Journal of Basic and Environmental Sciences

ISSN
Online:2356-6388
Print:2536-9202

Research Paper Open Access

Removal of Mn(II), Cd(II) and Ni(II) metal ions from aqueous solutions using modified chitosan by simple method

Noha T. Abo El-nassr [a], Abdou S. El-Tabl [b], Hossam S. Jahin [c], Mohammed H. H. Abu-Setta [b], Alaa. S. Amin [d], Islam. M. I. Moustafa [d]

[a] Basic Science Department, Higher Institute of Engineering and Technology, Menoufia, Egypt.
[b] Department of chemistry, Faculty of science, Menoufia university, Shebin El-kom. Egypt.
[c] Central Laboratory for Environmental Quality Monitoring, National Water Research Center, El-Kanater El-khayria 13621/6, Egypt.
[d] Chemistry Department, Faculty of Science, Benha University, Benha, Egypt.

Corresponding author: E-mail address: nohaaboelnassr@yahoo.com

Abstract

The adsorption capacities of modified chitosan towards Cd(II), Mn(II) and Ni(II) ions removal were examined. It verify the development of new groups, the modified chitosan characterized by X-ray, thermogravimetric analysis, field-emission (SEM), and IR. Variables including the impacts of pH, the dose of adsorbent, time, concentration and the temperature were used to examine the adsorption and kinetics studies of the process. The pseudo-second-order made well sense in the kinetic results. Removal effectiveness was found to rise with increasing time, temperature, and pH from 3 to 8 but decrease with increasing initial ions concentration and dose. Of these, the highest percentages of Cd(II), Mn(II) and Ni (II) removal were 67.15, 70.44, and 74.02%, respectively. An analysis of the isothermal properties was highly consistent with Langmuir's isotherm. D-R, Freundlich, and Langmuir models, the maximum uptake yields and isotherm parameter values were determined. Physical adsorption method was demonstrated by the relatively low average values of the energy of adsorption (1.48–2.26 kJ/mol). It was established that the thermodynamic parameters were endothermic (positive ΔH°) and spontaneous (negative ΔG°).

Keywords: *Heavy metals; modified chitosan; physico-chemical studies; Langmuir*

1. Introduction

Removing metals from industrial contaminants, water supplies, mine waters and other sources is a significant challenge in preventing important source's pollution in water and soil. Many techniques, including ion-exchange, adsorption, [1] electrolytic or liquid extraction, electrodialysis [2], chemical precipitation, membrane filtration and biosorption [3,4] have been presented to get rid of harmful metal ions presented in sea water and wastewater. Chelating resins have a wide range of real-world uses in chemical evaluation, environmental protection, water treatment, etc. [5]. Adsorption is one of these techniques that is frequently used to extract heavy metals from aqueous solutions because it is inexpensive, readily available and has advantage surface, chemical and physical properties [6-8]. It is believed that adsorption is a more effective beneficial method than alternative methods. Easy to use, rapid recovery, high enrichment factor, low chemical intake, fast kinetics, and reusable adsorbent are only a few of its many benefits [9-11]. As chelating adsorbents, polymers with synthetic or natural bases can be employed. Many materials can be employed as efficient adsorbents, including fly ash, activated carbon, zero valence iron, agricultural waste, zeolite, clay, lignocellulosic materials, bio-polymers, metal oxides, microorganisms, and sewage waste [12]. The best filtration and separation technique for removing heavy metals from industrial effluent is biosorption. It has several good biological properties, including good biocompatibility and biodegradation, as well as other functions like homeostatic activity, antithrombogenicity, immunity boosting, wound healing, and the ability to inhibit the growth of some bacteria [13]. Because of its hydrophilic nature, not being toxic reactive amine groups and chelating qualities, chitosan is an effective adsorber [14]. Furthermore, following modification, chitosan exhibits remarkable metal binding capabilities [15,16]. Compared to alkali and alkaline earth metals, chitosan aids in the more desirable adsorption of transition metals [17]. Due to particular interactions of the NH_2 group with heavy metals, chitosan is believed to have strong complexing ability [18]. At contrast to cellulose, chitosan has an NH_2 group at the C-2 position, whereas cellulose has an OH group. Quaternization of the amino group is the most frequent reaction involving the C-2 position in chitosan. [19]. A relatively simple polymer known as chitosan is the deacetylated residue of chitin. The rate of deacetylation in chitosan determines its molecular

weight.; widely accessible chitosan has a deacetylation degree ranging from 70 to 90 percent [20]. The properties of chitosan differentiate it from chitin and cellulose, and its N-deacetylation makes it soluble in formic and acetic acid dilutions in water. The solubility of chitosan, mostly due to the facility with which amino groups can be protonated in acids, is one of the primary problems restricting its application [21,22]. A strong metal ion-reactive amine functional group is present in chitosan, a copolymer of glucosamine and N-acetylglucosamine. Considerable research has been conducted recently on chitosan's ability to absorb metal cations [23]. Chitosan amine groups bind metal cations at almost neutral pH levels. Electrostatic force has a tendency to attach chitosan between anions because of its high protonation at lower pH levels. Heavy metals are generally extremely hazardous. and do not biodegrade in the environment [24,25]. Metals like zinc, manganese, mercury, cadmium, copper, nickel, cobalt, and ferrous have been shown to be hazard [26]. This publication aims to remove Cd(II), Mn(II), and Ni(II) cations from water-based solutions using modified chitosan.

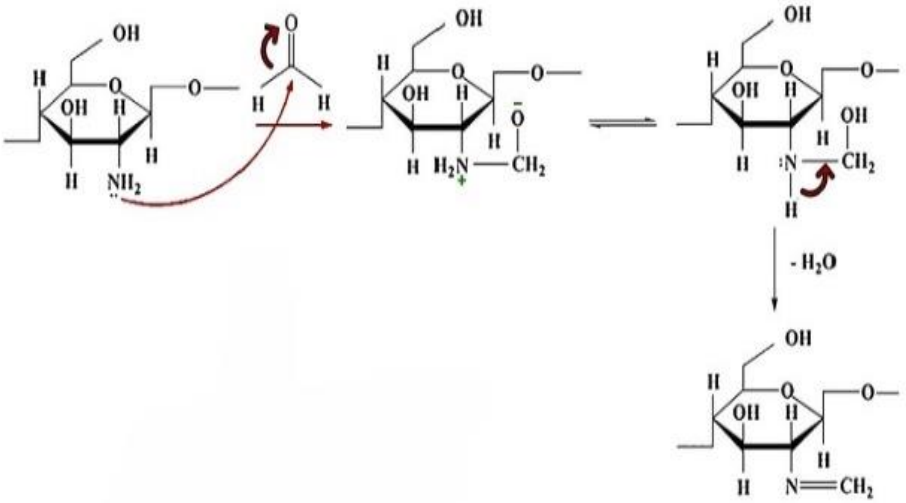
2. Experimental

2.1. Materials and methods

Chitosan (acetylation degree, DA:25%) was obtained from Roth chem germany, distilled water, concentrated acetic acid obtained from Daejung, formaldehyde obtained from Piochem, manganese sulphate ($MnSO_4.H_2O$) obtained from Alamia company for chemicals, nickel sulphate ($NiSO_4.7H_2O$) obtained from Alamia company for chemicals and cadmium sulphate octahydrate extra pure ($CdSO_4.8H_2O$) obtained from Oxford lab fine chemicals.

2.2. Method of modification of chitosan resin

0.5 g of chitosan had been immersed in the smallest amount of bidistilled water at ambient temperature and stirred for an hour, conc. CH_3COOH was inserted in drop wise, then the combination was agitated about an additional two hours. Next, 0.5 g of formaldehyde was introduced dropwise while stirring and two more hours were spent stirring the mixture before being dried in an oven for 30 minutes as demonstrated.



Chitosan derivative immobilization

2.3. Instruments

With ICP (Inductively Coupled Plasma), metal ions amounts were identified spectrophotometrically. In addition to TGA research, the produced resin was evaluated using spectrophotometric techniques such as IR, XRD, and SEM (scanning electron microscopy).

To obtain the (XRD), the Rigaku MiniFlex 600 was utilized. SEM pictures were captured using an EDS microscope (Jeol JMS-700). With an alpha II spectrometer, FTIR, was carried out.

3. Results and discussion

3.1. Characterization of modified resin

3.1.1. IR analysis for chitosan and modified chitosan

As seen in fig. (1), the chitosan's deravative band spectrum listed below displayed several distinct peaks. The absorption band in this spectrum corresponding to N-H expanding and the stretching of the O-H overlapped is 3444.87 cm^{-1}; extending aliphatic C-H, it is 2920.23 cm^{-1}; for C-O of primary alcoholic groups, it is 1398.39 cm^{-1} [27,28]. The strong peak is responsible for the chitosan polysaccharide's characteristic in-plane N-H bending vibration at 1635.64 cm^{-1} [29].

