45 °C for Cu^{2+} and 55 °C for Ni^{2+} ions. This is evident that the kinetic energy of Cu^{2+} and Ni^{2+} ions in that solution gradually raise with respect to the solution temperature resulting the % of elimination of Cu^{2+} and Ni^{2+} ions increased. After that, further raise the solution temperature from the optimum temperature, the % removal of Cu^{2+} and Ni^{2+} ions get decreased. This is due to the kinetic energy of Cu^{2+} and Ni^{2+} ions are very high at higher temperature. This may be attribute to the adsorbed metal ions collide with each other and weakening of Vander Waal's forces between adsorbate and adsorbent and hence the escaping tendency of metal ions from adsorbent surface increased. Therefore, the

rate of % removal of metal ions falls [24]. Hence, the optimum % removal has been found to be 75.5, 87.5, 91.5 and 93.6% for Cu^{2+} ions at solution temperature 45 °C and 74.7, 86.3, 90.8 and 92.9 % for Ni^{2+} ions at solution temperature 55 °C by β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent respectively. From these results it could be signified that the adsorption between adsorbent (β -CD, β -CDX1, β -CDX2 and β -CDX3) and adsorbate (Cu^{2+} and Ni^{2+} ions) is involvement of both physical and chemical adsorption. And adsorption of Cu^{2+} and Ni^{2+} ions onto β -CD, β -CDX1, β -CDX2 and β -CDX3 is an endothermic process.

3.2.5. Effect of contact time

The inspection of kinetic study for the adsorption of for the adsorption of Cu^{2+} & Ni^{2+} ions onto β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent is necessary for evaluation of the effect of time on % removal of Cu^{2+} & Ni^{2+} ions from wastewater in range of time 25 min to 300 min which has been represented in Figure 11 (a) and (b) respectively.

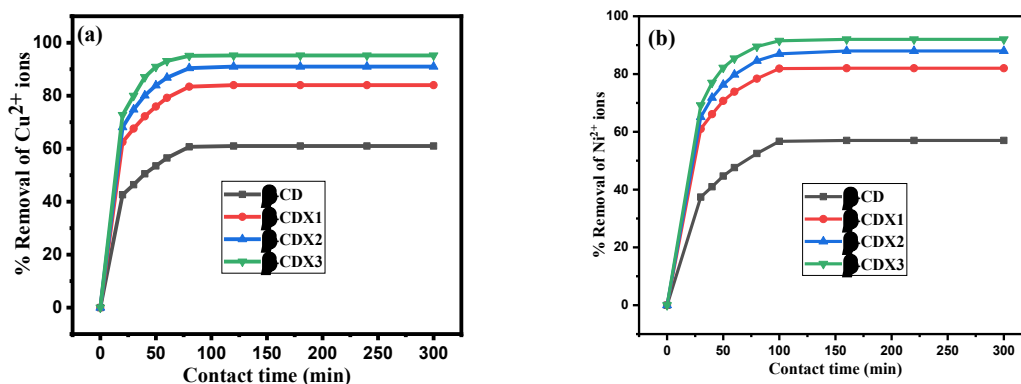


Figure 11. Effect of contact time on % removal of (a) Cu^{2+} (b) Ni^{2+} ion at optimum adsorbent dosage: 2.0 g/L, pH: 6.5, temperature: 45°C for Cu^{2+} and 55°C for Ni^{2+} , initial concentration: 1000 mg/L.

The result from experimental data shows that the % removal of Cu^{2+} & Ni^{2+} ions swiftly rise with rise in the contact time till 80 min for Cu^{2+} and 100 min for Ni^{2+} ions. After reaching the equilibrium concentration of Cu^{2+} & Ni^{2+} ions solutions at optimum contact time, further increasing the contact time, the % removal of these metal ions become constant. The reason behind for this event, the available active sites of xanthates to coordinate with heavy metal ions become saturated after reaching the equilibrium concentration of Cu^{2+} & Ni^{2+} ions solutions at optimum contact time 80 min for Cu^{2+} and 100 min for Ni^{2+} ions [39]. Hence, the

optimum % removal has been found to be 60.7, 83.4, 90.4 and 95.06 % for Cu²⁺ ions and 56.7, 81.9, 87.0 and 91.5% for Ni²⁺ ions by β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent respectively.

