International Journal of Applied Sciences: Current and Future Research Trends
(IJASCFRT)
ISSN: 2790-3990

https://ijascfrtjournal.isrra.org/index.php/Applied_Sciences_Journal

Capture and Removal of Heavy Metals from an Aqueous Media by Polymeric Adsorption

Rafia Sharif[a*], Prof. Azhari Hamid Nour[b], Dr. Issa Ismail Mohammed Ahmed[c]

[a,b]*International University of Africa, GHJ9+933, Madani St, Khartoum 12223,Khartoum ,Sudan*
[a]*Email: rafiasharif90@gmail.com,* [b]*Email: azharihamid@iua.edu.sd*

Abstract

In the present study, a bio-based composite was prepared by reacting chitosan and carboxymethyl cellulose (CMC) with citric acid (CA) and its ability to remove heavy metals [Cr (VI), Pb (II), Ni (II), Zn (II), Cu (II)] from an aqueous media were investigated. The best removal efficiency of heavy metals was noticed for the bio-based composite which were characterized by Fourier-transform Infrared Spectroscopy (FT-IR), Scanning electron microscopy (SEM) and Thermo gravimetric analysis (TGA). The effects of pH, contact time and the initial concentrations of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) on adsorption process were studied. The optimum conditions for the adsorption of heavy metals on chitosan/CMC bio-based composites were found between pH 2-6 and a contact time between 5-10 mints and initial concentration between 50-70 ppm. The FT-IR spectrum of chitosan/CMC with CA composite was clearly shown the presence of a peak at 1736 cm^{-1} which represents the formation of ester linkages between the two polymers (the citrate crosslinks). The SEM results were shown the homogeneous morphology of the composite. Around 50%-90% of heavy metals were removed from an aqueous media by chitosan/CMC bio-based composite. Furthermore, the results have shown that the adsorption process follows a pseudo-second order rate model generally while the Langmuir-Freundlich adsorption isotherm provides the best fit with a maximum adsorption capacity from 33.77 to 82.24 mg/g at 25 oC.

Keywords: Bio-based Composite; Cross linker; Chitosan/CMC; Citric Acid; Langmuir-Freundlich Adsorption isotherm.

1. Introduction

The removal of agricultural and industrial pollutants from sewage treatment and the possibility of re-use of water for agricultural purposes is the hottest topic, for most, of research papers now days. The chemical contaminants are the most harmful types of contaminants found in water. They are non- biodegradable and highly toxic. The most toxic heavy metals are lead, mercury and chromium [1].

---

* Corresponding author.

Because of economical and environmental concerns, researchers are trying to replace the synthetic polymers by naturally occurring polymer composites for the maximum utilization of bio-polymers in different areas of applications. The application of biopolymers in water treatment was thoroughly studied [2].

The various adsorbents like activated carbons, plant or lignocellulosic wastes, clays and biopolymers are among the common adsorbents used to remove different types of dyes and heavy metal ions from the wastewater. Chitosan is a good adsorbent biopolymer which is used to remove various kinds of anionic, cationic dyes and heavy metal ions [3]. Cellulose and chitosan being the first two abundant biopolymers in nature offer wide opportunities to be utilized for high–end applications such as water purification [4].

The reason for using polymer based composite is that they have strong chelating property with metals. Specifically, polymer-based nanocomposites have good physical, chemical and mechanical properties, as well as stronger compatibility [5], for example alginates and hybrid natural polymers have been used after preparing by sol gel method, or natural polymer based composite due to the presence of a number of free hydroxyl and carboxyl groups [6]. Natural polymers had restriction in term of their fixed structure and few functional groups. This issue has been solved by cross linking of two or more natural polymers for enhancing their physical properties as well as polysaccharide structure stability in aqueous medium [7].

II. Materials and method

2.1 Chemicals

Chitosan with deacetylation of 93% (Moisture ≤ 10%, Faint Beige to Beige powder) was obtained from Oxford Lab Co., Ltd (India) and used as it received. Carboxymethyl cellulose sodium salt (High viscosity) was supplied by Trust Chemical Laboratories (TCL) (India) and they were used as received. Citric acid Monohydrate (2-hydroxy-1, 2, 3-propanetricarboxylic acid monohydrate, M.W. 210.14) was supplied from CDH Fine Chemicals (India). Acetic acid (99.5%, Extra Pure), was purchased from LOBA Chemie LABORATORY REAGENTS & FINE CHEMICALS (India). Sulfuric acid was obtained from CDH Fine Chemicals (India). 1,5-diphenyl carbazide (m.p.173-176^{o}C, molecular mass,242.28g/mol) LabChem (USA). Acetone, CDH Fine Chemicals (India). Potassium dichromate ($K_2Cr_2O_7$) was purchased from CDH Fine Chemicals (India).

2.2 Preparation of chitosan/CMC bio-based composite samples

Stock solution of 1000 ppm acetic acid (AA) was prepared using 20 mL of the acid, completed to the mark in 1 liter volumetric flask using distilled water. This stock solution was used to dissolve chitosan, CMC and CA. Detailed method of preparation of composite samples is shown in Table 1.1. In each case, after the materials were mixed according to Table 3.1 the resulting solution was left for 48 hours, centrifuged (for 5 minutes), the deposited composite was washed thoroughly with distilled water and left to dry.

The resulting bio-based composite was used for the adsorption of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) from aqueous solution.

Table 2.1: Preparation of composite samples.

sample	Chitosan Solution in AA (g/ml)	CMC solution in AA (g/ml)	CA solution in AA (g/ml)	Total Volume (ml)	Amount of composite (g)
C1	0.1/40	0.9/50	0.0275/10	100	0.74
C2	0.1/100	0.9/90	0.0500/10	200	0.79
C3	0.5/150	0.5/140	0.0500/10	300	0.45
C4	0.1/100	0.9/95	0.0050/5	200	0.82
C5	0.9/150	0.1/140	0.0275/10	300	0.02
C6	0.5/150	0.5/145	0.0050/5	300	0.39
C7	0.5/100	0.5/90	0.0275/10	200	0.45
C8	0.5/40	0.5/50	0.0500/10	100	0.49
C9	0.9/100	0.1/90	0.0500/10	200	0.09
C10	0.1/150	0.9/140	0.0275/10	300	0.67
C11	0.9/40	0.1/50	0.0275/10	100	0.09
C12	0.5/100	0.5/90	0.0275/10	200	0.43
C13	0.5/45	0.5/50	0.0050/5	100	0.54
C14	0.9/100	0.1/95	0.0050/5	200	0.05
C15	0.5/100	0.5/90	0.0275/10	200	0.38

2.3 Removal of Cr(VI), Cu(II), Pb(II), Ni(II) and Zn(II) from aqueous solution using chitosan/CMC bio-based composite

A 1000 ppm Stock solutions of chromium(VI), copper(II),lead(II),nickel(II) and zinc(II) were prepared by dissolving a 0.2829g of potassium dichromate,0.393g of copper sulphate,0.159g of lead nitrate,0.405g of nickel chloride,0.2896g of zinc nitrate in distilled water and completed to the mark in 1 liter volumetric flask. From the previous stock solutions of chromium(VI),copper(II),lead(II),nickel(II) and zinc(II) another standard solutions of chromium(VI), copper(II),lead(II),nickel(II) and zinc(II) having 50 ppm concentrations were prepared and used for adsorption experiments. In a typical experiment, 10 mL of 50 ppm stock solutions of each metal salt solution was taken into 50mL of a plastic beaker and 0.02 g of bio-based composite was added and well stirred for 7 minutes. The beaker with its content was left for 24 hours at ambient conditions and Atomic absorption spectroscopy was used to determine the concentration of the remaining chromium (VI), copper (II), lead (II), nickel (II) and zinc (II)

2.4 Determination of Cr(VI), Cu(II), Pb(II), Ni(II) and Zn(II) concentration by atomic absorption spectroscopy using bio-based composite

AA500-Graphite Furnace-Atomic Absorption Spectrophotometer (PG Instruments) was used to determine the concentration of the remaining chromium (VI), copper (II), lead (II), nickel (II) and zinc (II)

The following analysis parameters were used:

Analytical line: 357.9 nm

Bandwidth: 0.4 nm

Filter factor: 1.0

Lamp current: 5.0 ma

Integration time: 3.0 sec

Background: None/SR

Flame type: N2O/Acetylene

Flame setting: Reducing Red Feather

Sensitivity: 0.05 mg/L

Detection limit: 0.005 mg/L

Working Range: 0.04-8.0 mg/L

A stock solution of chromium(VI), copper(II),lead(II),nickel(II) and zinc(II) having 1000 ppm concentration was used to prepare series of standard solutions (5, 10, 15, 20 and 25 ppm) of chromium(VI), copper(II),lead(II),nickel(II) and zinc(II).All solutions were acidified with 1% nitric acid to avoid precipitation. The efficiency was determined using the following equation:

$$\%E = \frac{Ci - Cf}{Ci} \text{ X } 100 \qquad (1.1)$$

Where Ci and Cf represent the initial and final concentrations of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II).

2.5.Determination of Cr(VI), Cu(II), Pb(II), Ni(II) and Zn(II) concentration by UV/Visible spectrophotometry using bio-based composite

The chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) concentrations in aqueous solutions was determined by JENWAY 7205 UV/Visible-spectrophotometer at 540-580 nm using 1,5-diphenylcarbazide (DPC) method for the Standard solution of Cr(VI) [8] and Xylenol orange method [9] for the Standard solutions of copper (II), lead (II), nickel (II) and zinc (II) with 50 ppm concentration was prepared from 1000 ppm stock solution of copper (II), lead (II), nickel (II) and zinc (II).Series of standard chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) solutions having different concentrations of 0.2, 0.4, 0.5, 0.8, and 1 ppm were prepared from the 50 ppm stock solution of Cr(VI). 1.0 mL of each of the standard Cr(IV) solutions was mixed with 9.0 mL of 0.2 M H_2SO_4 in a 10 mL volumetric flask then 0.2 mL of freshly prepared 0.25% (w/v) DPC in acetone was added into the volumetric flask. The mixture was stirred in a plastic beaker for 30 seconds and then let to stand for 15 minutes for full color development. The absorbance of the colored solution was measured at λmax 540 nm using distilled water as a reference, while the Series of standard copper (II), lead (II), nickel (II) and

zinc (II) metal ions solutions having different concentrations of 0.2, 0.4, 0.5, 0.8, and 1 ppm were prepared from the 50 ppm stock solution of copper (II), lead (II), nickel (II) and zinc (II).In a 100mL volumetric flask 0.2g of Xylenol Orange with 2.0mL of buffer solution of sodium acetate was added and dissolved with distilled water. In a typical experiment,0.1mL of each of the standard copper (II), lead (II), nickel (II) and zinc (II) solutions in a 10 mL volumetric flask with 0.1mL of freshly prepared Xylenol Orange was used. The mixture was stirred in a plastic beaker for 30 seconds and then let to stand for 15 minutes for full color development. The absorbance of the colored solution was measured at λmax 580 nm using distilled water as a reference. The absorbance-concentrations calibration curve was plotted with a correlation coefficient, of 0.9998. For the adsorption experiment, 10mL of 50 ppm chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) standard solution was taken into a conical flask and 0.02g of bio-based composite sample was added. The content was stirred for 7 minutes and the concentration of the remaining chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) was determined by UV/Visible spectrophotometry method for the standard chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) solutions. Absorbed chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) was calculated by equations 2.2 and 2.3

$$q_e = \frac{(c_o - c_f)V}{m} \quad (2.2)$$

$$q_t = \frac{(c_o - c_t)V}{m} \quad (2.3)$$

Where qe is the equilibrium adsorption capacity, qt adsorption capacity at time t, Co and Cf are the initial and final chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) concentrations, respectively, V is the volume of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) solution in a liter and m is the mass of the adsorbent in grams. Same experiment was repeated for finding out the Cr (VI), Cu (II), Pb(II), Ni(II) and Zn(II) concentration from aqueous solutions by bio-based composite.

2.5. Fourier Transform Infrared analysis

The infrared spectra of CMC, chitosan, bio-based composite and modified composite were obtained using Fourier transform infrared spectrometer, FT-IR, Shimadzu (model 8400S - Japan). Few milligrams of the each sample were mixed thoroughly with sufficient amount of KBr and pressed to form a transparent disk. The infrared spectrum was recorded between 400 and 4000 cm-1 using a resolution of 4cm-1 and 8 numbers of scans.

2.6. Scanning electron microscopy

SEM was used to investigate the morphology of the modified and bio-based composite samples through an InspectTM Scanning Electron Microscope (Inspect S50, Japan). 0.02g of sample was frozen under liquid nitrogen, mounted, sputter-coated with gold and allowed to dry in a vacuum system. The dried sample was viewed using an accelerating voltage of 5.00 kV.

2.7. Thermo gravimetric analysis

Thermogravimetric analysis was carried out using a Simultaneous Thermal Analyzer Neztsch STA449 F3 Jupiter. The analysis was carried out under nitrogen gas flow from room temperature to 700°C at a heating rate of 10°C/min.

2.8. Effect of time on removal of Cr (VI), Cu (II), Pb(II), Ni(II) and Zn(II) from aqueous solutions by bio-based composite

The effect of contact time on removal of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) was studied using bio-based composite. Contact times of 1, 2, 3, 4, 5, 7, 10, 12 and 15 minutes were selected to carry out the experimental work. Standard solution of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) with 50 ppm concentration was prepared from stock solution (1000 ppm) of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) and used for adsorption experiments. In a typical experiment, 10 ml of 50 ppm standard solutions of each metal was taken into a plastic beaker and 0.02g of bio-based composite was added and stirred well for 1 minute using a magnetic stirrer at ambient conditions and the remaining chromium (VI), copper (II), lead (II), nickel (II) and zinc (II)) was determined using UV/VIS spectrophotometry. Exactly typical steps were repeated but at different contact times of 2, 3, 4, 5, 7, 10, 12 and 15 minutes. A plot of the equilibrium adsorption capacity versus contact time was plotted.