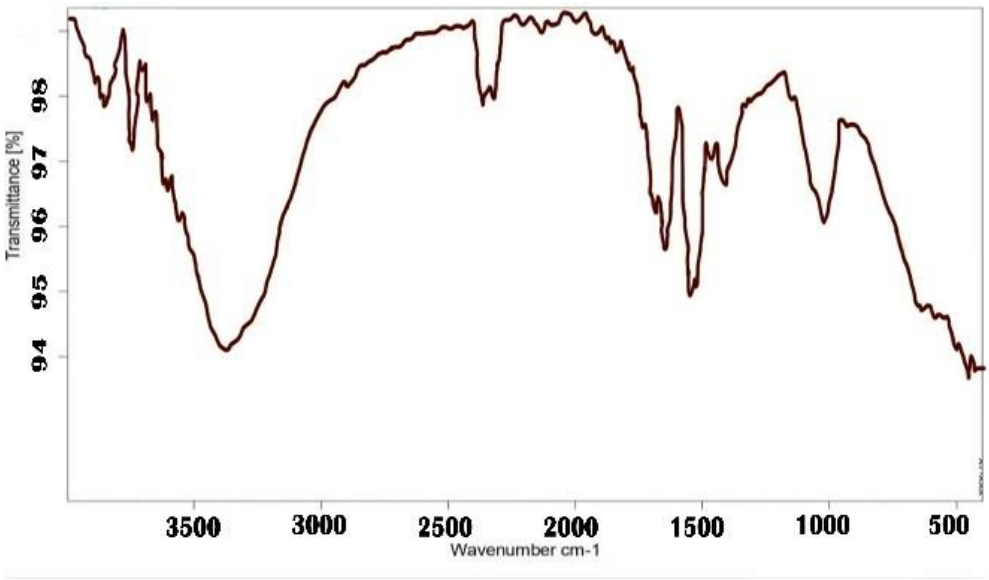


Fig. (1) IR of modified chitosan

3.1.2. Thermogravimetric analysis (TGA)

The initial phase of reducing weight was noted between 22 and 100°C, corresponds to a 10% reduction in moisture. Chitosan undergoes a non-oxidative thermal degradation between 248–600°C and indicates chitosan deacetylation as well as the process of vaporizing and eliminating substances that are volatile [30]. Amino groups that create unsaturated structures are the first step in the breakdown of chitosan [31]. A random splitting of the glycosidic linkages takes place during pyrolysis, and this is followed by breakdown and a sequence of lesser fatty acids [32]. As seen in fig. (2), the DSC revealed an exothermic elevated within 303.77 and 304.28°C and an endothermic peak between 77.78 and 80.44°C. The water loss linked to the hydrophilic groups of chitosan is attributed to the endothermic peak, which is also referred to as the dehydration temperature (T) [33,34]. Because of chitosan irregular composition and great affinity for water, it is efficiently hydrated [35]. This peak indicated that some bound water remained in the chitosan, indicating that it had not dried entirely. The heat breakdown of chitosan is associated with the exothermic peak [36, 37].

3.1.3. X-ray diffraction

Fig. (3) displays the sample's X-ray powder diffractogram. The pattern of chitosan resin modifications exhibited distinctive broad bending peak around 2θ equals 25.63°.

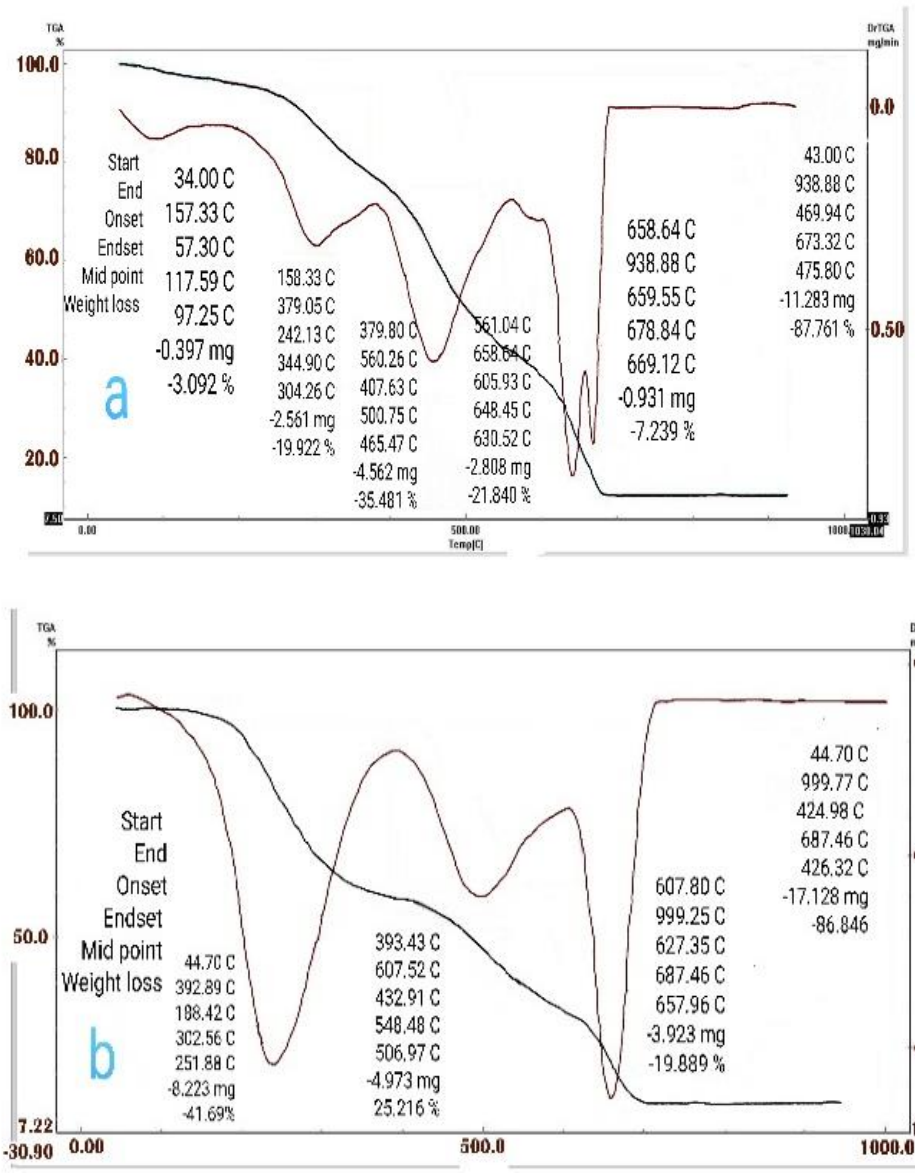


Fig. (2) TG/DTG patterns of (a) chitosan and (b) modified chitosan

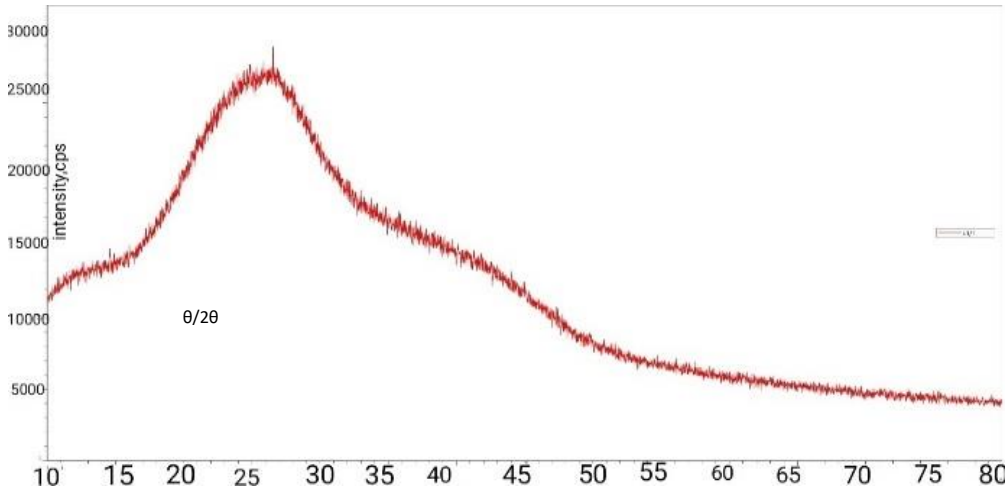


Fig. (3) XRD diffractogram of derivative of chitosan

3.1.4. SEM (scanning electron microscope)

The SEM micrograph appears the morphological features of modified chitosan as depicted in fig. (4). With strapping and shrinkage, the micrographs revealed a non-smooth and irregular surface [38].