3.3. Adsorption isotherm, kinetics and thermodynamic parameter study

The factors of the adsorption isotherms were derived by analyzing the slope of the linear plots and their intercept corresponding to Langmuir, Freundlich, and Temkin adsorption isotherm equations. Specifically, the plots employed were $1/C_e$ vs $1/q_e$, $\log C_e$ vs $\log q_e$, and $\log C_e$ vs q_e , respectively. The calculated values of the adsorption isotherm parameters for the Langmuir, Freundlich, and Temkin adsorption isotherm models, concerning the adsorption of Cu²⁺ and Ni²⁺ ions onto β -CD, β -CDX1, β -CDX2, and β -CDX3 adsorbents at various initial concentrations (100, 200, 400, 600, 800, and 1000 mg/L), are displayed in Table 2.

Table 2. Adsorption isotherm parameters for the adsorption of Cu²⁺ & Ni²⁺ onto β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent.

Adsorbent	Metals	Langmuir isotherm model			Freundlich isotherm model			Temkin isotherm model			
		M ²⁺	K _L (L/mg)	q _{max} (mg/g)	R ²	K _b (L/g)	1/n	R ²	B (mg/g)	A (L/g)	R ²
β -CD			0.0198	373.13	0.996	17.0718	0.5644	0.997	203.01	0.1849	0.959
β -CDX1			0.0526	467.28	0.997	33.2774	0.6099	0.981	255.61	0.5182	0.943
β -CDX2	Cu ²⁺		0.0660	480.76	0.996	39.8923	0.6049	0.982	258.88	0.6715	0.958
β -CDX3			0.0860	523.56	0.998	49.3844	0.6260	0.973	272.46	0.9392	0.953
β -CD			0.0184	257.06	0.995	13.002	0.6501	0.999	139.70	0.1659	0.974
β -CDX1	Ni ²⁺		0.0577	328.94	0.995	27.9634	0.6008	0.981	181.15	0.5322	0.960
β -CDX2			0.0632	381.67	0.998	32.0427	0.6044	0.993	199.28	0.6649	0.970
β -CDX3			0.0822	406.50	0.998	39.1282	0.6232	0.992	206.78	0.9090	0.973

The experimental results of all thermodynamic parameters value from Table (2) indicates the linear regression correlation coefficient (R²) values for Langmuir isotherm model is greater in comparison with the Freundlich and Temkin isotherm model. The R² values almost closed to 1, revealing the experimental figures were good fit with Langmuir model than that of Freundlich and Temkin isotherm model for Cu²⁺ & Ni²⁺ ions adsorption. This confirms the adsorption of Cu²⁺ & Ni²⁺ ions onto the β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent is monolayer [40]. The maximum adsorption capacities have been found to be

373.13, 467.28, 480.76 and 523.56 mg/g for Cu²⁺ and 257.06, 328.94, 381.67 and 406.50 mg/g for Ni²⁺ ions by β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent respectively.

The adsorption kinetic parameters like, rate constant and adsorption capacities were determined from the intercept and slope of the straight-line kinetic plots of $\ln(q_e - qt)$ vs t , t/qt vs t and qt vs $t^{1/2}$ for pseudo first order, pseudo second order and intraparticle diffusion model respectively. The calculated value of adsorption kinetic parameters corresponding with linear regression correlation coefficient (R^2) of Pseudo – first-order, Pseudo -second-order and Intra-particle-diffusion models for the adsorption of Cu²⁺ & Ni²⁺ ions onto β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent at different time intervals were presented in Table 3.

Table 3. Adsorption kinetic parameters for the adsorption of Cu²⁺ & Ni²⁺ onto β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent.