2.9 Effect of pH on removal of Cr (VI), Cu (II), Pb(II), Ni(II) and Zn(II) from aqueous solutions by bio-based composites

To determine the effect of pH the experiments were carried out at different pH values 2, 4, 6, 8 and 10. Standard solution of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) with 50 ppm concentration was prepared from 1000 ppm stock solution of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) and used for adsorption experiments. In a typical experiment, 10 ml of 50 ppm standard solution was taken into 50 ml beaker and the pH was adjusted to 2, 4, 6, 8 and 10 using 0.1M NaOH or 0.1M HCl solutions with the aid of a pH-meter. 0.02g of bio-based composite was added to contents of the beaker and stirred for 5 min on a magnetic stirrer at 150 rpm and then allowed to settle for 5 min to reach the equilibrium at ambient conditions. The remaining chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) was determined using UV/VIS spectrophotometry. A plot of the equilibrium adsorption capacity versus pH was carried out.

2.10 Effect of initial concentration on removal of Cr (VI), Cu (II), Pb(II), Ni(II) and Zn(II) from aqueous solutions by bio-based composite

The adsorption capacity of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) was studied at different concentrations 10, 20, 30, 40, 50 and 70 ppm. Standard solution of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) with 50 ppm concentration was prepared from stock solution (1000 ppm) of chromium (VI), copper (II), lead (II), nickel (II) and zinc (II) and used for adsorption experiments. In a typical experiment, 10 mL of 10 ppm standard solution was taken into a 50 mL beaker and 0.02 g of the bio-based composite was added and stirred well for 7 minutes using a magnetic stirrer at pH 5 which was previously adjusted using 0.1M HCl or 0.1M NaOH with the aid of a pH-meter. The remaining chromium (VI), copper (II), lead (II), nickel (II)

and zinc (II) was determined using UV/VIS spectrophotometry. The whole experiment was repeated again but using 20, 30, 40, 50, 60, 70, 80, 90 and 100 ppm of Cr (VI) in each case.

III. Results And Discussion

3.1 Optimization of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) uptake

To determine the polymer blend with the highest removal efficiency for chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) a series of experiments were carried out by varying the amounts of chitosan and CMC, the volumes of the stock solution of acetic acid that were used to dissolve the chitosan, CMC and citric acid and the amount of citric acid as a crosslinker. The initial and final concentrations of chromium (VI) were determined by atomic absorption spectroscopy and the results are shown in Table 3.1. As it is evident from the Table 3.1, sample bio-based composite) has the highest removal efficiency and hence were selected for further experimental work regarding the effects of different parameters on removal efficiency as well as adsorption kinetic and adsorption isotherms.

Table 3.1: Initial, final and maximum efficiency of Cr (VI), Cu (II), Pb (II), Ni (II) and Zn(II) concentration.

Sample	C_i	C_f	%E
C1	51.866	34.348	34
C2	51.866	30.970	40
C3	51.866	37.726	27
C4	51.866	34.348	34
C5	51.866	34.911	33
C6	51.866	33.222	36
C7	51.866	30.970	40
C8	51.866	23.652	54
C9	51.866	11.827	77
C10	51.866	17.907	65
C11	51.866	5.576	89
C12	51.866	21.622	58
C13	51.866	31.418	39
C14	51.866	17.907	65
C15	51.866	35.133	32

3.1.1 FTIR analysis

Figure 3.1, shows the infrared spectrum of chitosan. The band at around 3000 to 3600 cm^{-1} is characteristic of aromatic secondary amine N-H and –OH stretching vibrations.

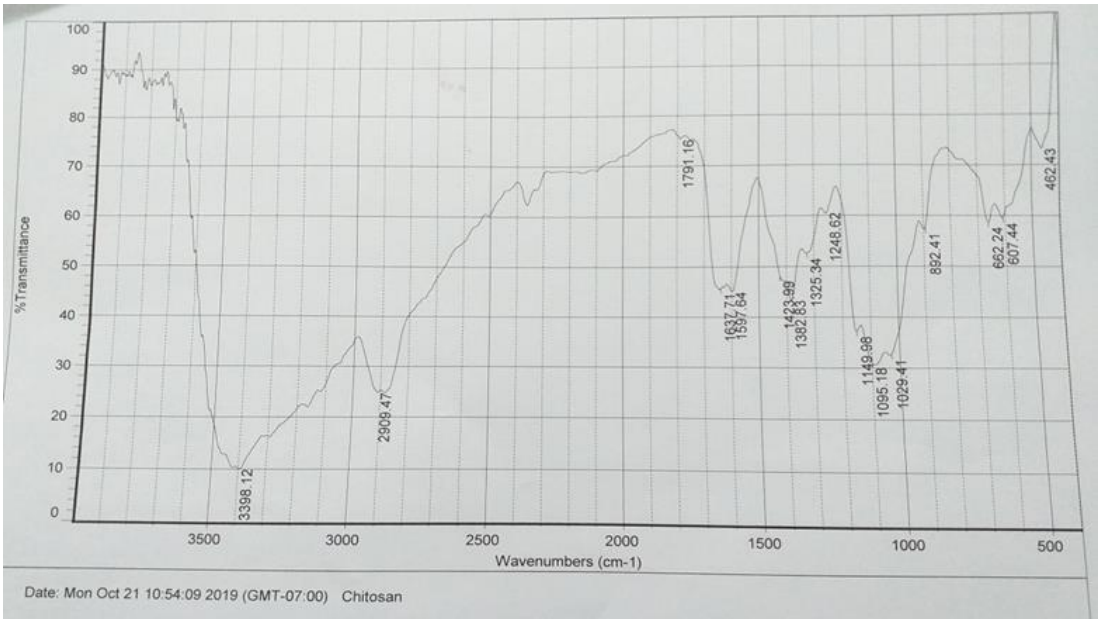


Figure 3.1: FTIR spectrum of chitosan polymer.

The absorption band at 2909 cm^{-1} is attributed to the C-H stretching vibration. The band at 1637 is due to the bending vibration of –OH group. The adsorption band at 1598 cm^{-1} shows the presence Of C=C asymmetrical stretches. The presence of symmetrical band C=C are confirmed by the bands at around 1637 cm^{-1}. The CH_2 and –C-N bending are cleared by the presence of bands at around 1423 and 1382 cm^{-1}, respectively. The absorption band at 1149 cm^{-1} also showing the asymmetric stretching of the C-O-C bridge. The bands at 1095 and 1029 cm−1 correspond to C-O stretching [10].Figure 3.2 displays the FTIR spectrum of CMC. As can be seen from the spectrum, the band at 3398 cm^{-1} corresponds to O–H stretching vibrations. The band at 2918 cm^{-1} represents saturated C–H stretching vibration. Finally, peak 1075 cm^{-1} represent the C–O–C stretching vibration [11].

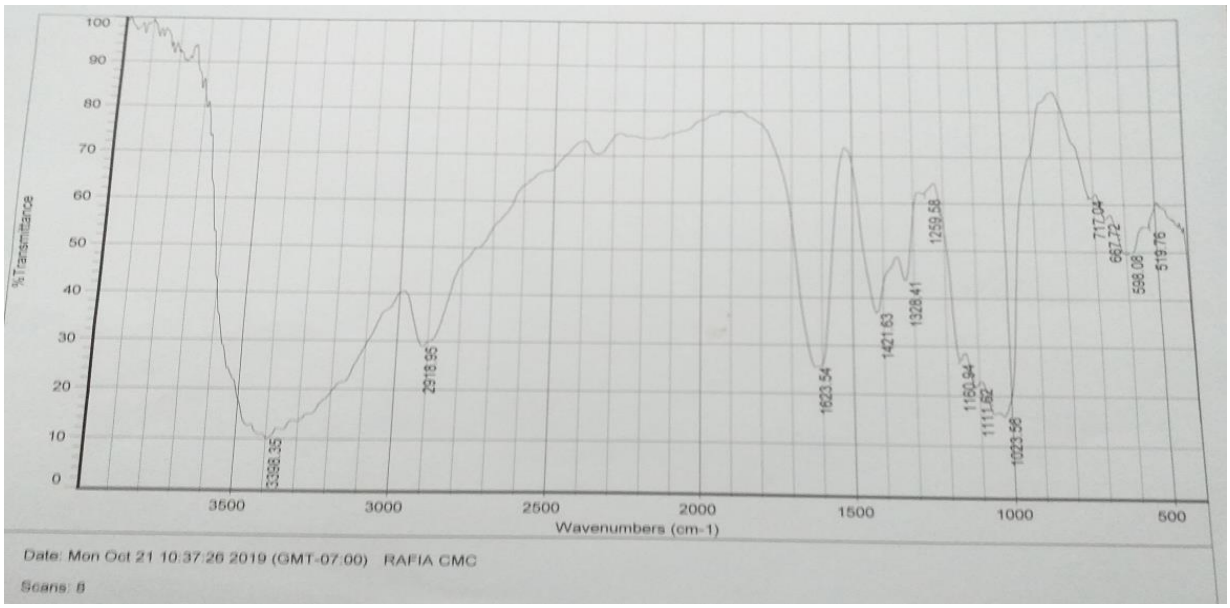


Figure 3.2: FTIR spectrum of CMC polymer.

Figure 3.3 shows the FTIR spectrum of the bio-based sample (C11). As it is evident from the figure, the presence of a peak at 1736 cm^{-1} represents the formation of ester linkages between the two polymers (the citrate crosslinks). The remaining peaks are typically similar to the ones that are shown already in Figures 3.2 and 3.3.The comparison between the FTIR spectra of chitosan and CMC clearly indicated a significant reduction in the absorption band at 1030 cm^{-1} associated with -OH group, which is a strong evidence of the carboxymethylation reaction occurring on the primary alcohol of chitosan [12].

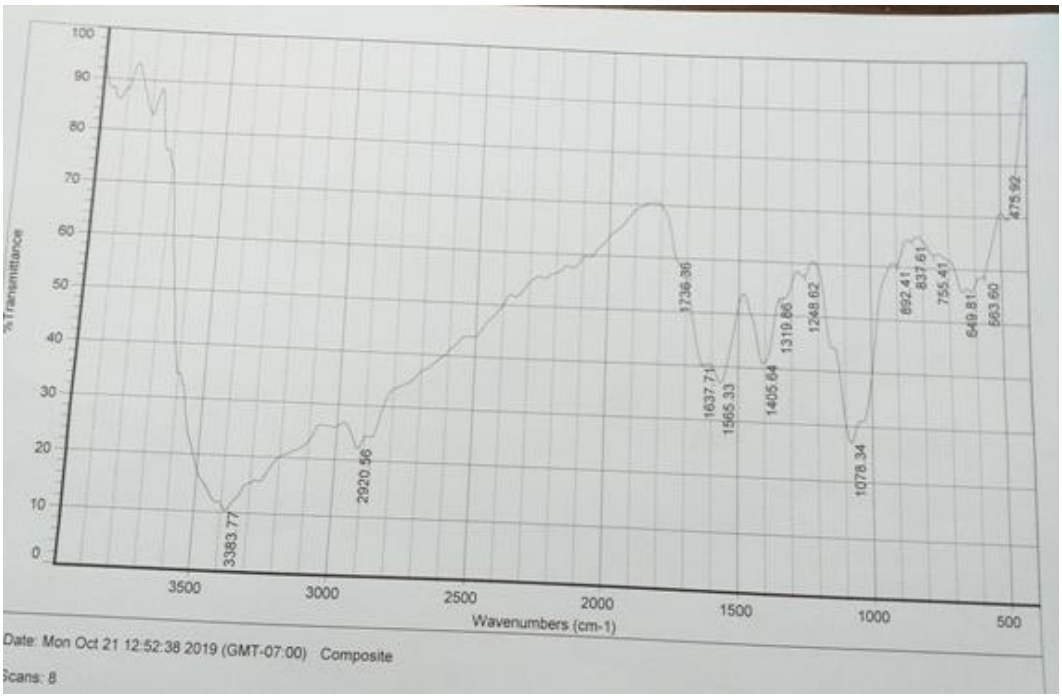


Figure 3.3: FTIR spectrum of bio-based composite sample (C11).

3.1.2 Scanning electron microscopy

SEM analysis in Figure 3.4 shows the morphology of the bio-based. The homogeneity of composite proves that bio-based composite have smooth large surface area for the adsorption of chromium(VI),copper(II),lead (II),nickel (II),and zinc(II).

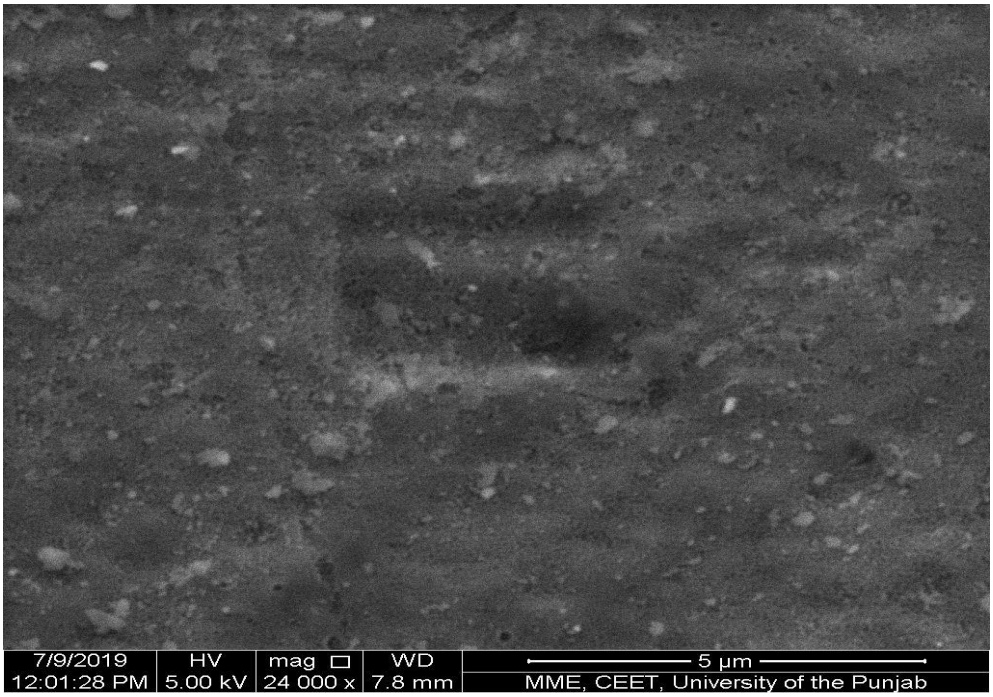


Figure 3.4: SEM micrograph of composite sample (C11).