3.1.5. Metal Ions Uptake

Each of the adsorption experiment was carried out in a bottle contains combination was agitated without heating using a mechanical stirrer. By diluting standard solutions, solutions with various starting amounts of manganese, nickel, and cadmium ions were obtained. All the tests for metal ions that were being investigated were conducted at a pH of 7-8. With the exception of the samples used to investigate the temperature effect. Eq. (1) was utilized to compute the capabilities of adsorption.

$$\text{Sorption uptake, } q = (C_o - C_e)\, V/W \qquad (1)$$

Where V is the volume's solution (L), C_e indicates final concentration (mg/L) after removal, q is the uptake, and W is the dose of modified chitosan (g). The formula used to determine the ion % removal eq. (2):

$$\%\text{removal} = (C_o - C_e)/C_o X100 \qquad (2)$$

3.1.6. Isotherm studies

Friendlylich, Langmuir, and (D–R) models [39,40] are the most often used isotherms have been utilized to characterize the adsorption properties for removal of ions from water-based solutions. By doing experiments at 303, 313, 323 and 333 K, adsorption isotherm data were acquired. This is the representation of the isotherm in linear form as represented in eq. (3,4):

Freundlich isotherm

$$\text{Log } q_e = \log k_F + (1/n) \log C_e \qquad (3)$$

Langmuir isotherm

$$C_e/q_e = C_e/Q_{max} + 1/KLQ_{max} \qquad (4)$$

The adsorption intensity is denoted by 1/n, the symbol for the greatest ability to adsorb is Q_{max}, the metal ion equiibrium concentration is C_e and the Langmuir binding constant K_L is associated with the adsorption energy (Lmg^{-1}).

Equation (R_L) eq. (5), also known as the equilibrium parameter or constant separation factor, can be utilized to specify the Langmuir isotherm's basic features [41].

$$R_L = \frac{1}{1 + K_L C_0} \qquad (5)$$

Values of $0 < R_L < 1$ indicated that, the adsorption procedure was appropriate.

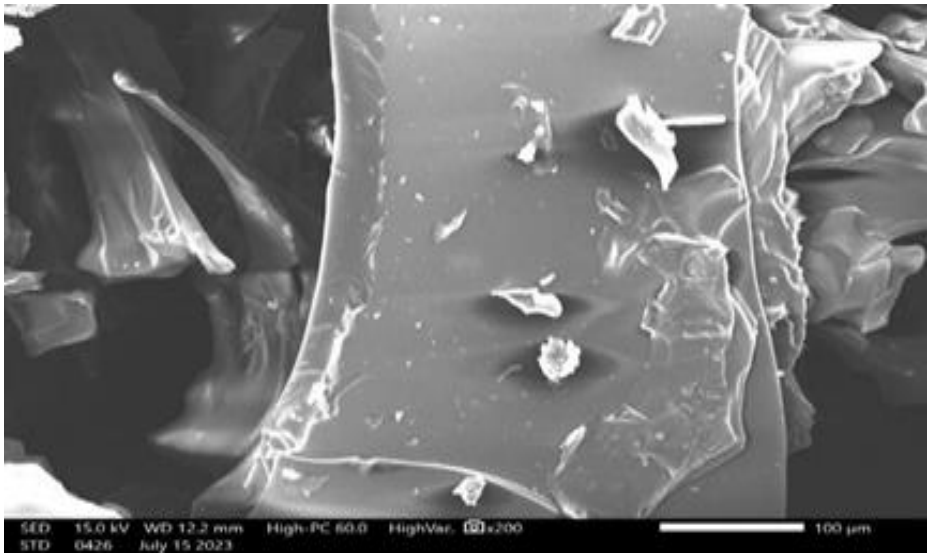


Fig. (4) SEM micrographs of modified chitosan

3.1.6. D–R isotherm [22]

$$lnq_e = lnK_{DR} - B\,\varepsilon^2 \quad (6)$$

$$\varepsilon = RT\,ln\left[1 + \frac{1}{C_e}\right] \quad (7)$$

$$E = \frac{1}{\sqrt{2B}} \quad (8)$$

As illustrated in eq. (6), K_{DR} is the highest possible capacity of adsorption, B is the adsorption energy measured in mol^2/kJ^2. B is obtained by plotting ln q_e versus ε^2. Eq. (7) can be used to compute the Polanyi potential (ε), where T represents temperature by kelvin and R indicates the constant of gas.

4. Adsorption techniques

4.1. Effects of different experimental conditions

This study investigates the temperature's impact, time, pH, concentration, amount of modified chitosan and other physical and chemical factors on adsorption.

4.1.1. Effect of pH

Among significant variables has an effect on the adsorption process is the initial pH. The initial pH was between 3–9 as shown in fig. (5). Because chitosan is soluble in very low pH, the adsorption investigation could not be conducted experimentally at pH levels below 3. The data indicates that at pH 8, the greatest percentages of Cd(II), Mn(II) and Ni(II) removal are 67.15, 70.44, and 74.02%, respectively. Because of the leftward shift of the equilibrium caused by a high level of H^+ in the adsorption medium at pH < 3, the reason for the zero percent removal at pH 1.

4.1.2. Effect of adsorbent dose

The amount of modified chitosan used in 30 ml of 2.6, 2.03, and 4.7 mgL^{-1} of Cd (II), Mn(II) and Ni(II) ions was distinct between 0.03 g to 1.00 g. The findings indicate that when the adsorbent dose for metals under investigation

increased,adsorption capacity of modified chitosan and the removal effectiveness (R) of the adsorbent decreased as shown in fig. (6). Removal percentage (R) fell from from 65.38 to 46.92% ,67.09 to 50.74%, and from 76.45 to 48.09% for Cd(II), Mn(II) and Ni(II), respectively. However, for Ni(II), R rose from 51.62 to 76.45% by dosage's raising dose from.03 to.05 g, and then fell by increasing the dose of modified chitosan. Active sites were used at higher dosages, all of the active sites were accessible for adsorption at lower dosages [42]. Moreover, aggregation brought on by high adsorbent dose might lower the adsorbent surface area and subsequently the absorption capacity [43,44]. Optimum dose was 0.03 g for Cd(II) and Mn(II) and was 0.05g for Ni(II). The highest removal percentage were 66.5, 68, and 76.45%.

4.1.3. Effect of contact time

Fig. (7) displays results of an investigation of metals on modified chitosan with time. The adsorbent was used for 10, 20, 30, 40, 50, 60, 90, 120, and 180 minutes.

The elimination reached equilibrium, according to the data, at approximately 60, 90, and 120 minutes for Cd(II), Mn(II), and Ni(II), respectively, with adsorption efficiencies of 66.08,68.18, and 75.53%, respectively. For Cd(II), Mn(II), and Ni(II), respectively, within the first ten minutes, over 50% of the absorbent content was reached. (60.77, 61.58, and 54.83%), indicating a rapid start to the adsorption process. This suggested that the modified chitosan has a rapid kinetic.

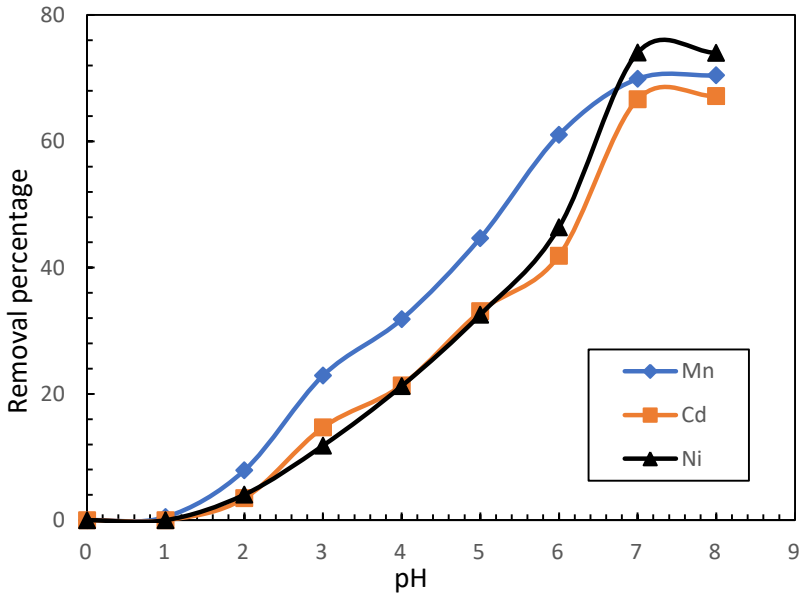


Fig. (**5**) Influence of pH on the removal percentage of studied metal ions on modified chitosan