Adsorbent	Metal s	Pseudo – first- order			Pseudo -second- order			Intra-particle- diffusion		
		K ₁ 1/min	q _e (mg g ⁻¹)	R ²	K ₂ g/(mg.min)	q _e (mg/g)	R ²	K _{diff} mg/(g.min ^{1/2})	q _e (mg/g)	R ²
β -CD		-0.014	209.41	0.999	1.79×10 ⁻⁴	357.14	0.995	20.63	120.80	0.997
β -CDX1	Cu ²⁺	-0.020	225.56	0.999	1.81×10 ⁻⁴	473.93	0.987	23.81	208.41	0.992
β -CDX2		-0.035	269.35	0.996	1.84×10 ⁻⁴	510.20	0.999	25.20	235.23	0.968
β -CDX3		-0.058	423.75	0.993	1.99×10 ⁻⁴	534.75	0.999	25.74	260.52	0.905
β -CD		-0.016	188.88	0.996	1.08×10 ⁻⁴	294.11	0.995	17.14	56.43	0.998
β -CDX1	Ni ²⁺	-0.020	198.97	0.998	1.45×10 ⁻⁴	384.61	0.999	18.34	148.58	0.976
β -CDX2		-0.025	221.06	0.997	1.46×10 ⁻⁴	408.16	0.999	19.11	164.58	0.947
β -CD		-0.032	247.19	0.996	1.57×10 ⁻⁴	423.72	0.999	19.29	184.85	0.903

As evident from Table 3, the R^2 values for both pseudo-first and pseudo-second-order kinetic models are nearly identical and close to 1. However, based on the adsorption capacities (q_e) values, the pseudo-second-order model surpasses the pseudo-first-order model. This suggests that the kinetic experimental data are best described by pseudo-second-order kinetic models, indicating that the rate of the adsorption process is governed by pseudo-second-order kinetics. This validates the conclusion that the adsorption of Cu²⁺ and Ni²⁺ ions onto β -CD, β -CDX1, β -CDX2, and β -CDX3 adsorbents involves chemical adsorption or chemisorption, which entails the exchange/sharing of valence electrons among the adsorbate and adsorbent

molecules. [41]. The maximum adsorption capacities have been found to be 357.14, 473.93, 510.20 and 534.75 mg/g for Cu²⁺ and 294.11, 384.61, 408.16, and 423.72 mg/g for Ni²⁺ ions β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent respectively.

The thermodynamic parameters, namely ΔG , ΔH , and ΔS , were calculated from the intercept and slope of the linear plots obtained by $\ln K_c$ versus $1/T$ from the Van't Hoff Equation. This analysis was conducted for the adsorption of Cu²⁺ and Ni²⁺ ions onto β -CD, β -CDX1, β -CDX2, and β -CDX3 adsorbents at an initial concentration of 1000 mg/L and temperatures of 293, 298, 303, 308, and 318 K. The resulting values for these thermodynamic parameters are provided in Table 4.

Table 4. Thermodynamic parameters for the adsorption of Cu²⁺ & Co²⁺ onto β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent

Adsorbent	Temperature (K)		Thermodynamics parameters							
			ΔG (KJ/mol)		ΔH (KJ/mol)		ΔS (J/mol K)		R ²	
	(Cu)	(Co)	(Cu)	(Co)	(Cu)	(Co)	(Cu)	(Co)	(Cu)	(Co)
β -CD	293	298	-0.047	-0.070						
	298	303	-0.276	-0.245						
	303	308	-0.521	-0.431	12.72	9.74	43.63	32.99	0.998	0.998
	308	313	-0.707	-0.589						
	318	328	-1.142	-1.062						
β -CDX1	293	298	-0.329	-0.276						
	298	303	-0.848	-0.785						
	303	308	-1.471	-1.290	34.77	28.01	119.65	95.06	0.998	0.998
	308	313	-2.039	-1.787						
	318	328	-3.312	-3.128						
β -CDX2	293	298	-0.540	-0.525						
	298	303	-1.220	-1.116						
	303	308	-2.006	-1.774	45.51	37.71	156.97	128.24	0.998	0.999
	308	313	-2.789	-2.434						
	318	328	-4.449	-4.353						
β -CDX3	293	298	-0.759	-0.759						
	298	303	-1.640	-1.471						
	303	308	-2.584	-2.231	52.30	42.70	181.11	145.88	0.999	0.999
	308	313	-3.526	-2.985						
	318	328	-5.260	-5.122						

The findings presented in Table 4 reveal that the negative ΔG values affirm spontaneous and feasible adsorption process for Cu²⁺ and Ni²⁺ ions onto β -CD, β -CDX1, β -CDX2, and β -CDX3 adsorbents. As the temperature elevates, the negative ΔG values also rise, indicating an enhanced adsorption capacity at elevated temperatures. The positive values of ΔH and ΔS further confirm that the adsorption process of heavy metal ions onto the adsorbent is endothermic in nature, contributing to an increased degree of randomness on the adsorbent surface. In essence, heat is consumed during the adsorption of Cu²⁺ and Ni²⁺ ions onto β -CD, β -CDX1, β -CDX2, and β -CDX3 adsorbents.