The composite homogeneous structure made the chitosan/cellulose composite film. However, the porosity of surface can also be seen because of crosslinker particles [13].

3.1.3 Thermogravimetric analysis

As shown in figure 3.5a and 3.5b the initial degradation rate is 100Co. At this stage the CMC and chitosan did not decompose properly and shows only the free water loss. The onset temperature for CMC and chitosan is 277 oC and 274 oC respectively which show a mass loss of 27.01% and 19.80%. The composite TGA curve Figure 3.5c shows the two clear peaks. The first peak is at about 100 Co to 150 oC and second peak rang is 250 oC to 350 oC, shows the mass change 24.82%. The second peak range also shows that it is the main peak where the decomposition occurred due the breaking of bonds. After 350 Co the mass changes is negligible. The bio-based TGA curve also shows that the temperature degradation rate at second peak is less than the second peak degradation rate of CMC and chitosan due to less mass loss of composite and because of crosslinker which provide the stability of the composite [13,14].

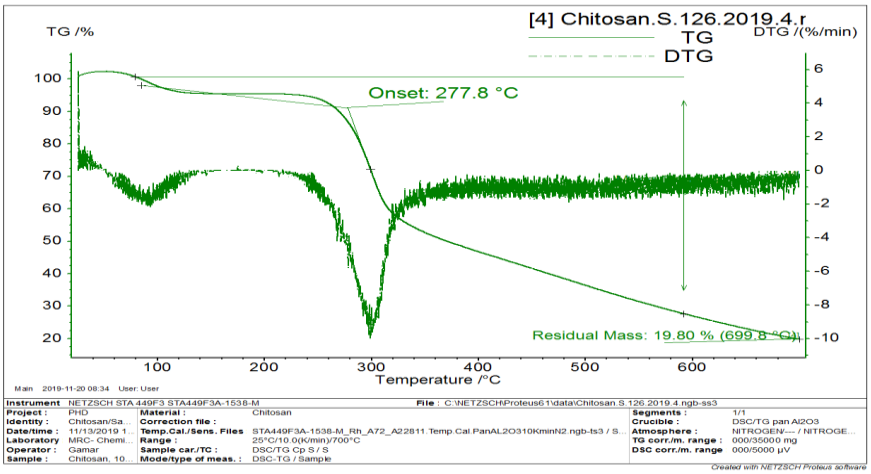


Figure 3.5a: TGA curve of chitosan sample.

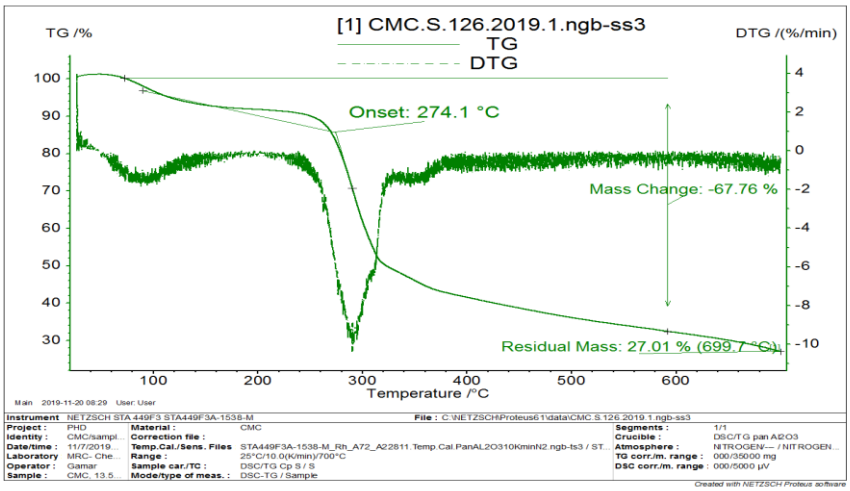


Figure 3.5b: TGA curve of CMC sample.

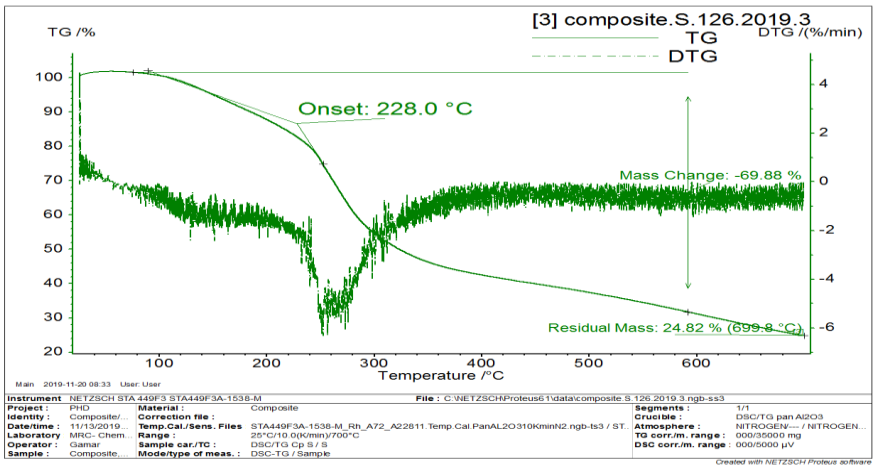


Figure 3.5c: TGA curve of composite sample (C11).

3.2 Effect of time on the removal of Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II) from aqueous solutions using bio-based composite

The effect of time on removal of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) from it is aqueous solutions was investigated using bio-based composite on different times. The initial and the final concentrations of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) were determined using UV/Visible spectrophotometry. The results are displayed in Figure 3.6. As it can be seen from the Figure 3.6, the equilibrium adsorption capacity was increased with time gradually and reached its plateau between 5 to 10 minutes, so 10 minutes were chosen as the optimum time for adsorption experiments.

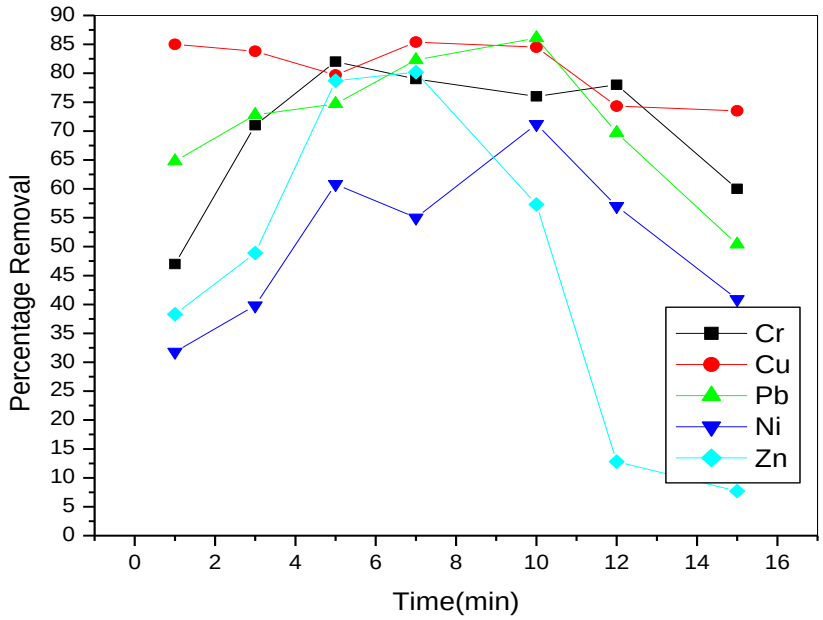


Figure 3.6: Effect of time on removal of Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

Figure 3.6 illustrates the result of comparative study of contact time by using bio-based composite. It is evident that optimum contact time for the bio-based composite was found to be 10 min with maximum removal. The trend of percentage adsorption was shown that with increased contact time there is more time for the chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions to make complex with the adsorbent. According to the results, the adsorbed amount of metal ions was improved by increasing the exposure time [14]. The uptake amount of heavy metal ions onto the bio-based followed the orders: Cu (II)>Cr (VI)>Pb (II)>Zn (II)>Ni (II).The percentage removal of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) by bio-based was 85.2%, 84.6%, 83.5%, 80.4% and 75.9% respectively.

3.3 Effect of initial concentration on removal of Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II) from aqueous solutions using bio-based composite

The effect of initial concentration on removal of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) from it is aqueous solutions were investigated using different concentrations by using bio-based. The initial and the final concentrations of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) were determined using UV/Visible spectrophotometry. It can be seen in Figure. 3.7, when the initial chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) concentration was increased, the amount of substance retained per unit adsorbent mass (qe) increased and the percentage of adsorption decreased. The percentage removal is at its peak on between 50g/mL to 60g/mL. The reason of the decrease in the percentage of adsorption as concentration increases is that the amount of adsorbate per each active site on the adsorbent surface increased, because amount of adsorbent is constant. Thus, as the concentration increases, the amount of adsorbate that cannot be adsorbed by the adsorbent also increases. The reason for the increase in the amount of substance retained per unit adsorbent mass is that the amount of retaining substance increased at the active sites. This allows the adsorbent to approach its maximum capacity [15]. The uptake amount of heavy metal ions onto the bio-based followed the orders: Pb (II)>Cr (VI)>Ni (II)>Zn (II)>Cu (II).The percentage removal of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) by bio-based was 95.2%, 75.6%, 63.5%, 34.4% and 25.9% respectively.

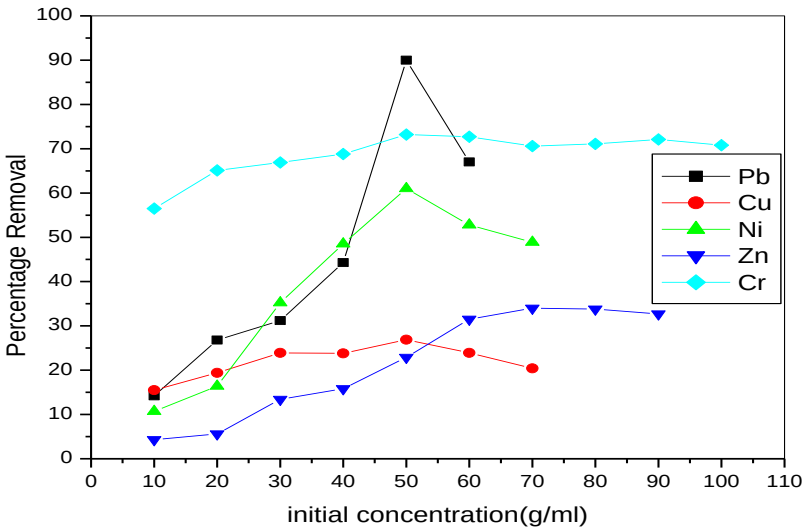


Figure 3.7: Effect of initial concentration on removal of Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

3.4 Effect of pH on removal of Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II) from aqueous solutions using bio-based composite

The effect of pH on removal of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) from it is aqueous solutions were investigated using 2,4,6,8 and 10 pH solutions. The results are displayed in Figure 3.8. As can be seen from the Figure 4.8, the percentage removal was increased with pH decreases and reached its maximum between 2 to 6 pH. With increasing the pH level, the electrostatic repulsive forces between metals ions and negative charge on the surface of the adsorbent becomes strong and resultant reduces the adsorption capacity (Wang and Chen 2014). In the acidic pH range, hydronium ions (H^+) exist in the solution. They have the

potential to protonate the electron-rich groups like amino (NH_2) to ammonium group (NH_3^+), carboxyl group (COO–), hydroxyl group (OH) etc. At lower pH, due to higher (H^+) concentration, more protonation will occur and hence the adsorbent surface will be highly positive. On the other hand, in basic pH range due to the presence of negatively charged hydroxyl groups (OH–), the surface starts having negative charges as well. However, the total charges on the surface also depend on the number of functional groups and the affinity of the functional group to the (H+),and (OH–) ions. Hence, for heavy metal ions existing as negative ions in water, low pH (2–4) is more suitable. On the other hand, heavy metal ions like chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) exist as positive ions only, So negative charged adsorbent surface favors the adsorption [16]. The results of other researches similarly indicate the effect of the pH level on chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) adsorption capacity by different adsorbents [17,18].