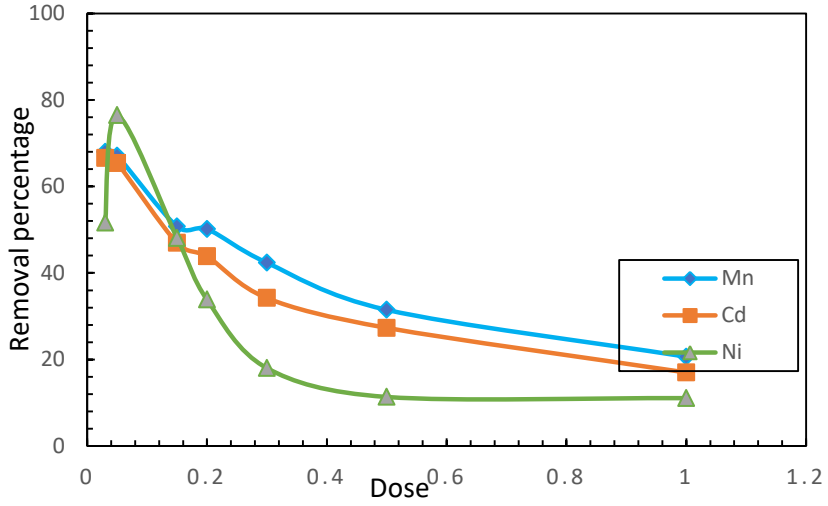


Fig. (**6**) Modified chitosan dosage on removal of metal ions

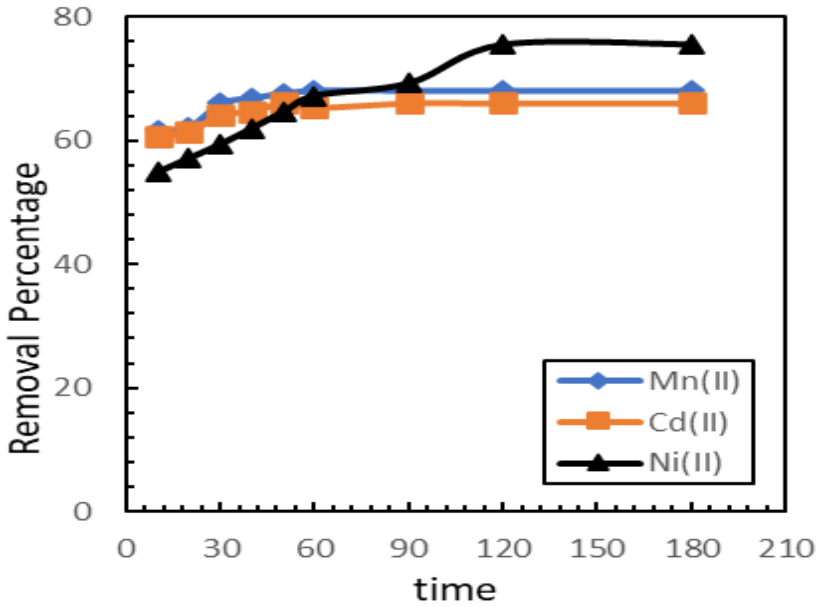


Fig. (7) Effect of time on modified chitosan's absorption of the investigated ions

4.1.4. Effect of concentration

Fig. (8) illustrates how concentration affects the proportion of metals removed using modified chitosan. The chart shows that when initial heavy metal concentration increased, the percentage removal steadily drops for Mn(II) and Cd(II) ions, but for Ni(II) increased in the beginning, then decreased.

4.1.5. Effect of temperature

It became known that temperature significantly impacted the adsorption action, as indicated by the superimposition of the curves at various temperatures (30, 40, 50, and 60 °C) as depicted in fig (9). It was shown that the adsorption capacity and percent of elimination rose for the three tested metal ions as the temperature rose [45].