3.4. Paper industry wastewater (real) treatment

The effect of β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent for the treatment of real lignin enriched paper industry wastewater has been presented in Figure 12.

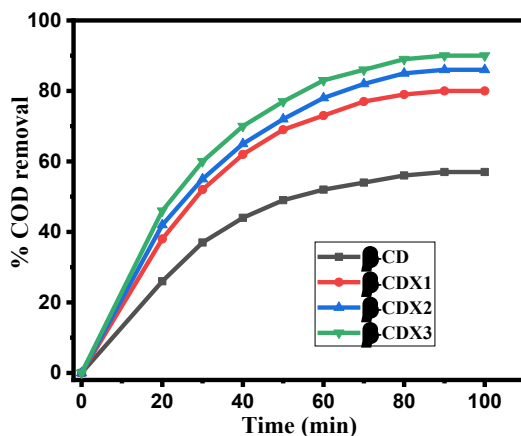


Figure 12. Effect of adsorbents for LEPIW treatment (Condition: adsorbent dose: 2.0 g/L, pH: 7, operating temperature: 40 °C; Initial COD:1000 mg/L)

As demonstrated the results from Figure (12) the % COD removal increase with increasing contact time in the treatment of lignin enriched paper wastewater. This may be concern that the presence of many functional groups like, $-C(=S)S^-$, $-COO^-$, $-OH$, and $-COOCH_3$ in β -CD and β -CDXs adsorbent which is responsible for removal of pollutant (lignin) from paper wastewater [42]. The maximum % COD removal has been found to be 56, 79, 85 and 89 % from lignin enriched paper wastewater at 80 min optimum contact time. These data indicated the efficiently removal of lignin from real wastewater by β -CD and β -CDXs adsorbent.

3.5. Comparative study of β -CDXs adsorbent with reported xanthates adsorbents

Comparing the adsorption efficiency of the β -CDXs adsorbent with similar reported xanthates such as bagasse, wood, chitosan, sawdust, orange peel, hydroxypropyl cellulose, and lactose is challenging due to the considerable variability in the conditions used for synthesizing these adsorbents, as well as differences in the conditions during the adsorption process. Despite this complexity, it is essential to underscore the significance of the study by highlighting that β -CDX3 exhibits a maximum adsorption capacity of 534.75 mg/g for Cu^{2+} and 423.72 mg/g for Ni^{2+} . However, when compared to other similar reported xanthates, the adsorption capacity of β -CDX3 appears notably low, as illustrated in Table 5. Despite this, the comparative

study suggests that the prepared β -CDXs adsorbent demonstrates a commendable capacity for the adsorption of Cu^{2+} and Ni^{2+} ions.

Table 5. Comparison of adsorption capacity of β -CDX3 with similar reported xanthates.

S.N.	Name of adsorbent	Metals	pH	T ($^{\circ}$ C)	q_e (mg/g)	Ref.
1.	Insoluble bagasse xanthate	Cu^{2+}	5.0 ± 0.1	18 - 21	26.9	[43]
2.	Insoluble wood xanthate	Cu^{2+}	5.0 ± 0.1	18 - 21	27.8	[43]
3.	Xanthate- modified magnetic chitosan	Cu^{2+}	6.0	30	34.5	[44]
4.	Modified sawdust xanthate	Cu^{2+} , Ni^{2+}	6.0 ± 0.1	25	64.58, 40.86	[19]
5.	Orange peel xanthate	Cu^{2+} , Ni^{2+}	5.0 - 5.5	25	77.60, 15.45	[45]
6.	X-CS/NIPAAm composite hydrogel	Cu^{2+} , Ni^{2+}	5	~ 25	115.1, 66.9	[46]
7.	Hydroxypropyl cellulose Xanthate	Cu^{2+} , Ni^{2+}	5.0 - 5.5	30	129.58, 114.29	[17]
8.	Lactose-xanthate	Cu^{2+} , Ni^{2+}	5	25	234.78, 239.35	[39]
9.	β -CDX3	Cu^{2+} , Ni^{2+}	6.5	45-55	534.75, 423.72	Present study