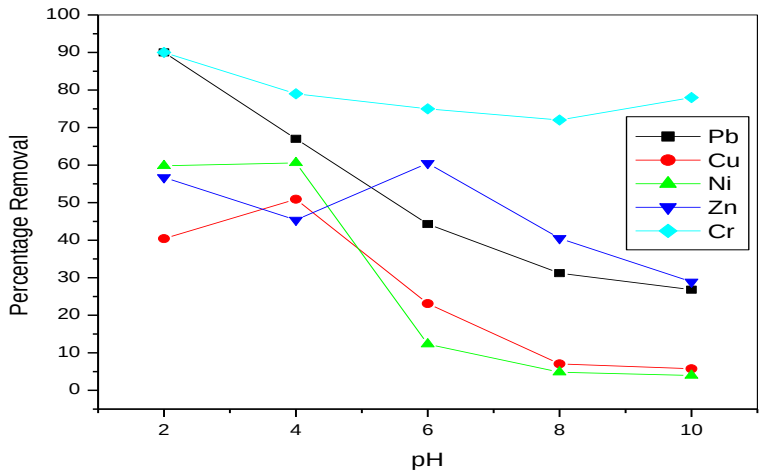


Figure 3.8: Effect of pH on removal of Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

3.5 Adsorption isotherms

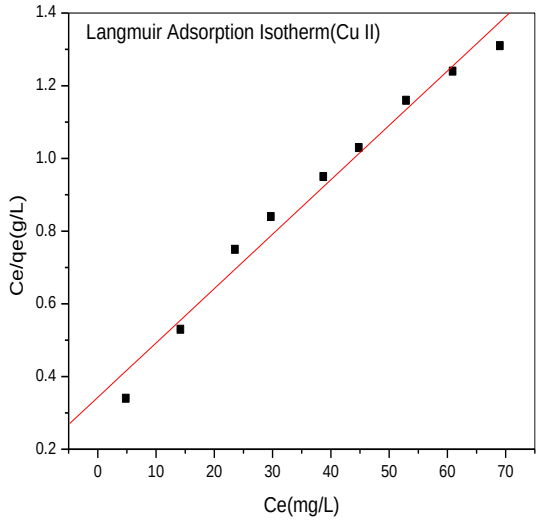
The behaviors like capacity and the interaction between the unmodified adsorbent and chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions at moderate temperature can be described by adsorption isotherms. The adsorption process has been interpreted by applying many isotherms like Langmuir equations 3.7, 3.8, Freundlich equations 3.9, Langmuir- Freundlich 3.10, Temkin equation 3.11 and Dubinin– Radushkevich (DR) adsorption isotherms equation 3.12, 3.13, 3.14 to deduce the adsorption of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions on the bio-based. Linear form of Langmuir adsorption isotherm is given as follow.

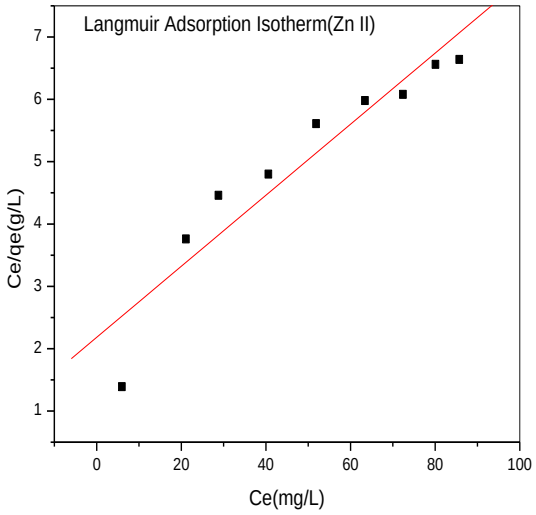
$$\frac{Ce}{qe} = \frac{1}{KLqm} + \frac{Ce}{qm} \qquad (3.7)$$

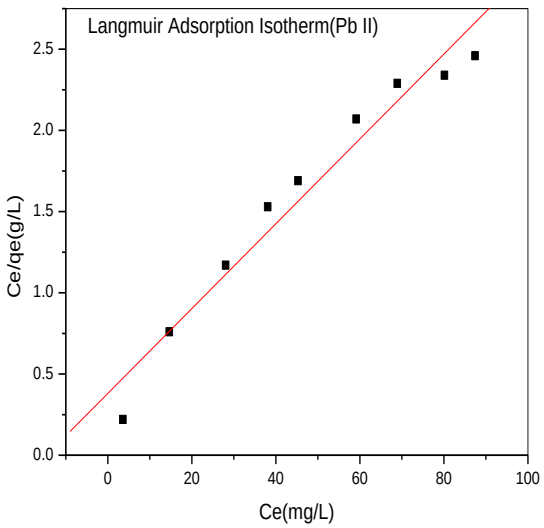
$$RL = \frac{1}{1+KLCo} \qquad (3.8)$$

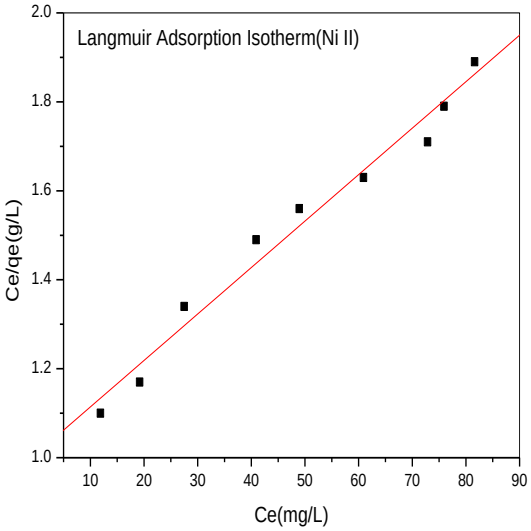
In equation 3.7, qe (mg/g) is the amount of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) adsorbed at equilibrium per unit mass of adsorbent, Ce (mg/L) is the concentration in aqueous solution of

chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions at equilibrium, qm gives the theoretical maximum adsorption capacity, KL describes the affinity of the surface for the solute and Co is the initial chromium (IV), copper (II), lead (II), nickel (II) and zinc (II)concentration. The Langmuir isotherm model indicates formation of a monolayer of adsorbed molecules on the surfaces of adsorbent, with adsorption sites equally available for adsorption and non-interaction between adjacent adsorbed molecules [19].It is also applied to explain the equilibrium inveterate between metal ions in solution and the amount of metal ions adsorbed on the surface of composite [20].Experimental data (ce/qe verses ce) was fitted onto Langmuir isotherm model for copper (II), lead (II), nickel (II) and zinc (II) ions. The value of RL (separation factor) in equation 4.8 gives the information about the adsorption process. RL values indicate the adsorption to be unfavorable when RL > 1, linear when RL = 1, favorable when 0 < RL < 1, and irreversible when RL = 0 [21]. The RL values calculated are represented in Table 4.2 which are between 0 and 1 indicating that, the adsorption of metal ions are favorable [22]. Similar results are available in the literature [23, 24, 25, 26, 27].









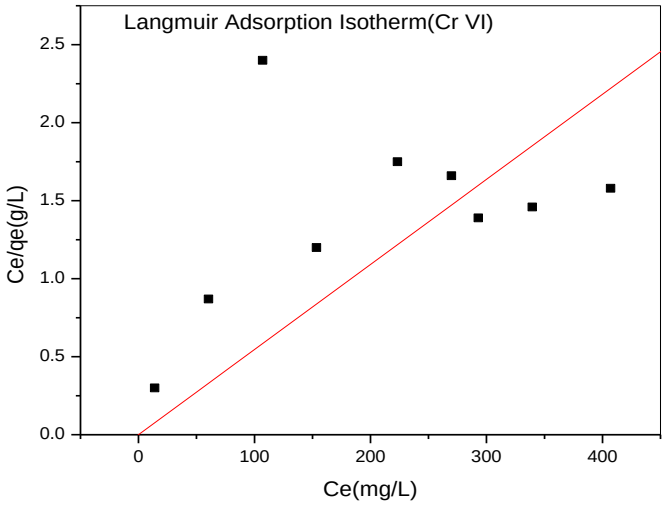


Figure 3.9: Langmuir adsorption isotherm for Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

Freundlich isotherm explains the adsorption processes on heterogonous surfaces as well as it also specifies the relative distribution of the energy and the heterogeneity of the adsorbate sites [28]. The linear form of Freundlich adsorption isotherm is given as follow:

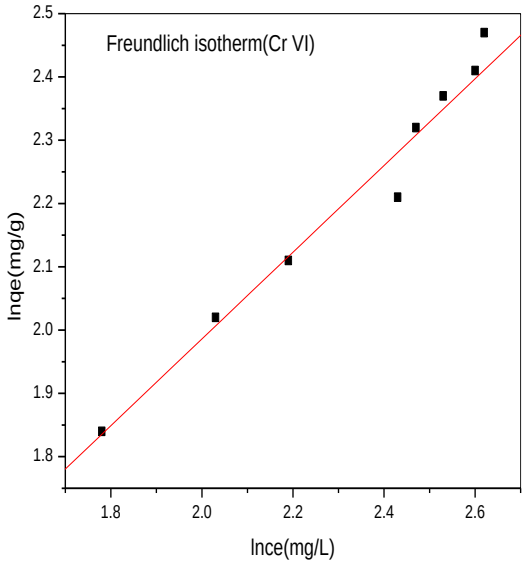
$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \qquad (3.9)$$

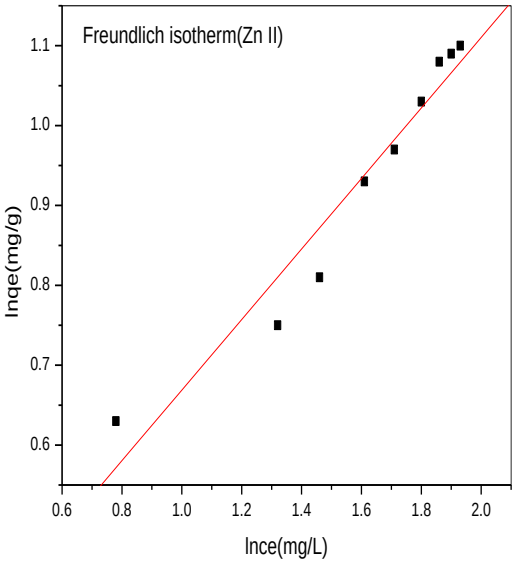
Where Ce is the equilibrium concentration of the adsorbate in mg/L, qe is the amount of adsorbate adsorbed at equilibrium (mg/g), 1/n is the adsorption intensity and KF is the relative adsorption capacity. The plot of lnqe against lnCe according to Equation 3.9 is shown in Figure 3.9. The values of Freundlich constants such as 1/n and KF were calculated from slope and intercept of the plot, respectively and their values are given in Table 3.2. The smaller the value of 1/n means greater extent of heterogeneity of adsorbent surface [29]. The experimental data show best fit for Freundlich isotherm model for chromium (IV), copper (II), nickel (II) and zinc (II) ions but not for lead (II) ions adsorption on bio-based. For the lead (II) ions, compared with the Freundlich isotherm, Langmuir isotherms provided a better fitted results (R_2 =0.966), suggesting that the monolayer adsorption dominate the adsorption process and no apparent interference between the adsorbed lead (II) ions on adjacent sites [30].Langmuir-Freundlich model is a combined form of Langmuir and Freundlich expression for the prediction of the heterogeneous adsorption. At low adsorbate concentration, it reduces to Freundlich isotherm, whereas it predicts a monolayer adsorption capacity characteristic of Langmuir isotherm at high adsorbate concentration [31]. It is expressed as follows:

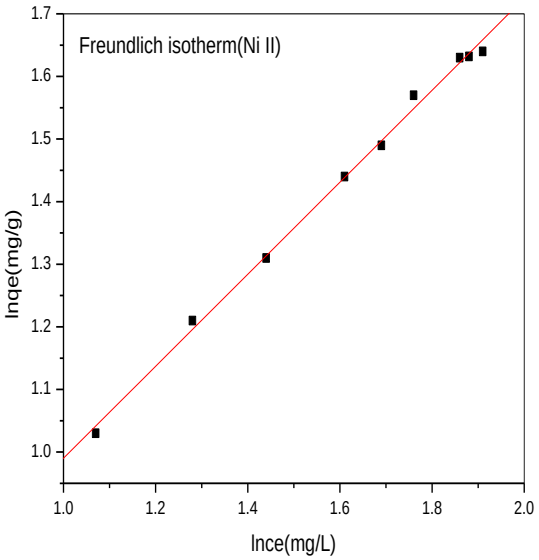
$$qe = \frac{qm(bce)1/n}{1+(bce)1/n} \qquad (3.10)$$

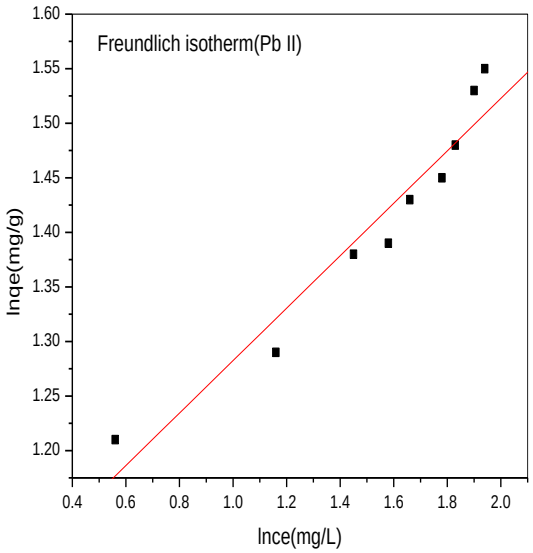
where b (L/mg) is the Langmuir-Freundlich isotherm constant and the parameter n′ could be regarded as the parameter characterizing the system heterogeneity. The larger is this parameter n′, the more heterogeneous is the system. The fitting results getting from the isotherms were shown in Figures 3.9 and 3.10 and the values of

correlation coefficients and other parameters obtained from the adsorbent were given in Table 4.2.As can be seen from the adsorption isotherms Figures 3.9 and 3.10 and the correlation coefficients (R^2) Table 3.2, Langmuir-Freundlich model fitted the adsorption isotherm of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) best, among the four isotherm models (Langmuir, Freundlich, Temkin and Dubinin– Radushkevich (DR) adsorption isotherms).