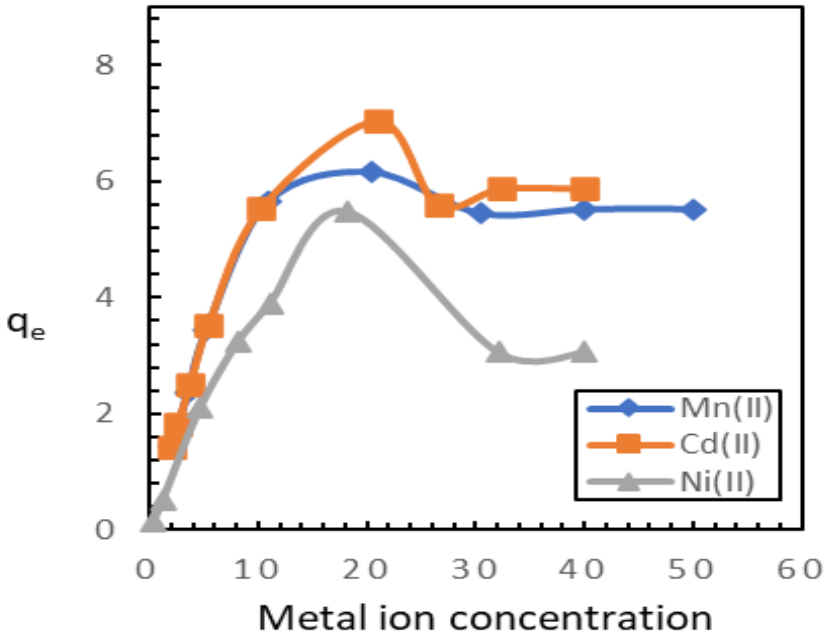


Fig. (8) Conc.'s effect on the elimination

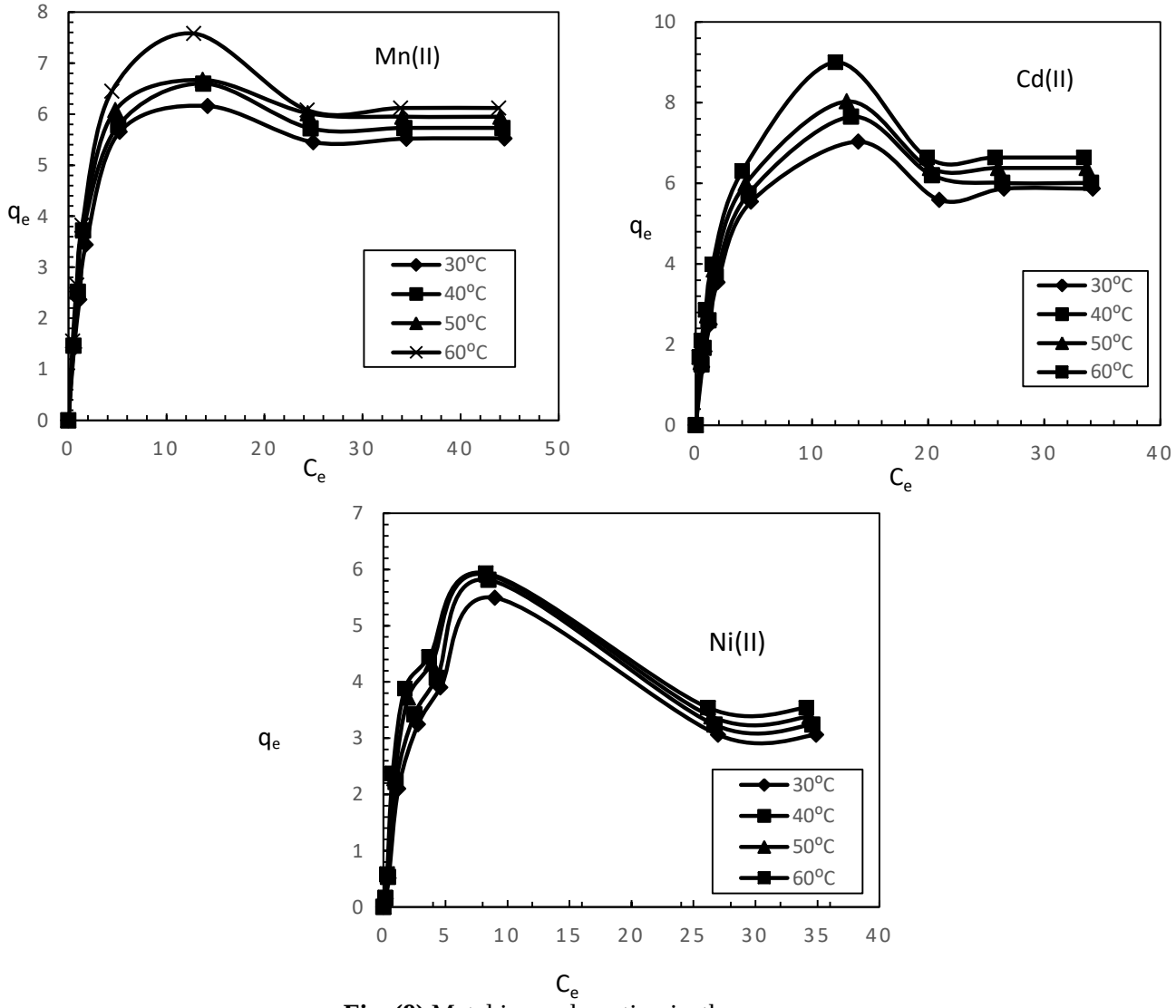


Fig. (9) Metal ions adsorption isotherms

4.2. Adsorption kinetics

Adsorption kinetic mechanism investigation of metal ions onto the modified chitosan is carried out using three kinetic models: intraparticle diffusion models, pseudo-first-order model and pseudo-second-order model. The adsorption of metals on modified chitosan is represented with kinetic parameters in fig. (10) and table (1). The coefficient determination (R^2) of the set data, as shown by the R^2 result, indicates that the experiment fits the pseudo-second-order model perfectly [46,47]. Intraparticle diffusion of uptake of studied heavy metals on modified chitosan was shown in fig. (11).

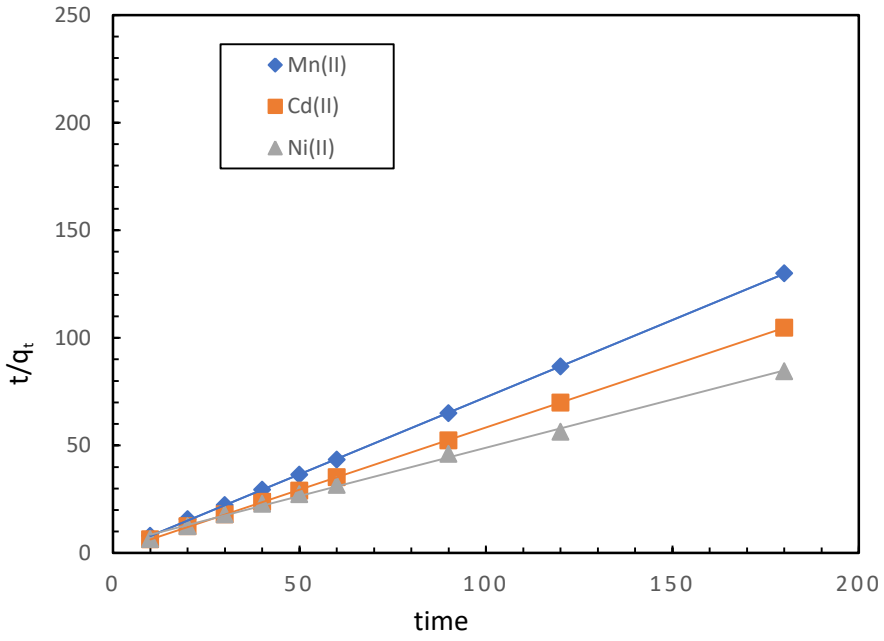


Fig. 10. Pseudo-second order model

Table 1 Kinetic characteristics of metal ions

Metal ion	q_e (exp.)	Pseudo-first order .			Pseudo-second order .		
		q_e (calc.)	k_1 (min^{-1})	R^2	q_e (calc.)	k_2 x10^{-5} (gmg^{-1} min^{-1})	R^2
Mn(II)	1.38	0.03	0.03	0.21	1.39	0.63	0.99
Cd(II)	1.72	0.05	0.03	0.31	1.73	0.58	1.00
NI(II)	2.13	0.33	0.004	0.16	2.22	0.19	0.99

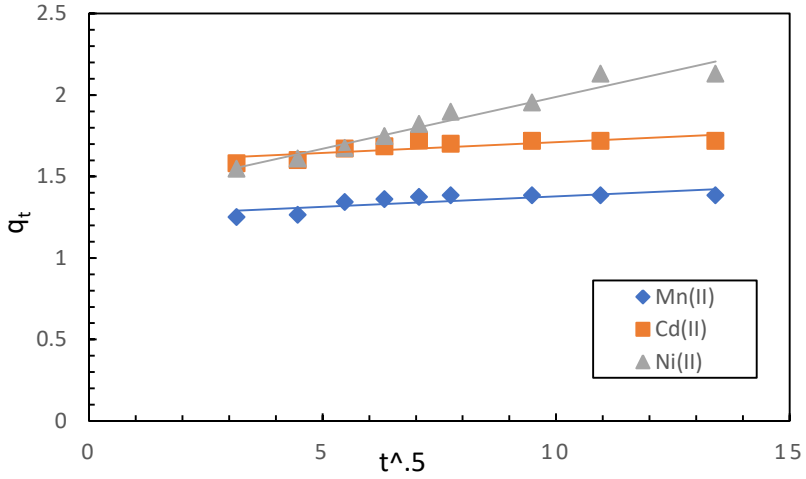


Fig. (11) Intraparticle diffusion of metal's elimination

Table 2 Intraparticle diffusion of of metal's elimination

Heavy metal	K_i	X	R^2
Mn(II)	0.013	1.250	0.611
Cd(II)	0.013	1.579	0.640
NI(II)	0.064	1.353	0.953

The coefficient of efficiency, or R^2, shows how dependent two variables are on one another as shown in table 2 [48]. R^2 values close to 1 indicate that the outcome fits that model. The adsorption is demonstrated to follow pseudo-second order [49].

4.3. Adsorption models

In order to align with the isothermal experimental data, various isothermal models were utilized [50]. Assuming an equivalent and energetically identical adsorption site, Langmuir assumes a monolayer covering adsorption approach [51,52]. In linearized form, it can be represented as eq. (9):

$$C_e/q_e=C_e/q_e+1/(K_LQ_{max}) \quad (9)$$

The graph of C_e/q_e vs. C_e showed an equal slope and intercept of $1/Q_{max}$ and $1/K_LQ_{max}$, respectively fig. (12). At all temperatures, At the identical temperature, the adsorption behavior was nearly monolayer, obeyed the isotherm of Langmuir, and had similar experimental and anticipated Q_{max} values. This occurred in spite of the adsorber's diverse nature. [53-56].

Multi-layer adsorption across a heterogeneous surface can be modeled using the Freundlich isotherm model [57,58]. To express the linearized form, use equation (10):

$$\text{Ln } q_e = \ln K_f - (1/n) \ln C_e \quad (10)$$

The adsorption capacity is expressed as K_f (mg/g). Based on the (1/n) value, the isotherm's kind is identified. However, absorption of ions was clearly more with line with the Langmuir model than the Freundlich model [59].