4. Conclusions

The result discloses that, in comparison to another reported adsorbent, β -CD based-xanthate can be employed as a competent adsorbent. It might be utilized to treat both heavy metal ion-containing wastewater and lignin enriched paper industry wastewater. The maximum % removal has been found to be 73.6, 91.9, 93.4 and 95.8 % for Cu^{2+} ions and 65.8, 88.6, 91.3 and 94.1 % for Ni^{2+} ions at optimum adsorbent dosage 2.0 g/L, pH 6.5, solution temperature 45 $^{\circ}$ C for Cu^{2+} and 55 $^{\circ}$ C Ni^{2+} ions, initial concentration 1000 mg/L and contact time 80 min for Cu^{2+} and 100 min for Ni^{2+} by β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent respectively. This result indicates that the β -CDX3 is the best grade adsorbent as compare to others and have the highest metal ion removal capacity. This result shows that highest amount of metal ions removal is with best grade β -CD based-xanthate i.e., β -CDX3. While the efficacy of LEPIW treatment for β -CD, β -CDX1, β -CDX2 and β -CDX3 adsorbent has been demonstrated to be 56, 79, 85, and 89% for starting COD: 1000 mg/L, this implies that it might be successful for colored/organic wastewater. The experimental data exhibited a perfect fit for both Langmuir and Freundlich isotherm models in the adsorption of Cu^{2+} and Ni^{2+} ions. This suggests that both physical and chemical phenomena are involved in the adsorption process, signifying monolayer adsorption of Cu^{2+} and Ni^{2+} ions on the β -CDXs adsorbent surface. The kinetic data were perfectly-suited for the pseudo-first-order kinetic model, indicating a chemisorption process. The maximum adsorption capacity was determined to be 534.75 mg/g for Cu^{2+} and 423.72 mg/g for Ni^{2+} ions, respectively.

Acknowledgement

One of the authors (Arbind Chaurasiya) thankfully acknowledges to University Grants Commission (UGC), Department of Higher Education, Ministry of Education, Government of India for providing the Senior Research Fellowship (SRF) for this research work.

Data availability

The information utilized to substantiate the conclusions of this research can be obtained by contacting the corresponding author.

References

- [1] A. Hojjati-Najafabadi, M. Mansoorianfar, T. Liang, K. Shahin, and H. Karimi-Maleh, "A review on magnetic sensors for monitoring of hazardous pollutants in water resources," *Sci. Total Environ.*, vol. 824, p. 153844, Jun. 2022, doi: 10.1016/j.scitotenv.2022.153844.
- [2] P. Govind and S. Madhuri, "Heavy metals causing toxicity in humans, animals and environment," *Res. J. Anim. Vet. Fish. Sci.*, vol. 2, no. 2, pp. 17–23, 2014.
- [3] M. A. Barakat, "New trends in removing heavy metals from industrial wastewater," *Arab. J. Chem.*, vol. 4, no. 4, pp. 361–377, Oct. 2011, doi: 10.1016/j.arabjc.2010.07.019.
- [4] Hina Khatoun and J. P. N. Rai, "Agricultural Waste Materials As Biosorbents for the Removal," *Octa J. Environ. Res.*, vol. 4, no. 3, pp. 208–229, 2016, [Online]. Available: <http://www.sciencebeingjournal.com>
- [5] N. A. A. Qasem, R. H. Mohammed, and D. U. Lawal, "Removal of heavy metal ions from wastewater: a comprehensive and critical review," *npj Clean Water*, vol. 4, no. 1, 2021, doi: 10.1038/s41545-021-00127-0.
- [6] Y. S. Chang *et al.*, "Adsorption of Cu(II) and Ni(II) ions from wastewater onto bentonite and bentonite/GO composite," *Environ. Sci. Pollut. Res.*, vol. 27, no. 26, pp. 33270–33296, Sep. 2020, doi: 10.1007/s11356-020-09423-7.
- [7] Y. B. Onundi, A. A. Mamun, M. F. Al Khatib, and Y. M. Ahmed, "Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon," *Int. J. Environ. Sci. Technol.*, vol. 7, no. 4, pp. 751–758, Sep. 2010, doi: 10.1007/BF03326184.
- [8] M. Fernández-García, A. Martínez-Arias, J. C. Hanson, and J. A. Rodriguez, "Nanostructured Oxides in Chemistry: Characterization and Properties," *Chem. Rev.*, vol. 104, no. 9, pp. 4063–4104, Sep. 2004, doi: 10.1021/cr030032f.