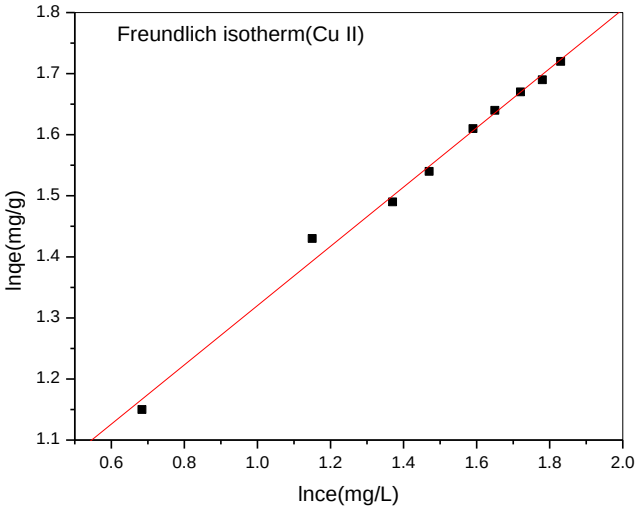


Figure 4.10: Freundlich adsorption isotherm for Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

Temkin isotherm interprets the interactions between adsorbents and metal ions to be adsorbed in adsorption process [32]. Temkin model assumes a linear decrease in the adsorption heat with surface coverage. Besides, Temkin equation also describes the behavior of many sorption systems on the heterogeneous surface [33]. The linear form of the Temkin isotherm is represented as:

$$q_e = \beta \ln K_T + \beta \ln C_e \qquad (3.11)$$

Where C_e is the equilibrium concentration of the adsorbate in mg/L, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), β (J/mol) is a heat adsorption constant and K_T is the equilibrium binding constant (L/min) parallel to the maximum binding energy [34].A plot of q_e versus $\ln C_e$ assists the determination of constants β and K_T via slope and intercept. The values of R^2, K_T (L/g), β (J/mol) are given in Table 3.2. Fitting the obtained experimental data to Temkin model demonstrated that the adsorption of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) onto bio-based obeys this model to a greater degree.

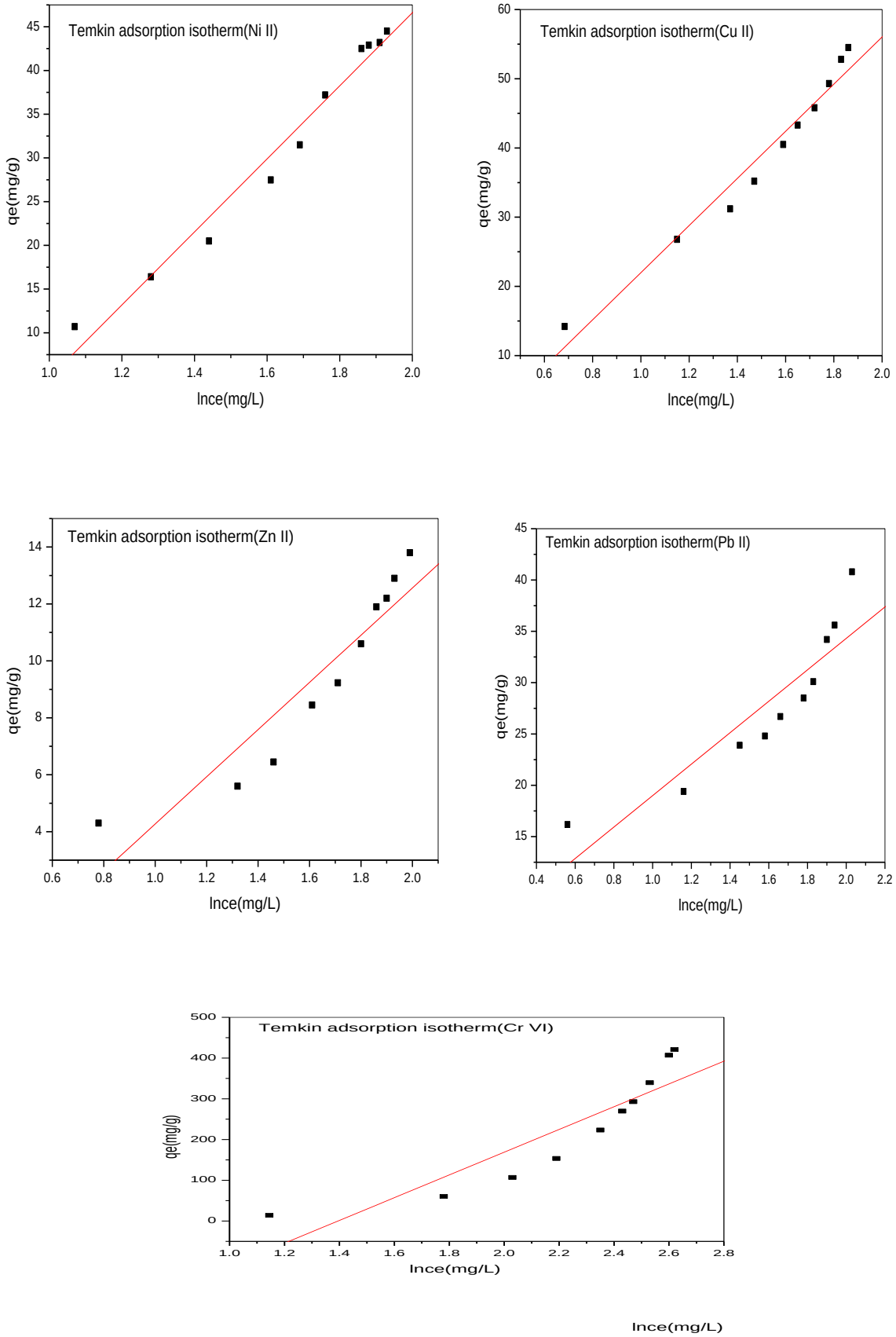


Figure 3.11: Temkin adsorption isotherm for Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

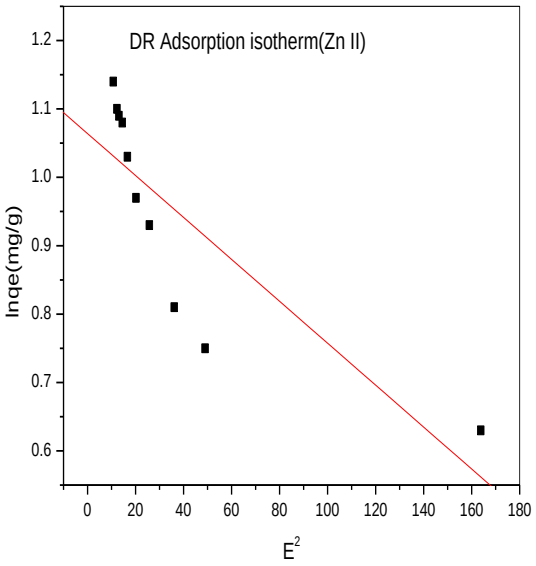
Dubinin-Radushkevich model evaluates the heterogeneity of the surface energies. The linear form of DR isotherm equation is represented as:

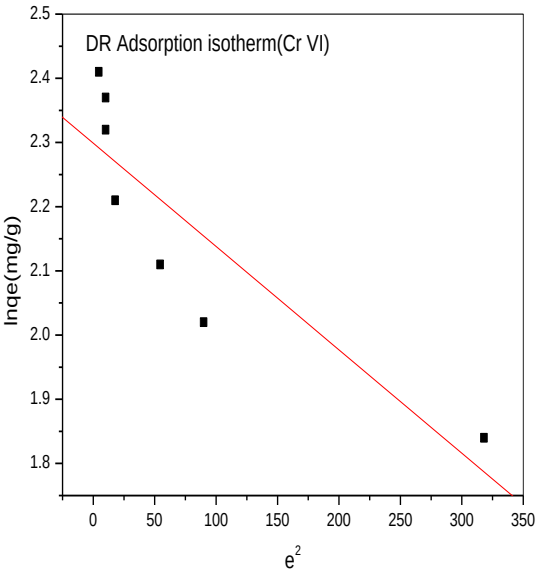
$$\ln q_e = \ln q_{DR} - \beta_D \varepsilon^2 \quad (3.12)$$

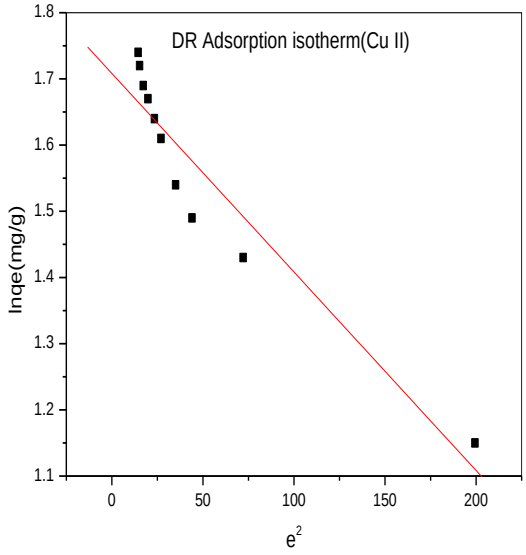
$$\varepsilon = RT \ln\left[1 + \frac{1}{Ce}\right] \quad (3.13)$$

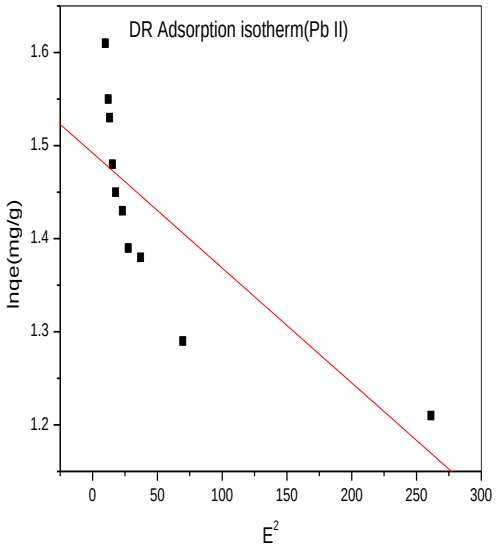
$$E_S = \frac{1}{\sqrt{2\beta D}} \quad (3.14)$$

Where q_m is the theoretical saturation capacity (mol/g), β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol /J) and ε is the potential, C_e is the equilibrium concentration of adsorbate in solution (mol/L), R ($Jmol^{-1}K^{-1}$) is the gas constant and T (K) is the absolute temperature. The DR constants q_m and β were calculated from the linear plots of $\ln q_e$ versus ε^2 and are given in Table 3.2. Value of E_S was calculated from equation 3.14 using the value of β_D. It gives information about the nature of adsorption process. Value of E_S (kJ/mol) found less than 8kJ/mol specify the presence of physical interactions and existence of van der wall's forces between adsorbate and adsorbent [35]. [36] stated that the values of E_S between 8 and 16 kJ/mol indicates the occurrence of physisorption, while the values higher than16 kJ/mol correspond to chemical adsorption. In this study, value of E_S was found to be 0.225, 13.13, 20.41, 7.581, 12.71,20.41 kJ/mol which was proof of formation of physical interaction between chromium (IV),copper (II), nickel (II) and zinc (II) ions and functional groups of bio-based while Pb(II) ions show the chemical adsorption with the functional groups of bio-based [37].Decreasing order of validity of various adsorption isotherms in term of their value of correlation coefficient (R^2) to best interpret the adsorption of chromium (IV) ions from aqueous medium on bio-based was found to be Freundlich > Langmuir >Temkin > DR with R^2 values 0.9797 > 0.9437 > 0.7301 > 0.3751, respectively, for the copper (II) ions Freundlich > Langmuir >Temkin > DR with R^2 values 0.989 > 0.996 > 0.983 > 0.950, respectively,for the lead (II) ions, Freundlich > Langmuir >Temkin > DR with R^2 values 0.978 > 0.966 > 0.906 > 0.783, for the nickel (II)) ions Freundlich > Langmuir >Temkin > DR with R^2 values 0.988 > 0.998 > 0.987 > 0.974 and for the zinc (II) ions Freundlich > Langmuir >Temkin > DR with R^2 values 0.944 > 0.9704> 0.933 > 0.831.


DR Adsorption isotherm(Zn II)
lnqe(mg/g)
E²


DR Adsorption isotherm(Cr VI)
lnqe(mg/g)
e²


DR Adsorption isotherm(Cu II)
lnqe(mg/g)
e²


DR Adsorption isotherm(Pb II)
lnqe(mg/g)
E²

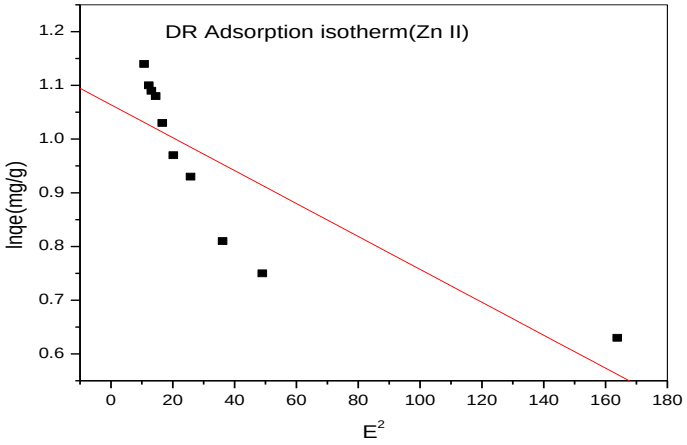


Figure 3.12: Dubinin-Radushkevich adsorption isotherm for Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

Table 32: Different isotherm parameters for Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II) ions on bio-based.