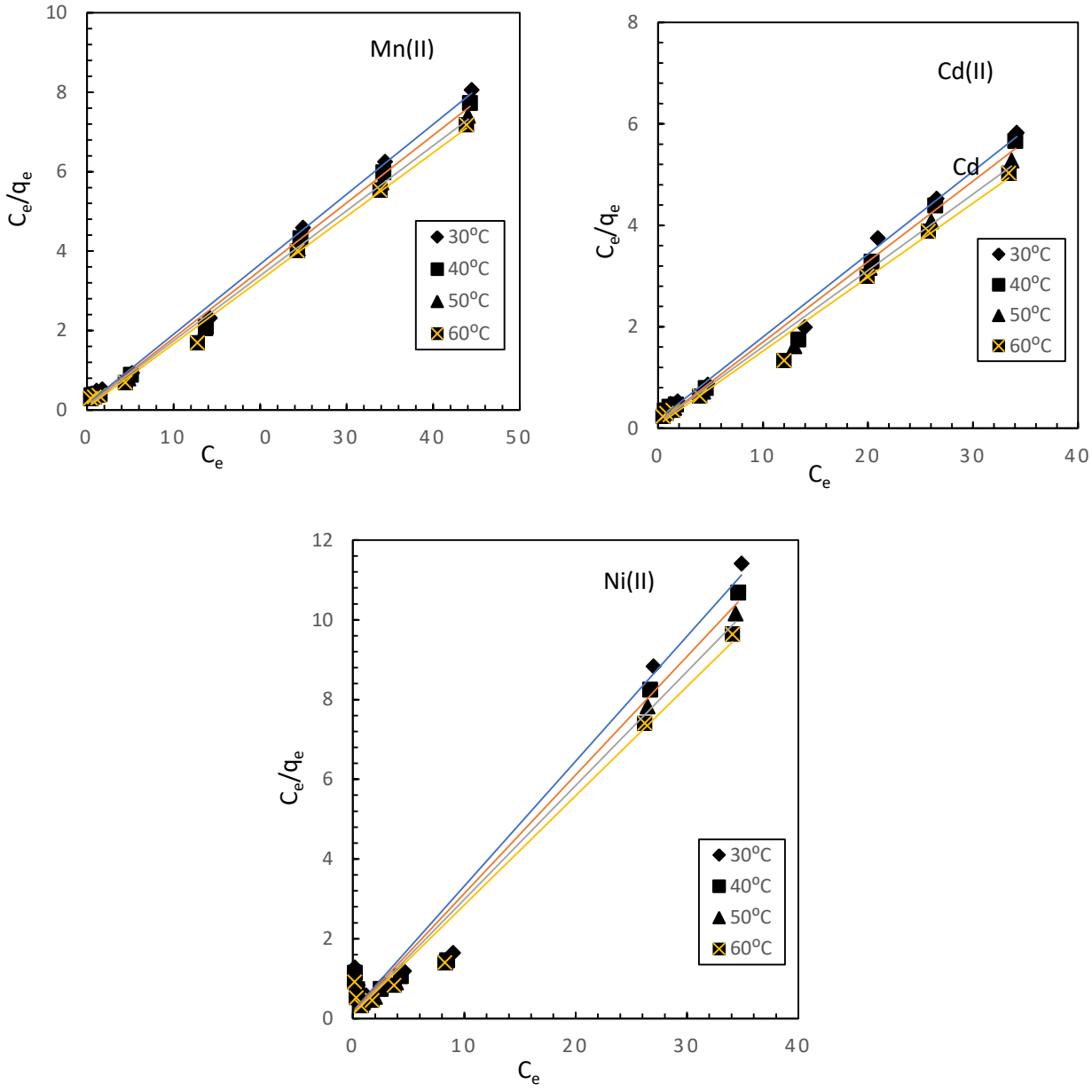


Fig. (12) isotherm of Langmuir ion uptake

4.3.1.The D-R dubinin-rdushkevich

An isotherm is a model that depends on temperature and can be utilized to identify the kind of adsorption mechanism (physical or chemical) by analyzing how energy is distributed on a surface that is heterogeneous [60,61].

As to the article, physisorption takes place when E < 8 $kJmol^{-1}$, but chemisorption happens when E the value within 8 −16

$kJmol^{-1}$. The findings showed that physisorption is responsible for the uptake of metals on modified chitosan [62].

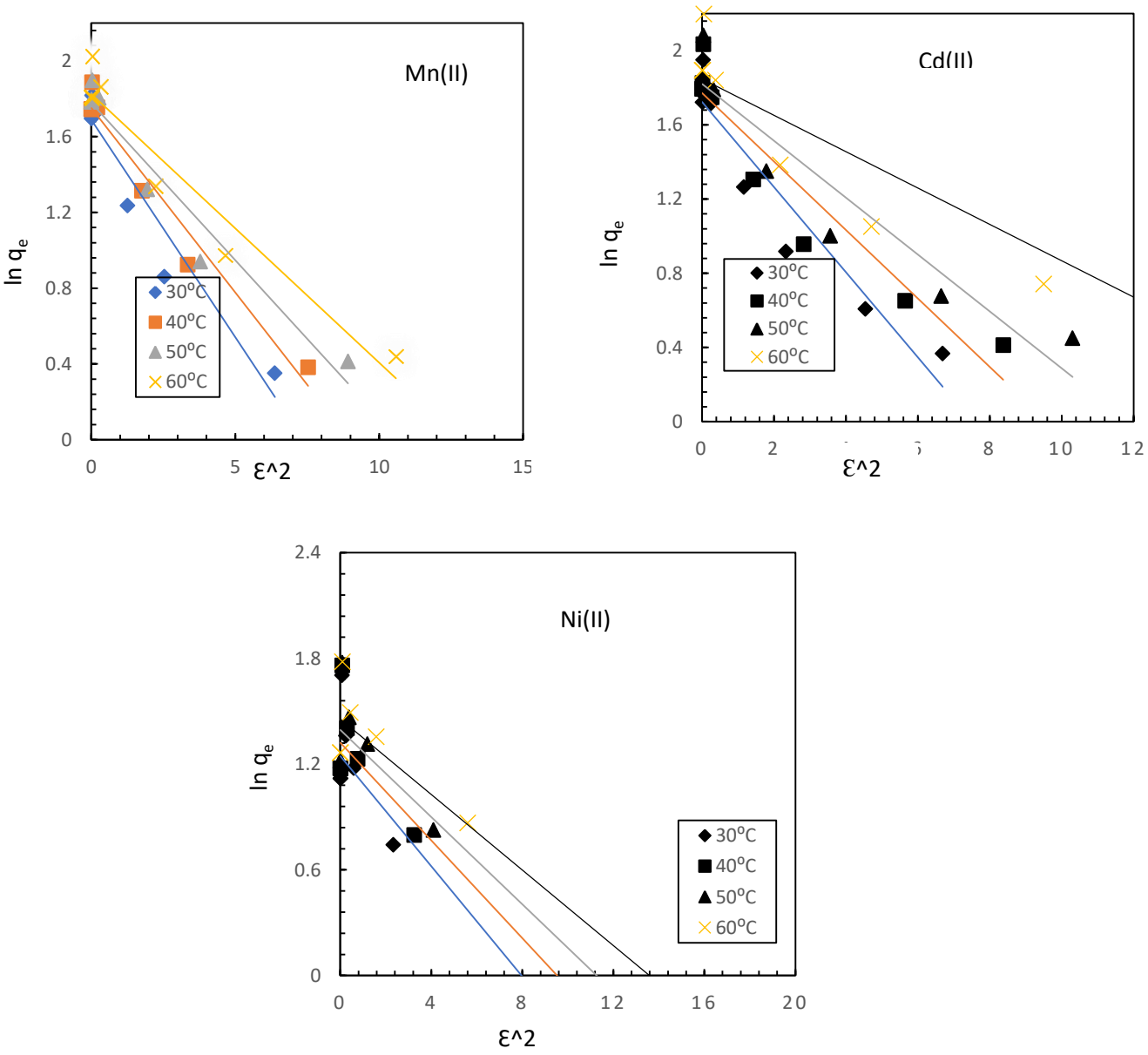


Fig. (13) Plot of the Dubinin-Radushkevich isotherm for metal ion adsorption

Table (3) Dubinin–Radushkevich for metal's sorption

Temp.	Mn(II)			Cd(II)			Ni(II)		
	k_{DR} (mg /g)	B (mol^2 kJ^{-2})	E (kJ /mol)	k_{DR} (mg /g)	B (mol^2 kJ^{-2})	E (kJ /mol)	k_{DR} (mg /g)	B (mol^2 kJ^{-2})	E (kJ /mol)
303	5.41	0.23	1.48	5.61	0.23	1.48	3.48	0.16	1.79
313	5.77	0.19	1.60	5.89	0.18	1.65	3.75	0.14	1.9
323	5.92	0.17	1.74	6.18	0.15	1.81	4.03	0.12	2.01
333	6.21	0.14	1.88	6.34	0.1	2.26	4.29	0.11	2.16

4.3.2. Thermodynamic treatment of studied ions sorption process

The following equations (14,15) were used to obtain the thermodynamic variables shown in table 4, Entropy change (ΔS), enthalpy change (ΔH), and standard Gibbs free energy change (ΔG) are among them.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

$$\Delta G^\circ = -RT\ln K_o \quad (12)$$

By using the Khan and Singh method [63], plotting ln (q_e/C_e) against C_e at different temperatures allowed for the calculation of the sorption distribution coefficient K_0. After then, the coefficient was extrapolated to zero C_e. The negative value of ΔG° demonstrated the spontaneous character of the adsorption reaction [64-66]. The ΔG° negative value rose with increasing temperatures, suggesting that high temperatures are more favorable for the investigated uptake [67,68]. Because |ΔH°| is smaller than |TΔS°| and the TΔS° value changed very little for each metal ion at all temperatures, the adsorption process was dominated by entropic rather than enthalapic changes [69].