- [9] M. S. Mauter and M. Elimelech, "Environmental Applications of Carbon-Based Nanomaterials," *Environ. Sci. Technol.*, vol. 42, no. 16, pp. 5843–5859, Aug. 2008, doi: 10.1021/es8006904.
- [10] M. Varsha, P. Senthil Kumar, and B. Senthil Rathi, "A review on recent trends in the removal of emerging contaminants from aquatic environment using low-cost adsorbents," *Chemosphere*, vol. 287, p. 132270, Jan. 2022, doi: 10.1016/j.chemosphere.2021.132270.
- [11] G. C. Panda, S. K. Das, and A. K. Guha, "Biosorption of cadmium and nickel by functionalized husk of *Lathyrus sativus*," *Colloids Surfaces B Biointerfaces*, vol. 62, no. 2, pp. 173–179, Apr. 2008, doi: 10.1016/j.colsurfb.2007.09.034.
- [12] Z. D. Liu and R. C. Hider, "Design of iron chelators with therapeutic application," *Coord. Chem. Rev.*, vol. 232, no. 1–2, pp. 151–171, Oct. 2002, doi: 10.1016/S0010-8545(02)00050-4.
- [13] A. Al-Fahdawi and E. Alsalihi, "Synthesis and Characterization of Iron(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Complexes Using Diphenylmethyl Xanthate Ligand," *ARO-The Sci. J. Koya Univ.*, vol. 6, no. 1, pp. 33–37, May 2018, doi: 10.14500/aro.10243.
- [14] S. Vastag, L. Markó, and A. L. Rheingold, "Mononuclear cobalt carbonyls containing monodentate thiolate or xanthate groups. The structures of $\text{PhSCo}(\text{CO})_2(\text{PPh}_2\text{OMe})_2$ and $\text{MeOCS}_2\text{Co}(\text{CO})_2(\text{PPh}_2\text{iBu})_2$," *J. Organomet. Chem.*, vol. 397, no. 2, pp. 231–238, Nov. 1990, doi: 10.1016/0022-328X(90)80241-Q.
- [15] R. Sachar and S. Kapoor, "Synthesis and characterization of the adducts of Bis(O-ethylthiocarbonato)nickel(II) with substituted pyridines," *Orient. J. Chem.*, vol. 25, no. 4, pp. 1133–1136, 2009, doi: 10.1155/2013/502856.
- [16] H.-T. Kim and K. Lee, "Application of insoluble cellulose xanthate for the removal of heavy metals from aqueous solution," *Korean J. Chem. Eng.*, vol. 16, no. 3, pp. 298–302, May 1999, doi: 10.1007/BF02707116.
- [17] Y. Zhang *et al.*, "Modified adsorbent hydroxypropyl cellulose xanthate for removal of Cu^{2+} and Ni^{2+} from aqueous solution," *Desalin. Water Treat.*, vol. 57, no. 56, pp. 27419–27431, 2016, doi: 10.1080/19443994.2016.1177733.
- [18] S. LIANG, X. GUO, N. FENG, and Q. TIAN, "Effective removal of heavy metals from aqueous solutions by orange peel xanthate," *Trans. Nonferrous Met. Soc. China*, vol. 20, pp. s187–s191, May 2010, doi: 10.1016/S1003-6326(10)60037-4.
- [19] L. XIA, Y. HU, and B. ZHANG, "Kinetics and equilibrium adsorption of copper(II) and nickel(II)