Langmuir isotherm parameters for Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II)	
R2	0.9397, 0.989, 0.9788, 0.988, 0.944
q_m (mg/g)	0.37, 0.01, 0.02, 0.01, 0.05,
b (L/mg)	71.12, 194.9, 100.7, 95.24, 80.55
R_L	0.271, 0.148, 0.025, 0.0102, 0.054
Freundlich isotherm parameters for Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II)	
R2	0.989, 0.996, 0.966, 0.998, 0.9704
N	0.685, 0.485, 0.240, 0.735, 0.441
1/n	1.46, 2.06, 4.15, 1.36, 2.26
K_F (L/g)	0.21, 0.08, 0.02, 0.59, 0.64
Temkin isotherm parameters for Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II)	
R2	0.9523,0.983,0.906,0.987,0.933
K_T (L/g)	2.69, 1.037, 1.428, 0.123, 0.724
β (J/mol)	0.0035, 34.05, 15.319, 41.76, 8.288
DR isotherm models for Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II)	
R2	0.714, 0.950, 0.7834, 0.974, 0.8312
E_S (kJ/mol)	0.225, 13.13, 20.41, 7.581, 12.71
q_{DR} (mg/g)	0.7806, 0.535, 0.4001, 0.541, 0.62

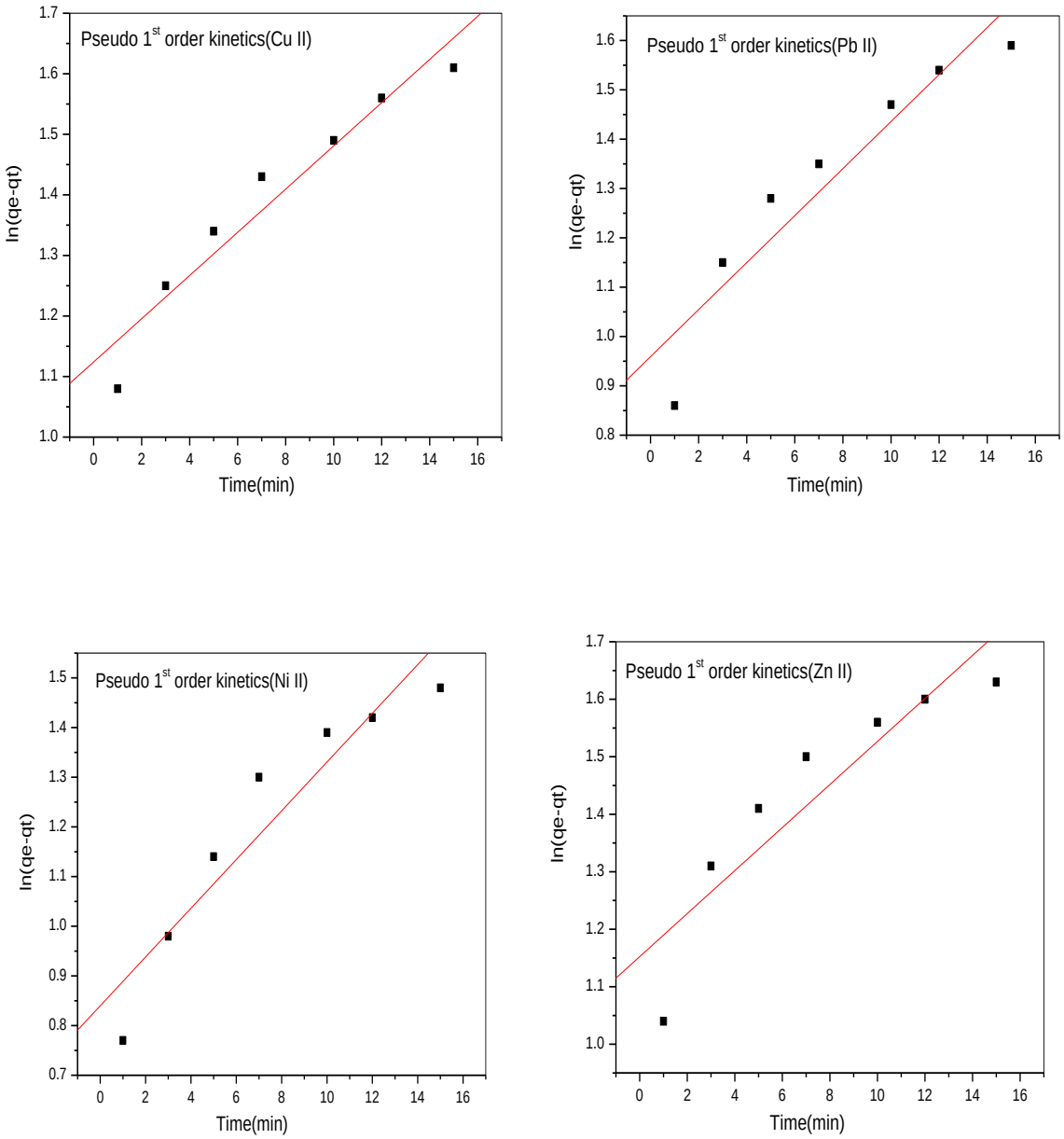
3.6 Kinetic study of adsorption process

To investigate the rate of adsorption and the adsorption mechanism of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) onto bio-based composite, the pseudo first order, pseudo second order, Intra-particle diffusion and Elovich kinetic models were applied to adsorption data [38]. Pseudo first order assumes that metal ions are bound only to one binding site on the cell surface [39]. The kinetic rate is proportional to the number of free binding sites [40]. Linear forms of pseudo first order kinetic equation is given as follow:

$$\ln(qe - qt) = \ln qe - k1t \qquad (3.15)$$

In the equation 3.15, qe (mg/g) refers to the concentration of chromium (IV), copper (II), lead (II), nickel (II)

and zinc (II) ions adsorbed on the active sites of composite at equilibrium while qt (mg/g) is the concentration of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions adsorbed on biomass at any time. k1 is first order rate constant and its units are min−1. The value of ln(qe−qt) was plotted against t using equation 3.15 to find the pseudo first order kinetics parameters [41].Values of k1 and qe were calculated from the slope and the intercept of the plot and their values are given in Table 3.3.



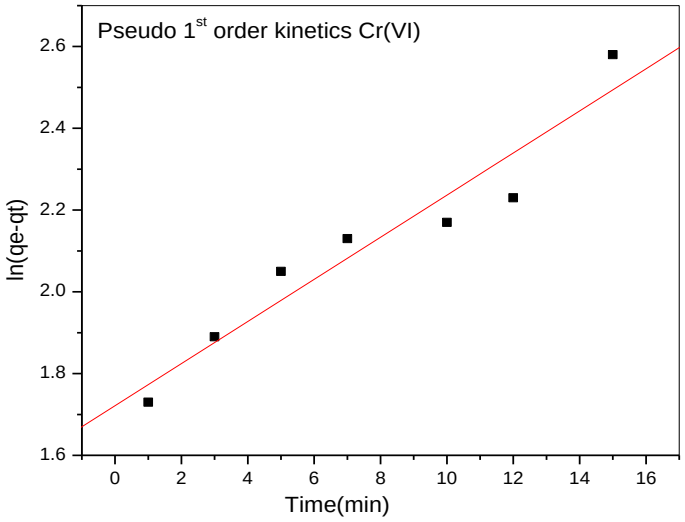


Figure 3.13: Pseudo 1st order kinetics for Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

The pseudo-second-order kinetic model assumes the presence of chemisorption that involves electrons exchange between the –OH or the ligand groups and the metal ions [42, 43].Linear form of pseudo second order kinetic equation is as follow:

$$t/qt = \frac{1}{K2.qe2} + \frac{t}{qe} \qquad (3.16)$$

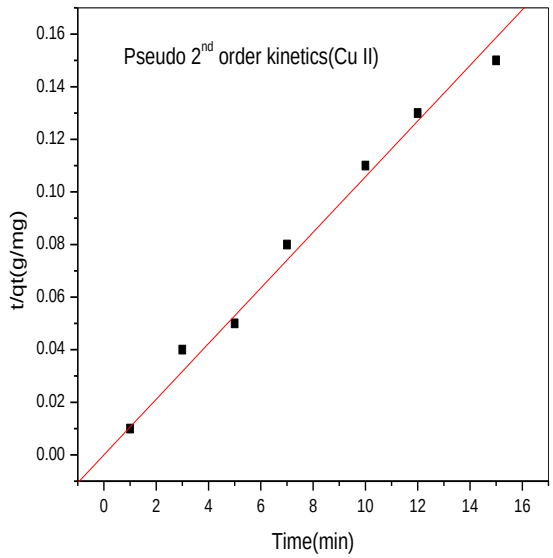
In equation 3.16, K_2 is pseudo second order rate constant and its unit is g/mg·min. The plot of t/q_t vs. t according to equation 3.16 is shown in Figure 3.13 and value of q_e and K_2 were calculated from the slope and the intercept of the plot, respectively. The initial adsorption rate represented by ho is defined as follow:

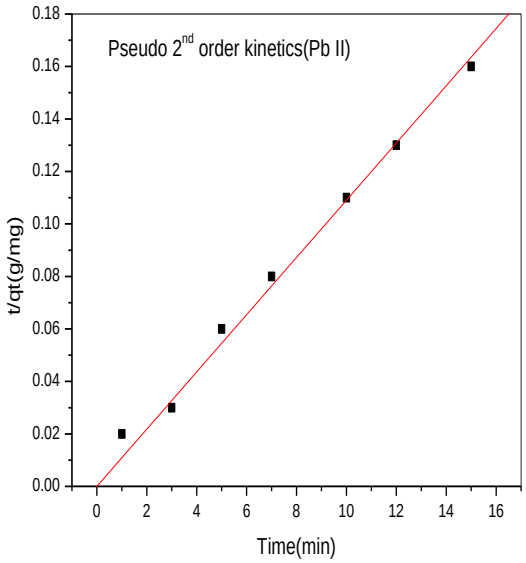
$$ho = k_2 qe^2 \qquad (3.17)$$

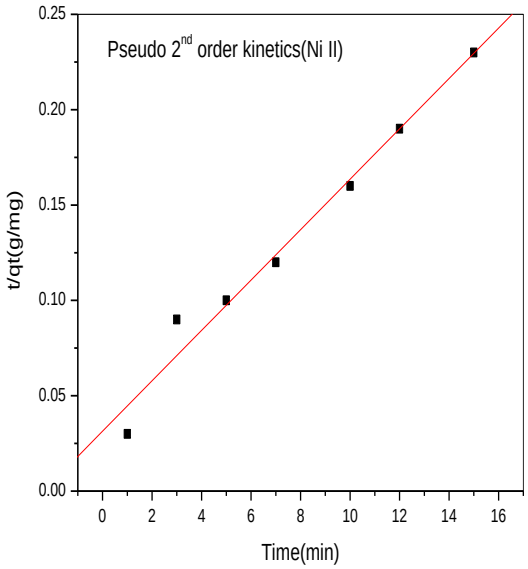
While the time required attaining the half of the equilibrium concentration of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions adsorbed on bio-based was calculated using the relation as given below:

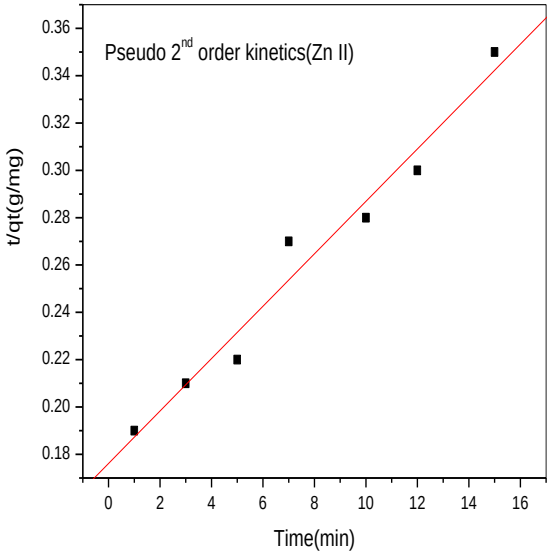
$$t_{1/2} = 1/k_2 q_e^2 \qquad (3.18)$$

In equations 3.17 and 3.18, k2 and qe are the pseudo second order rate constant and equilibrium concentration of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions adsorbed on bio-based. Value of k2, qe, R2, ho and t1/2 for pseudo second order kinetic model are given in Table 3.3.


Pseudo 2nd order kinetics(Cu II)
t/qt(g/mg)
Time(min)


Pseudo 2nd order kinetics(Pb II)
t/qt(g/mg)
Time(min)


Pseudo 2nd order kinetics(Ni II)
t/qt(g/mg)
Time(min)


Pseudo 2nd order kinetics(Zn II)
t/qt(g/mg)
Time(min)

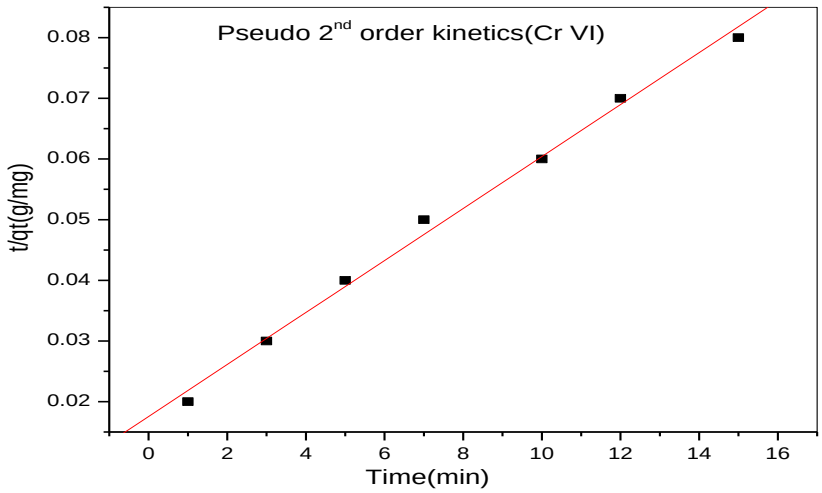
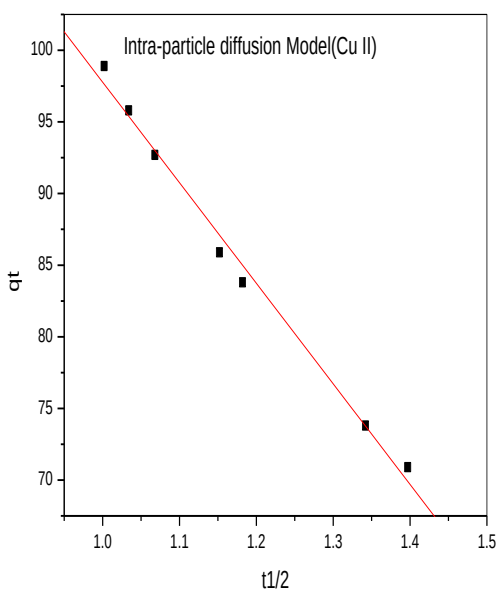