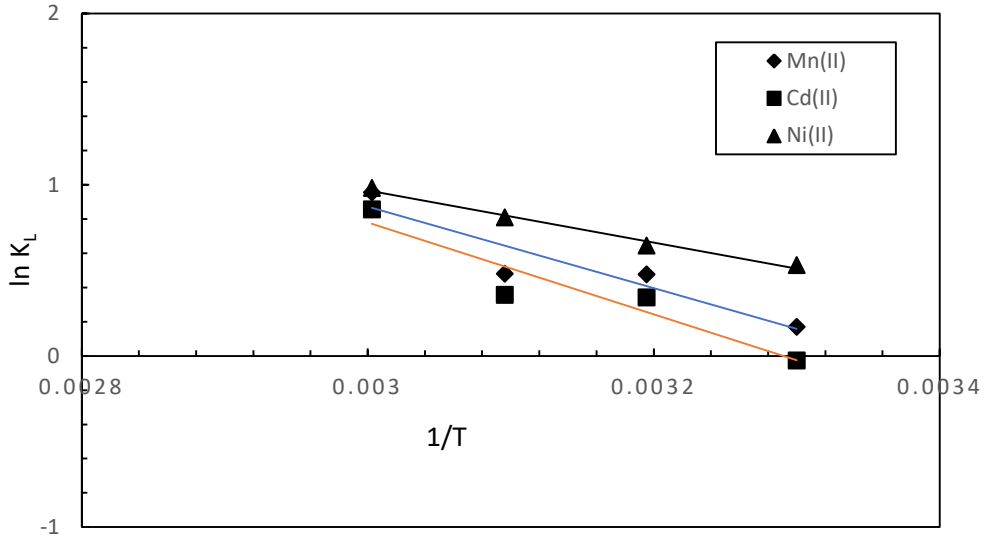


Fig. (14) Van't Hoff plots for the uptake of metals

Table 4. Thermodynamic characteristics of metal adsorption

Heavy metal	ΔH° (kJ/mol)	ΔS° (kJ/mol)	Temp.(K)	ΔG° (kJ/mol)	TΔS° (kJ/mol)
Mn(II)	19.75	0.07	303	-0.4	20.15
			313	-1.06	20.82
			323	-1.73	21.48
			333	-2.39	22.14
Cd(II)	22.31	0.07	303	0.07	22.24
			313	-0.66	22.97
			323	-1.40	23.71
			333	-2.13	24.44
Ni(II)	12.68	0.05	303	-1.29	13.97
			313	-1.75	14.43
			323	-2.21	14.89
			333	-2.67	15.35

5. Metal desorption and adsorbent recycling

The goal of the regeneration studies was to evaluate the adsorbent's reusability and identify the optimal reagent for metal's cations adsorption. By employing potent chelating agents, heavy metals can be eliminated using this technique [70]. In this instance, the loaded adsorbent with the heavy metals under investigation was shaken and exposed to ethanol for about an hour. During several adsorption/desorption five cycles, the regenerate resin showed an equivalent capacity to absorb.

6. Application of modified chitosan for industrial wastewater treatment

utilizing real samples with high levels of multi-metal ions, the modified chitosan's

adsorption capacity was tested utilizing a water pump near an agricultural drain and adjacent to agricultural land as shown in (table 5).

Table 5. ICP results of real samples before and after treatment with modified chitosan

Metal ion	Water pump sample 1 next to agricultural land			Water pump sample2 next to agricultural drain		
	C_i (mgL^{-1})	C_f (mgL^{-1})	Removal %	C_i (mgL^{-1})	C_f (mgL^{-1})	Removal %
Mn	0.88	0.175	80.20	0.8	0.14	82.5
Cd	0.4	0.075	81.25	0.37	0.07	81.43
Ni	0.03	0.004	86.67	0.025	0.003	86.8
Ba	0.16	0.04	75	0.12	0.028	76.42
Cu	0.09	0.02	78.02	0.086	0.018	79.07

7. Conclusions

Formaldehyde was added to chitosan to modify it. The generated adsorbent was characterized using several technologies. Many parameters (adsorbent dose, pH, duration, and adsorbate concentration) affected the adsorption process. The adsorbent showed rapid kinetics for the studied ions, with maximum absorption taking place in 60 minutes. The adsorption capacity for three ions rose as the adsorbate concentration was increased until saturation was reached. We used the D-R, Freundlich, and Langmuir adsorption isotherm models. The adsorption was found to be consistent with the Langmuir adsorption isotherm model. for five cycles, the adsorbent was regenerated in order to efficiently reabsorb metal ions. It was discovered that the adsorbent worked incredibly well to treat actual water pump samples.

8. References

1. **A. Bashir, L. A. Malik, S. Ahad, T. Manzoor, M. A. Bhat, A. H. Pandith, "Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods." Environ. Chem. Lett. 17 (2019): 729-754.**
2. **M. D. M. C. Gonzalez, M. V. Guzman, J. M. R. Maroto, J. M. P. Garcia, "Metal recovery from wastewater using electrodialysis separation." *Metals* 14 (2023): 38-55.**
3. **N. C. Joshi, R. Sharma, A. Singh, "Biosorption: A review on heavy metal toxicity and advances of biosorption on conventional methods." J. Chem. Chem Sci .7 (2017): 714-724.**

4. **S. L. R. K. Kanamarlapudi, V. K. Chintalpudi, S. Muddada, "Application of biosorption for removal of heavy metals from wastewater." Biosorption 18 (2018): 70-116.**
5. **P. K. Patel, L. M. Pandey, R. V. S. Uppaluri, "Highly effective removal of multi-heavy metals from simulated industrial effluent through an adsorption process employing carboxymethyl-chitosan composites. " *Environ. Res.* 240 (2024): 117502-117516.**
6. **R. Chakraborty, A. Asthana, A. K. Singh, B. Jain, A. B. H. Suzan, "Adsorption of heavy metal ions by various low-cost adsorbents: a review." J. Environ. Anal. Chem. 102 (2022): 342-379.**
7. **M. O. Idris, A. A. Yaqoob, M. N. M. Ibrahim, A. Ahmad, M. B. Alshammari, "Introduction of adsorption techniques for heavy metals remediation." Emerging Techniques for Treatment of Toxic Metals from Wastewater. Elsevier,18(2023): 1-18.**
8. **M. Z. A. Zaimee, M. S. Sarjadi, M. L. Rahman, "Heavy metals removal from water by efficient adsorbents." Water 13 (2021): 2659-2670.**
9. **S. D. Gisi, G. Lofrano, M. Grassi, M. Notarnicola, "Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment" A review. Sustain. Mater. Technol. 9 (2016): 10-40.**
10. **Z. Raji, A. Karim, A. Karam, S. Khalloufi, "Adsorption of heavy metals: mechanisms, kinetics, and applications of various adsorbents in wastewater remediation—a review." *Waste*.1 (2023): 775-805.**
11. **Z. U. Zango, N. S. Sambudi, K. Jumbri, A. Ramli, N. H. H. A. Bakar, B. Saad, M. N. H. Rozaini, H. A. Isiyaka, A. M. Osman, A. Sulieman, "An overview and evaluation of highly porous adsorbent materials for polycyclic aromatic hydrocarbons and phenols removal from wastewater." Water 12 (2020): 2921-2960.**
12. **M. D. H. Rahaman, M. D. A. Islam, M. D. A. Rahman, S. M. N. Alam, "Biodegradable composite adsorbent of modified cellulose and chitosan to remove heavy metal ions from aqueous solution." *Curr. Res. Green Sustain.* 4 (2021): 100119-100126**
13. **D. Mahlangu, K. Mphahlele, F. D. Paola, N. H. Mthombeni, "Microalgae-mediated biosorption for effective heavy metals removal from wastewater: A review." *Water* 16 (2024): 718-740.**
14. **U. Upadhyay, I. Sreedhar, S. A. Singh, C. M. Patel, K. L. Anitha, "Recent advances in heavy metal removal by chitosan based adsorbents." Carbohydr. Polym. 251 (2021): 117000-117028.**

15. **S. Shahraki, H. S. Delarami, F. Khosravi, R. Nejat, "Improving the adsorption potential of chitosan for heavy metal ions using aromatic ring-rich derivatives." J. Colloid Interface Sci. 576 (2020): 79-89.**

16. **Y. Zhang, M. Zhao, Q. Cheng, C. Wang, H. Li, X. Han, Z. Fan, G. Su, D. Pan, Z. Li, "Research progress of adsorption and removal of heavy metals by chitosan and its derivatives: A review." Chemosphere 279 (2021): 130927-130943.**

17. **I. O. Saheed, W. D. Oh, F. B. M. Suah, "Chitosan modifications for adsorption of pollutants–A review ".J. Hazard. Mater. 408 (2021): 124889- 124950.**

18. **F. G. L. M. Borsagli, A. Borsagli, "Chemically modified chitosan bio-sorbents for the competitive complexation of heavy metals ions: a potential model for the treatment of wastewaters and industrial spills." J. Environ. Polym. Degrad. 27 (2019): 1542-1556.**