- ions from aqueous solution using sawdust xanthate modified with ethanediamine,” *Trans. Nonferrous Met. Soc. China*, vol. 24, no. 3, pp. 868–875, Mar. 2014, doi: 10.1016/S1003-6326(14)63137-X.
- [20] H. Kim and H. M. Removal, “Application of Insoluble Cellulose Xanthate for the Removal of Heavy Metals from Aqueous Solution,” vol. 16, no. 3, pp. 298–302, 1999.
- [21] S. Sharan *et al.*, “Treatment of lignin enriched paper industry wastewater by electrocoagulation: Modelling approach and economic evaluation,” *Chem. Eng. Res. Des.*, vol. 197, pp. 708–720, Sep. 2023, doi: 10.1016/j.cherd.2023.07.034.
- [22] S. B. Rahardjo, T. E. Saraswati, A. Masykur, N. N. F. Finantrena, and H. Syaima, “Synthesis and Characterization of Tetrakis(2-amino-3-methylpyridine)copper(II) Sulfate Tetrahydrate,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 349, p. 012056, Apr. 2018, doi: 10.1088/1757-899X/349/1/012056.
- [23] Q. Mohammed Salman, “Spectroscopic study of UV-VIS electronic transitions of Ni 2+ ions in different phases of Sol-Gel process,” *J. Univ. Kerbala*, vol. 14, no. 4, 2016, [Online]. Available: <https://www.iasj.net/iasj?func=fulltext&aId=118310>
- [24] A. Chaurasiya, P. P. Pande, R. Shankar, A. Nath, and N. P. Tripathi, “Synthesis and characterization of pectin-xanthate and their application in heavy metal and lignin enriched paper industry wastewater treatment,” *Sep. Sci. Technol.*, pp. 1–17, Nov. 2023, doi: 10.1080/01496395.2023.2279942.
- [25] Y. Zhang *et al.*, “Modified adsorbent hydroxypropyl cellulose xanthate for removal of Cu 2+ and Ni 2+ from aqueous solution,” *Desalin. Water Treat.*, vol. 57, no. 56, pp. 27419–27431, Dec. 2016, doi: 10.1080/19443994.2016.1177733.
- [26] R. M. Silverstein and G. C. Bassler, “Spectrometric identification of organic compounds,” *J. Chem. Educ.*, vol. 39, no. 11, p. 546, Nov. 1962, doi: 10.1021/ed039p546.
- [27] G. T. Rekso, “Chemical and Physical Properties of Cassava Starch–CM–Chitosan–Acrylic Acid Gel Copolymerization by Gamma Irradiation,” *Indones. J. Chem.*, vol. 14, no. 1, pp. 37–42, Mar. 2014, doi: 10.22146/ijc.21265.
- [28] F. J. Stevenson and K. M. Goh, “Infrared spectra of humic acids and related substances,” *Geochim. Cosmochim. Acta*, vol. 35, no. 5, pp. 471–483, May 1971, doi: 10.1016/0016-7037(71)90044-5.
- [29] A. Mahmood, M. Ahmad, R. M. Sarfraz, and M. U. Minhas, “β-CD based hydrogel microparticulate system to improve the solubility of acyclovir: Optimization through in-vitro, in-vivo and

- toxicological evaluation,” *J. Drug Deliv. Sci. Technol.*, vol. 36, pp. 75–88, Dec. 2016, doi: 10.1016/j.jddst.2016.09.005.
- [30] J. Shaikh, S. V. Deshmane, R. N. Purohit, and K. R. Biyani, “BEHAVIOURAL STUDY OF CYCLODEXTRIN INCLUSION COMPLEX ON ENHANCEMENT OF SOLUBILITY OF ACECLOFENAC,” *INDIAN DRUGS*, vol. 52, no. 11, pp. 19–23, Nov. 2015, doi: 10.53879/id.52.11.10325.
- [31] H. N. Tran, S.-J. You, and H.-P. Chao, “Effect of pyrolysis temperatures and times on the adsorption of cadmium onto orange peel derived biochar,” *Waste Manag. Res. J. a Sustain. Circ. Econ.*, vol. 34, no. 2, pp. 129–138, Feb. 2016, doi: 10.1177/0734242X15615698.
- [32] H.-J. Schneider, F. Hacket, V. Rüdiger, and H. Ikeda, “NMR Studies of Cyclodextrins and Cyclodextrin Complexes,” *Chem. Rev.*, vol. 98, no. 5, pp. 1755–1786, Jul. 1998, doi: 10.1021/cr970019t.
- [33] E. Meez, A. Rahdar, and G. Z. Kyzas, “Sawdust for the Removal of Heavy Metals from Water: A Review,” *Molecules*, vol. 26, no. 14, p. 4318, Jul. 2021, doi: 10.3390/molecules26144318.
- [34] Z. U. Zango and S. Shehu Imam, “Evaluation of Microcrystalline Cellulose from Groundnut Shell for the Removal of Crystal Violet and Methylene Blue,” *Nanosci. Nanotechnol.*, vol. 8, no. 1, pp. 1–6, 2018, doi: 10.5923/j.nn.20180801.01.
- [35] T. S. Anirudhan and S. S. Sreekumari, “Synthesis and characterization of a functionalized graft copolymer of densified cellulose for the extraction of uranium(VI) from aqueous solutions,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 361, no. 1–3, pp. 180–186, May 2010, doi: 10.1016/j.colsurfa.2010.03.031.
- [36] J. Duan *et al.*, “Synthesis of a novel flocculant on the basis of crosslinked Konjac glucomannan-graft-polyacrylamide-co-sodium xanthate and its application in removal of Cu²⁺ ion,” *Carbohydr. Polym.*, vol. 80, no. 2, pp. 436–441, Apr. 2010, doi: 10.1016/j.carbpol.2009.11.046.
- [37] Y. P. Kumar, P. King, and V. S. R. K. Prasad, “Removal of copper from aqueous solution using *Ulva fasciata* sp.—A marine green algae,” *J. Hazard. Mater.*, vol. 137, no. 1, pp. 367–373, Sep. 2006, doi: 10.1016/j.jhazmat.2006.02.010.
- [38] O. E. Abdel Salam, N. A. Reiad, and M. M. ElShafei, “A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents,” *J. Adv. Res.*, vol. 2, no. 4, pp. 297–303, Oct. 2011, doi: 10.1016/j.jare.2011.01.008.