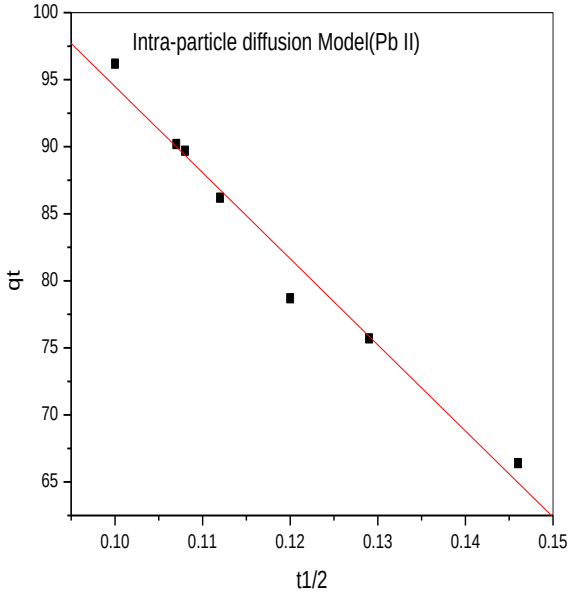
Figure 3.14: Pseudo 2nd order kinetics for Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

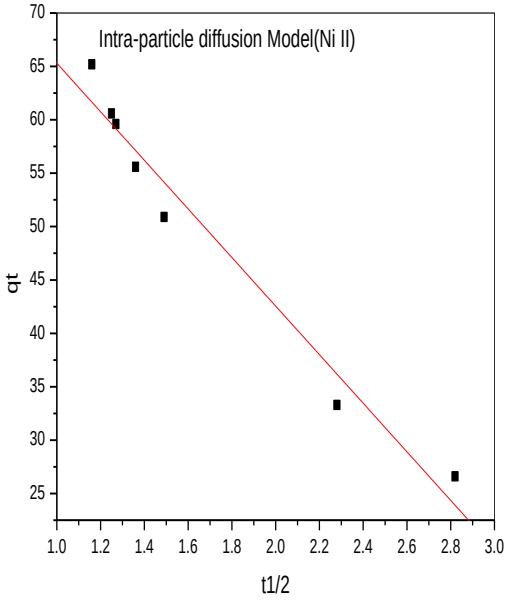
The intra-particle diffusion model assumes that the effectiveness of the adsorption center and the mass transfer process are the most important factors affecting adsorption kinetics. If the straight line passes through the origin, it indicates that intra -particle diffusion is the rate -limiting step to control the adsorption process; if the origin is not passed, the adsorption process is jointly controlled by other adsorption stages [44].Intra-particle diffusion model was applied to elaborate the diffusion mechanism of adsorption of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions on bio-based using equation 3.19 as given below:

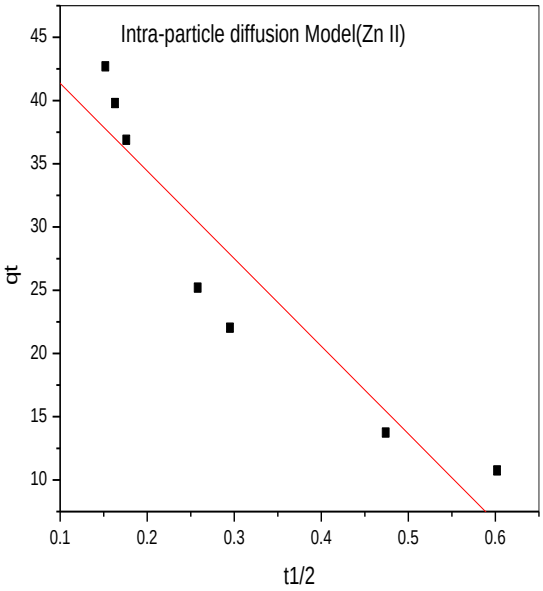
$$qt = kipdt^{1/2} + C \qquad (3.19)$$

In equation 3.19, kipd (mg/g·min$^{1/2}$) is intra-particle diffusion constant while C is the constant which is relevant to thickness of the boundary layer. If the value of C is greater, it interprets the higher surface adsorption [45]. The value of kipd and C was determined from slope and intercept of the plot of q_t vs. $t^{1/2}$, respectively. Values of parameters of intra-particles diffusion model are given in Table 3.3.


Intra-particle diffusion Model(Cu II)
qt
t1/2


Intra-particle diffusion Model(Pb II)
qt
t1/2


Intra-particle diffusion Model(Ni II)
qt
t1/2


Intra-particle diffusion Model(Zn II)
qt
t1/2

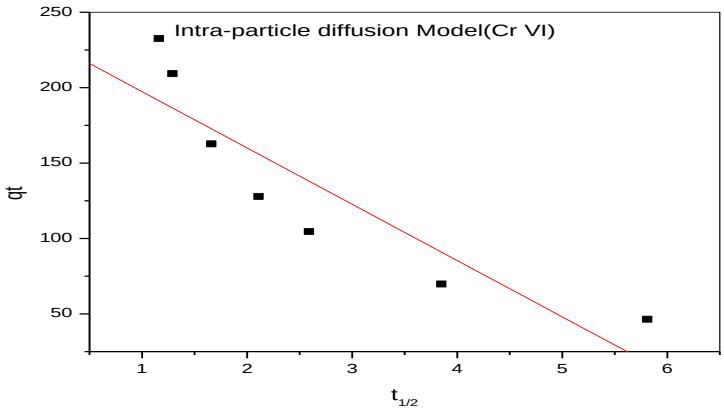


Figure 3.15: Intra-particle diffusion kinetics for Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II).

The heterogeneous diffusion process is expressed by the Elovich model [46] which is governed by the reaction rate with diffusion coefficient [47]. Linear form of Elovich model is as follow:

$$qt = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (3.20)$$

In equation 3.20, α (mg/g·min) and β (g·mg) are the Elovich parameters. α represents the initial adsorption rate while β designates the desorption constant. Elovich parameters such as β and α were determined from slope and intercept of plot of qt vs. lnt according to equation 3.20 and their values are given in Table 3.3. Values of regression factor (R^2) for chromium (IV), adsorption on bio-based composite were found to be 0.9478, 0.997, 0.899 and 0.971,for the copper (II) ions 0.966,0.995,0.996 and 0.958 ,for lead(II) ions 0.949,0.998,0.989 and 0.983 ,for the nickel(II) ions 0.945,0.989,0.984 and 0.971 and for zinc (II) ions 0.908,0.948,0.939 and 0.936,for pseudo first order, pseudo second order, intra-particle diffusion model and Elovich model, respectively. The value of regression factor (R^2) for adsorption of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) ions on bio-based were approaches to unity for pseudo second order kinetics which indicates that it best interprets the adsorption process as compared to pseudo first order, intra-particles diffusion and Elovich models.

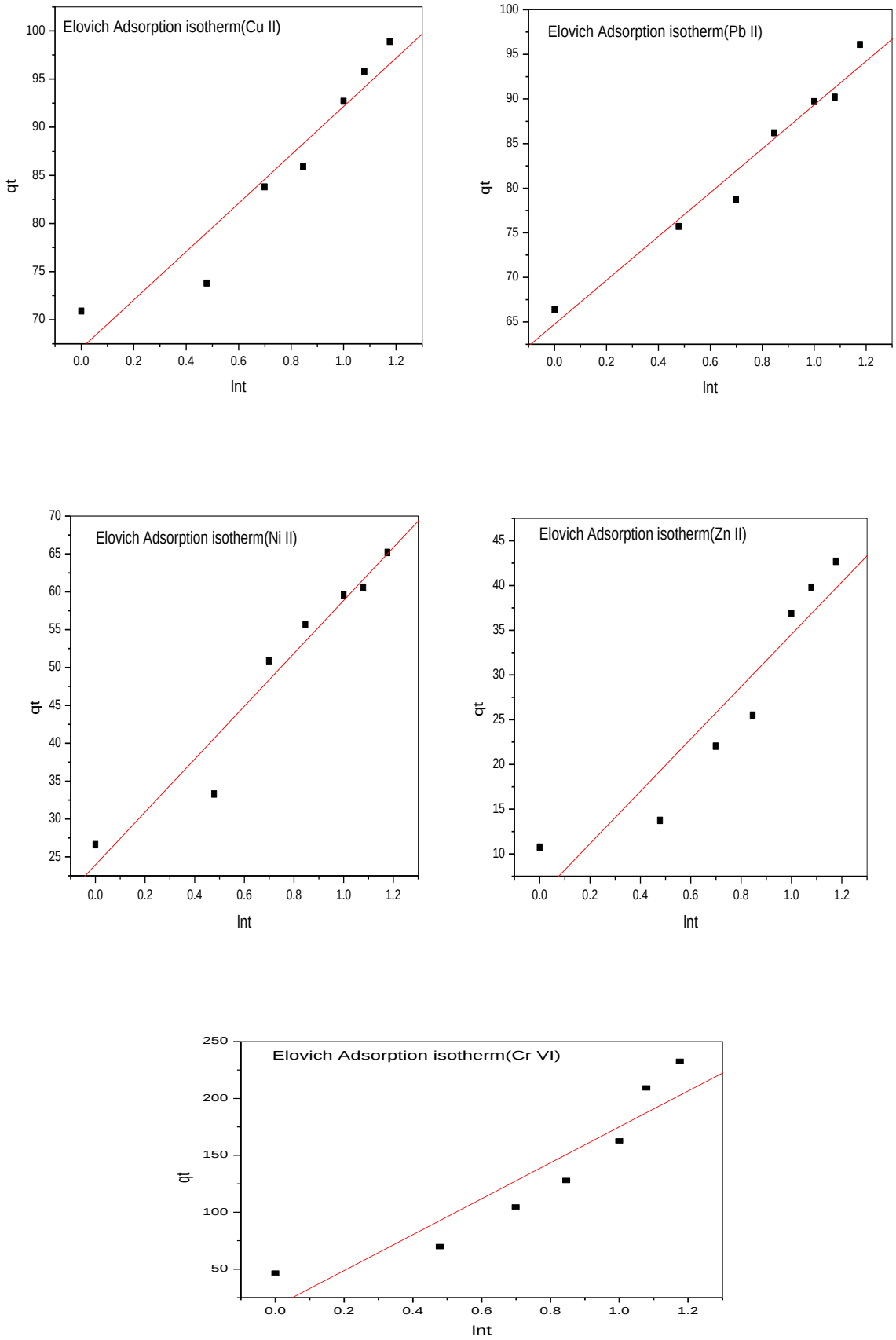


Figure 3.16: Elovich kinetics for Cr (VI), Cu (II), Pb (II), Ni (II) and Zn (II)

Table 3.3: Kinetic parameters for adsorption of Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II) ions on bio-based.

Pseudo 1st order kinetics of Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II)	
R2	0.9478,0.966,0.949,0.945,0.908
qe (mg/g)	0.246,0.117,0.046,0.174,0.1419
k1 (min-1)	0.042,0.0357,0.048,0.049,0.037
Pseudo 2nd order kinetics Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II)	
R^2	0.9971,0.995,0.998,0.989,0.928
q_e (mg/g)	0.537,2.104,16.35,0.421,1.198
h (mg/g·min)	0.012,0.045,27.53,0.024,0.221
$t_{1/2}$ (min)	83.3,22.32,59.4,427.4,5.42
k_2 (g/mg·min)	0.0047,0.010,0.103,0.013,0.154
Intra-particles diffusion model Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II)	
R^2	0.8998,0.996,0.989,0.984,0.939
C (mg/g)	234.7,167.9,158.7,88.04,48.29
k_{ipd} (mg/g·min)	6.28,2.393,0.247,3.871,0.696
Elovich model Cr (IV), Cu (II), Pb (II), Ni (II) and Zn (II)	
R^2	0.9712,0.958,0.983,0.971,0.936
α (mg/g·min)	3.39,1.83,1.81,1.37,0.721
β (g/mg)	157.56,25.13,24.57,34.94,29.23

Conclusion

In conclusion, optimization of the preparation conditions has revealed that the removal efficiency of unmodified and modified composites for different metals like chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) from its aqueous solutions at different parameters like solution pH, contact time and initial concentration of metal ions in aqueous solution is different. The uptake amount of heavy metal ions onto the unmodified composite followed the orders: Pb (II)>Cr (VI)>Ni (II)>Zn (II)>Cu (II).The percentage removal of chromium (IV), copper (II), lead (II), nickel (II) and zinc (II) by unmodified composite was 95.2%, 75.6%, 63.5%, 34.4% and 25.9% respectively.

Acknowledgment

I would also like to express my sincerest gratitude to my supervisor the Prof. Azhari Hamid Nour, for his support and kindness. I am also thankful to co-supervisor Dr.

Essa Esmail Mohammad at Sudan University of Science and Technology, for his skillful guidance, extrovert support, his critical valuable comments and suggestions throughout the research.

References

[1] Abdel-Raouf, M.S. and Abdul-Raheim, A.R.M. Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: A Review, *Journal of Pollution Effects and Control*, 5(1) (2017): pp.15-19.

[2] El Knidri, Hakima, Raja Belaabed, Abdellah Addaou, Ali Laajeb, and Ahmed Lahsini. "Extraction, chemical modification and characterization of chitin and chitosan." *International journal of biological macromolecules* 120 (2018): pp.1181-1189.

[3] Fu, Fenglian, and Qi Wang. "Removal of heavy metal ions from wastewaters: a review." *Journal of environmental management* 92, no.3, (2011): pp 407-418.

[4] Kanth, Vanarchi Rajini, Praveen B. Kajjari, Priya M. Madalageri, Sakey Ravindra, Lata S. Manjeshwar, Tejraj M. Aminabhavi, and Vijaya Srinivasu Vallabhapurapu. "Blend hydrogel microspheres of carboxymethyl chitosan and gelatin for the controlled release of 5-fluorouracil." *Pharmaceutics* 9, no. 2 (2017): pp 13.

[5] Zhao, Guixia, Xiubing Huang, Zhenwu Tang, Qifei Huang, Fenglei Niu, and Xiangke Wang. "Polymer-based nanocomposites for heavy metal ions removal from aqueous solution: a review." *Polymer Chemistry* 9, no. 26 (2018): pp 3562-3582.

[6] Abdel-Halim, E. S., and Salem S. Al-Deyab. "Removal of heavy metals from their aqueous solutions through adsorption onto natural polymers." *Carbohydrate Polymers* 84, no. 1 (2011):pp 454-458.

[7] Aravamudhan, Aja, Daisy M. Ramos, Ahmed A. Nada, and Sangamesh G. Kumbar. "Natural polymers: polysaccharides and their derivatives for biomedical applications." In *Natural and synthetic biomedical polymers*, Elsevier, no.4 (2014): pp. 67-89.

[8] Sanchez-Hachair, Arnaud, and Annette Hofmann. "Hexavalent chromium quantification in solution: Comparing direct UV–visible spectrometry with 1, 5-diphenylcarbazide colorimetry." *Comptes Rendus Chimie* 21, no. 9 (2018):pp. 890-896.

[9] Wang, Jiangjiang, Jia Zhao, Xia Liu, Lijun Zhang, Qingyin Zhang, and Yugao Guo. "Combining Ultraviolet-Visible Spectrometry And Chemometrics For Simultaneous Determination Of Copper, Chrome And Nickel Ions In Water." *International Journal of Science* 3 no.8 (2016): ISSN: 1813-4890.

[10] Valizadeh, Shahriyar, Mahmood Naseri, Sedighe Babaei, Seyed Mohammad Hashem Hosseini, and Ahmad Imani. "Development of bioactive composite films from chitosan and carboxymethyl cellulose using glutaraldehyde, cinnamon essential oil and oleic acid." *International Journal of Biological Macromolecules* 134 (2019):pp. 604-612.

[11] Huang, Guolin, Hongyan Zhang, Jeffrey X. Shi, and Tim AG Langrish. "Adsorption of chromium (VI) from aqueous solutions using cross-linked magnetic chitosan beads." *Industrial & Engineering Chemistry Research* 48, no. 5 (2009):pp. 2646-2651.

[12] Borsagli, Fernanda GL Medeiros, Alexandra AP Mansur, Poliane Chagas, Luiz CA Oliveira, and Herman S. Mansur. "O-carboxymethyl functionalization of chitosan: complexation and adsorption of Cd (II) and Cr (VI) as heavy metal pollutant ions." *Reactive and Functional Polymers* 97 (2015):pp. 37-47.

[13] Sun, Yongjun, Aowen Chen, Shu-Yuan Pan, Wenquan Sun, Chengyu Zhu, Kinjal J. Shah, and Huaili

Zheng. "Novel chitosan-based flocculants for chromium and nickle removal in wastewater via integrated chelation and flocculation." *Journal of Environmental Management* 248 (2019):pp. 109241.

[14] Wu, Shuping, Jiarui Kan, Xiangzi Dai, Xiaojuan Shen, Kan Zhang, and Maiyong Zhu. "Ternary carboxymethyl chitosan-hemicellulose-nanosized TiO 2 composite as effective adsorbent for removal of heavy metal contaminants from water." *Fibers and Polymers* 18 (2017): pp.22-32.

[15] Olivera, Sharon, Handanahally Basavarajaiah Muralidhara, Krishna Venkatesh, Vijay Kumar Guna, Keshavanarayana Gopalakrishna, and Yogesh Kumar. "Potential applications of cellulose and chitosan nanoparticles/composites in wastewater treatment: A review." *Carbohydrate polymers* 153 (2016):pp. 600-618.

[16] Sheth, Yashvi, Swapnil Dharaskar, Mohammad Khalid, and Shriram Sonawane. "An environment friendly approach for heavy metal removal from industrial wastewater using chitosan based biosorbent: A review." *Sustainable Energy Technologies and Assessments* 43 (2021): pp.100951.

[17] Lam, Boukary, Sébastien Déon, Nadia Morin-Crini, Gregorio Crini, and Patrick Fievet. "Polymer-enhanced ultrafiltration for heavy metal removal: Influence of chitosan and carboxymethyl cellulose on filtration performances." *Journal of cleaner production* 171 (2018): pp. 927-933.

[18] Luo, Jingqi, Chuanjie Fan, Zhi Xiao, Tianshu Sun, and Xiaodong Zhou. "Novel graphene oxide/carboxymethyl chitosan aerogels via vacuum-assisted self-assembly for heavy metal adsorption capacity." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 578 (2019): pp.123584.

[19] Naseem, Khalida, Zahoor H. Farooqi, Robina Begum, Muhammad Zia Ur Rehman, Aiman Shahbaz, Umar Farooq, Muhammad Ali, Hafiz Muhammad Abd Ur Rahman, Ahmad Irfan, and Abdullah G. Al-Sehemi. "Removal of cadmium (II) from aqueous medium using vigna radiata leave biomass: equilibrium isotherms, kinetics and thermodynamics." *Zeitschrift für Physikalische Chemie* 233, no. 5 (2019):pp. 669-690.

[20] Ayawei, Nimibofa, Augustus Newton Ebelegi, and Donbebe Wankasi. "Modelling and interpretation of adsorption isotherms." *Journal of chemistry* 2017 (2017):pp.11

[21] Abou El-Reash, Y. G., M. Otto, I. M. Kenawy, and A. M. Ouf. "Adsorption of Cr (VI) and As (V) ions by modified magnetic chitosan chelating resin." *International Journal of Biological Macromolecules* 49, no. 4 (2011):pp. 513-522.

[22] Touihri, Manel, Fatma Guesmi, Chiraz Hannachi, Béchir Hamrouni, Lotfi Sellaoui, Michael Badawi, Jordi Poch, and Núria Fiol. "Single and simultaneous adsorption of Cr (VI) and Cu (II) on a novel Fe3O4/pine cones gel beads nanocomposite: Experiments, characterization and isotherms modeling." *Chemical Engineering Journal* 416 (2021):pp. 129101.

[23] Ai, Tian, Xiaojun Jiang, and Qingyu Liu. "Chromium removal from industrial wastewater using Phyllostachys pubescens biomass loaded Cu-S nanospheres." *Open Chemistry* 16, no. 1 (2018):pp. 842-852.

[24] Hajizadeh, Zoleikha, Kobra Valadi, Reza Taheri-Ledari, and Ali Maleki. "Convenient Cr (VI) removal from aqueous samples: executed by a promising clay-based catalytic system, magnetized by Fe3O4 nanoparticles and functionalized with humic acid." *Chemistry Select* 5, no. 8 (2020):pp. 2441-2448.

[25] Jung, Chanil, Jiyong Heo, Jonghun Han, Namguk Her, Sung-Jae Lee, Jeill Oh, Jaena Ryu, and Yeomin Yoon. "Hexavalent chromium removal by various adsorbents: powdered activated carbon, chitosan,

and single/multi-walled carbon nanotubes." *Separation and purification technology* 106 (2013): pp.63-71.

[26] Rhaman, Md Masudur, Md Rezaul Karim, MK Mohammad Ziaul Hyder, Yunus Ahmed, and Ranjit K. Nath. "Removal of chromium (VI) from effluent by a magnetic bioadsorbent based on Jute Stick powder and its adsorption isotherm, kinetics and regeneration study." *Water, Air, & Soil Pollution* 231 (2020):pp. 1-18.

[27] Rahaman, Md Hafezur, Md Ataul Islam, Md Monjurul Islam, Md Aminur Rahman, and SM Nur Alam. "Biodegradable composite adsorbent of modified cellulose and chitosan to remove heavy metal ions from aqueous solution." *Current Research in Green and Sustainable Chemistry* 4 (2021):pp. 100119.

[28] Das, Biswajit, NABA KUMAR MONDAL, and PALAS ROYand SOUMYA CHATTARAJ. "Equilibrium, kinetic and thermodynamic study on chromium (VI) removal from aqueous solution using Pistia stratiotes biomass." *Chemical Science Transactions* 2, no. 1 (2013): pp.85-104.

[29] Ahmad, Rais, Imran Hasan, and Alok Mittal. "Adsorption of Cr (VI) and Cd (II) on chitosan grafted polyaniline-OMMT nanocomposite: isotherms, kinetics and thermodynamics studies." *Desalin Water Treat* 58 (2017): pp.144-153.

[30] Wu, Pian, Yayuan He, Siyu Lu, Shanlin Wang, Jiecan Yi, Yafei He, Jingwen Zhang et al. "A regenerable ion-imprinted magnetic biocomposite for selective adsorption and detection of Pb2+ in aqueous solution." *Journal of Hazardous Materials* 408 (2021):pp. 124410.

[31] Wang, Yaoguang, Di Wu, Qin Wei, Dong Wei, Tao Yan, Liangguo Yan, Lihua Hu, and Bin Du. "Rapid removal of Pb (II) from aqueous solution using branched polyethylenimine enhanced magnetic carboxymethyl chitosan optimized with response surface methodology." *Scientific reports* 7, no. 1 (2017): pp.10264.

[32] Altun, Türkan, and Hüseyin Ecevit. "Cr (VI) removal using Fe2O3-chitosan-cherry kernel shell pyrolytic charcoal composite beads." *Environmental Engineering Research* (2020). https://doi.org/10.4491/eer.2019.112.

[33] Li, Weikun, Hongliang Wei, Yuhua Liu, Songmao Li, Gang Wang, Tao Guo, and Huayun Han. "An in situ reactive spray-drying strategy for facile preparation of starch-chitosan based hydrogel microspheres for water treatment application." *Chemical Engineering and Processing-Process Intensification* 168 (2021): pp.108548.

[34] Pietrelli, Loris, Iolanda Francolini, Antonella Piozzi, Maria Sighicelli, Ilaria Silvestro, and Marco Vocciante. "Chromium (III) removal from wastewater by chitosan flakes." *Applied Sciences* 10, no. 6 (2020): pp.1925.

[35] Schmuhl, R., H. M. Krieg, and Klaas Keizer. "Adsorption of Cu (II) and Cr (VI) ions by chitosan: Kinetics and equilibrium studies." *Water Sa* 27, no. 1 (2001):pp. 1-8.

[36] Manzoor, Kaiser, Mudasir Ahmad, Suhail Ahmad, and Saiqa Ikram. "Synthesis, characterization, kinetics, and thermodynamics of EDTA-modified chitosan-carboxymethyl cellulose as Cu (II) ion adsorbent." *ACS omega* 4, no. 17 (2019):pp. 17425-17437.

[37] Plesu, Nicoleta, Lavinia Macarie, Adriana Popa, and Gheorghe Ilia. "Polymeric supports for water treatment applications." *In Water-Formed Deposits*, 19 (2022):pp. 397-433.

[38] Jung, Chanil, Jiyong Heo, Jonghun Han, Namguk Her, Sung-Jae Lee, Jeill Oh, Jaena Ryu, and Yeomin

Yoon. "Hexavalent chromium removal by various adsorbents: powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes." *Separation and purification technology* 106 (2013):pp. 63-71.

[39] Chojnacka, Katarzyna. "Biosorption and bioaccumulation–the prospects for practical applications." *Environment international* 36, no. 3 (2010): pp.299-307.

[40] Ghaedi, Mehrorang, Shaaker Hajati, Behnaz Barazesh, Farahnaz Karimi, and Gholamreza Ghezelbash. "Saccharomyces cerevisiae for the biosorption of basic dyes from binary component systems and the high order derivative spectrophotometric method for simultaneous analysis of Brilliant green and Methylene blue." *Journal of Industrial and Engineering Chemistry* 19, no. 1 (2013): pp.227-233.

[41] González, Aridane G., Oleg S. Pokrovsky, J. Magdalena Santana-Casiano, and Melchor González-Dávila. "Bioadsorption of heavy metals." *Prospects and challenges in algal biotechnology* (2017):pp. 233-255.

[42] Al-Qodah, Zakaria, Mohd Adib Yahya, and Mohammad Al-Shannag. "On the performance of bioadsorption processes for heavy metal ions removal by low-cost agricultural and natural by-products bioadsorbent: a review." *Desalin Water Treat* 85 (2017):pp. 339-357.

[43] Demirbas, E., N. Dizge, M. T. Sulak, and M. Kobya. "Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon." *Chemical Engineering Journal* 148, no. 2-3 (2009): pp.480-487.

[44] Jiang, Huabin, Yuru Yang, Zongkun Lin, Binchan Zhao, Jing Wang, Jun Xie, and Aiping Zhang. "Preparation of a novel bio-adsorbent of sodium alginate grafted polyacrylamide/graphene oxide hydrogel for the adsorption of heavy metal ion." *Science of The Total Environment* 744 (2020): pp.140653.

[45] Li, Haibo, Shaodan Bi, Long Liu, Weifang Dong, and Xin Wang. "Separation and accumulation of Cu (II), Zn (II) and Cr (VI) from aqueous solution by magnetic chitosan modified with diethylenetriamine." *Desalination* 278, no. 1-3 (2011):pp. 397-404.

[46] Pan, Min, Xumeng Lin, Jingjing Xie, and Xiaoming Huang. "Kinetic, equilibrium and thermodynamic studies for phosphate adsorption on aluminum hydroxide modified palygorskite nano-composites." *RSC advances* 7, no. 8 (2017):pp. 4492-4500.

[47] Pal, Dan Bahadur, Arvind Singh, Jay Mant Jha, Neha Srivastava, Abeer Hashem, Maha Abdullah Alakeel, Elsayed Fathi Abd_Allah, and Vijai Kumar Gupta. "Low-cost biochar adsorbents prepared from date and delonix regia seeds for heavy metal sorption." *Bioresource technology* 339 (2021): pp.125606.