- [39] A. Nath, Anamica, P. Prakash Pande, and R. Sahankar, "Synthesis of Disaccharide-Based Xanthates for the Removal of Some Heavy Metals from Aqueous Solutions," *Iran. J. Chem. Chem. Eng.*, vol. 41, no. 4, pp. 1137–1150, 2022, doi: 10.30492/IJCCE.2021.127412.4123.
- [40] A. G. Ibrahim, A. S. Saleh, E. M. Elsharma, E. Metwally, and T. Siyam, "Chitosan-g-maleic acid for effective removal of copper and nickel ions from their solutions," *Int. J. Biol. Macromol.*, vol. 121, pp. 1287–1294, Jan. 2019, doi: 10.1016/j.ijbiomac.2018.10.107.
- [41] Y. . Ho and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochem.*, vol. 34, no. 5, pp. 451–465, Jul. 1999, doi: 10.1016/S0032-9592(98)00112-5.
- [42] K. B. Dawadi, M. Bhattarai, and P. L. Homagai, "Adsorptive Removal of Methyl Red from Aqueous Solution using Charred and Xanthated Sal (*Shorea robusta*) Sawdust," *Amrit Res. J.*, vol. 1, no. 1, pp. 37–44, Sep. 2020, doi: 10.3126/arj.v1i1.32451.
- [43] S. Chakraborty and V. Tare, "Role of various parameters in synthesis of insoluble agrobased xanthates for removal of copper from wastewater," *Bioresour. Technol.*, vol. 97, no. 18, pp. 2407–2413, Dec. 2006, doi: 10.1016/j.biortech.2005.10.010.
- [44] L. Dong *et al.*, "Characterization and Mechanistic Study of Heavy Metal Adsorption by Facile Synthesized Magnetic Xanthate-Modified Chitosan/Polyacrylic Acid Hydrogels," *Int. J. Environ. Res. Public Health*, vol. 19, no. 17, p. 11123, Sep. 2022, doi: 10.3390/ijerph191711123.
- [45] S. Liang, X. Y. Guo, N. C. Feng, and Q. H. Tian, "Effective removal of heavy metals from aqueous solutions by orange peel xanthate," *Trans. Nonferrous Met. Soc. China (English Ed.)*, vol. 20, no. SUPPL.1, pp. s187–s191, 2010, doi: 10.1016/S1003-6326(10)60037-4.
- [46] S. Wu *et al.*, "Fabrication of xanthate-modified chitosan/poly(N-isopropylacrylamide) composite hydrogel for the selective adsorption of Cu(II), Pb(II) and Ni(II) metal ions," *Chem. Eng. Res. Des.*, vol. 139, no. Ii, pp. 197–210, 2018, doi: 10.1016/j.cherd.2018.09.035.