19. **Laroche, Celine, Delattre, Cedric, M. Baouche, "Bioactivity of chitosan and its derivatives." Curr. Org. Chem. 22 (2018): 641-667.**

20. **C. M. D. Moura, J. M. D. Moura, N. M. Soares, L. A. D. A. Pinto, "Evaluation of molar weight and deacetylation degree of chitosan during chitin deacetylation reaction: Used to produce biofilm." Chem. Eng. Process.: Process Intensification 50 (2011): 351-355.**

21. **B. Bellich, L. D'Agostino, S. Semeraro, A. Gamini, A. Cesàro, "The good, the bad and the ugly" of chitosans." Mar. Drugs 14 (2016): 99-129.**

22. **L. Casettari, D. Vllasaliu, J. K. W. Lam, M. Soliman, L. Illum, "Biomedical applications of amino acid-modified chitosans: a review." Biomater. 33 (2012): 7565-7583.**

23. **M. Muhaidin, F. H. Naning, J. M. Saad, R. Wahi, T. Zangina, "Heavy Metal Ion Adsorbent in Aqueous Solution: A Review on Chitosan and Chitosan Composites."** ***Adv. Res. In Micro. Nano Eng.*****18 (2024): 78-102.**

24. **J. Desbrières, E. Guibal, "Chitosan for wastewater treatment." Polym. Int. 67 (2018): 7-14.**

25. **X. Tan, Z. Tian, Y. Liu, F. Xiao, H. Zhang, "Facile fabrication of chitosan /bone/bamboo biochar beads for simultaneous removal of co-existing Cr (VI) and bisphenol a from water."** ***J. Environ. Health, 59*** **(2024): 507-520.**

26. **K. K. Lawal, L. K. Ekeleme, C. M. Onuigbo, V. O. Ikpeazu, S. O. Obiekezie, "A review on the public health implications of heavy metals." WJARR 10 (2021): 255-265.**

27. **S. C. Dey, M. A. Amin, T. U. Rashid, M. Z. Sultan, M. Ashaduzzaman, M. Sarker, S. M. Shamsuddin, "Preparation, characterization and performance evaluation of chitosan as**

an adsorbent for remazol red." Int. J. Latest Res. Eng. Technol 2 (2016): 52-62.

28. F. G. L. M. Borsagli, A. Borsagli, "Chemically modified chitosan bio-sorbents for the competitive complexation of heavy metals ions: a potential model for the treatment of wastewaters and industrial spills." J. Environ. Polym. Degrad. 27 (2019): 1542-1556.

29. S. C. Deya, M. A. Aminb, T. U. Rashidc, M. Ashaduzzamand, S. M. SDey, S. Chandra, "pH induced fabrication of kaolinite-chitosan biocomposite." Int. Lett. Chem. Phys. Astron 68 (2016): 1-9.

30. M. A. Ibrahim, M. H. Alhalafi, El. A. M. Emam, H. Ibrahim, R. M. Mosaad, "A review of chitosan and chitosan nanofiber: Preparation, characterization, and its potential applications." Polym. 15 (2023): 2820-2854.

31. S. A. Othman, S. N. F. A. Rahman, "Chitosan Properties: A Preliminary Review." *JAMEA* 5 (2024): 8-12.

32. N. Sh. Lebedeva, S. S. Guseinov, E. S. Yurina, Y. A. Gubarev, A. I. V'yugin, "Pyrolysis of Complexes of Metallo sulpho phthalocyanines with Chitosan for Obtaining Graphite-like structures." *J. Inorg. Organomet. Polym. Mater.* 31 (2021): 3991-4000.

33. C. Thambiliyagodage, M. Jayanetti, A. Mendis, G. Ekanayake, H. Liyanaarachchi, S. Vigneswaran, "Recent advances in chitosan-based applications—a review." *Materials* 16 (2023): 2073-2130

34. W. K. Restu, R. S. Mawarni, E. Triwulandari, M. Ghozali, T. O. Zahra, N. Rachmadona, P. Sugita, H. A. Restu, "Baked hydrogel from palm starch and modified chitosan for water contaminant removal." *Chem. Pap.* 78 (2024): 2977-2986.

35. B. L. Tardy, B. D. Mattos, C. G. Otoni, M. Beaumont, J. Majoinen, T. Kämäräinen, O. J. Rojas, "Deconstruction and reassembly of renewable polymers and biocolloids into next generation structured materials." Chem. Rev. 121 (2021): 14088-14188.

36. C. Rodrigues, J. M. M. D. Mello, F. Dalcanton, D. L. P. Macuvele, N. Padoin, M. A. Fiori, C. Soares, H. G. Riella, "Mechanical, thermal and antimicrobial properties of chitosan-based-nanocomposite with potential applications for food packaging." J. Environ. Polym. Degrad. 28 (2020): 1216-1236.

37. N. H. I. Kamaludin, H. Ismail, A. Rusli, "Thermal behavior and water absorption kinetics of polylactic acid/chitosan biocomposites." Iran. Polym. J. 30 (2021): 135-147.

38. Y. Mahmud, Yead, N. Uddin, T. Acter, M. M. Uddin, A. M. S. Chowdhury, M. L. Bari, A. I. Mustafa, S. M. Shamsuddin, "Enhancement of antimicrobial properties of shoe lining leather using chitosan in leather finishing." Adv. Mater. Res. 9 (2020): 233-250.

39. Balarak, Davoud, Mostafapour, Ferdos, Azarpira, Hossein, Joghataei, Ali, "Langmuir, Freundlich, Temkin and Dubinin–radushkevich isotherms studies of equilibrium sorption of ampicilin unto montmorillonite nanoparticles." J. Pharm. Res. Int. 20 (2017): 1-9.

40. M. Monir, R. E. Elsayed, R. A. Azzam, T. M. Madkour, "Novel High-Performance Functionalized and Grafted Bio-Based Chitosan Adsorbents for the Efficient and Selective Removal of Toxic Heavy Metals From Contaminated Water." *Polym.* 16(2024): 1718-1737.

41. Q. Hu, Y. liu, C. Feng, Z. Zhang, Z. Lei, K. Shimizu, "Predicting equilibrium time by adsorption kinetic equations and modifying Langmuir isotherm by fractal-like approach." J. Mol. Liq. 268 (2018): 728-733.

42. H. A. Mohammed, L. S. Eddine, G. G. Hasan, S. Meneceur, C. Salmi, J. A. A. Abdullah, M. M. S. Abdullah, F. Menaa, "Efficient Removal of Heavy Metals, Dyes, and Contaminants from Industrial Wastewater Using Chitosan-Coated Fe_3O_4 Nanocomposites: Biosynthesis, Characterizations, and Performance Evaluation." *Biomass Convers. Biorefin.* 14 (2024): 1-16.

43. M. J. Ahmed, B. H. Hameed, E. H. Hummadi, "Review on recent progress in chitosan/chitin-carbonaceous material composites for the adsorption of water pollutants." *Carbohydr. Polym.*247 (2020): 116690-116762

44. D. Chandra, Md. T. H. Molla, Md. A. Bashar, Md. S. Islam, Md. Sh. Ahsan "Chitosan-based nano-sorbents: synthesis, surface modification, characterisation and application in Cd (II), Co (II), Cu (II) and Pb (II) ions removal from wastewater." *Sci. Rep.* 13 (2023): 6050-6066.

45. T. F. Akinhanmi, E. A. Ofudje, A. I. Adeogun, P. Aina, I. M. Joseph, "Orange peel as low-cost adsorbent in the elimination of Cd (II) ion: kinetics, isotherm, thermodynamic and optimization evaluations." *Bioresour. Bioprocess.* 7 (2020): 1-16.

46. D. Hao, Y. Liang, "Adsorption of $Cu^{2+,}$ Cd^{2+} and Pb^{2+} in wastewater by modified chitosan hydrogel. " *Environ. Technol.* 43 (2022): 876-884.

47. S. S. Elanchezhiyan, P. Karthikeyan, K. Rathinam, M. H. Farzana, C. M.

Park, "Magnetic kaolinite immobilized chitosan beads for the removal of Pb (II) and Cd (II) ions from an aqueous environment." *Carbohydrate Polym.* 261 (2021): 117892-117902.

48. Akbari, Mona, and Maryam Akbari. "Modeling of Preparation of Chitosan/Tripolyphosphate Nanoparticles Using Machine-Learning Techniques." *Iran. J. Chem. Chem. Eng. (IJCCE) Research Article* 43 (2024): 1-12.

49. V. Micle, G. E. Damian, G. C. Rogozan, L. M. Sur, "Non-Linear Regression Model for Estimating the Efficiency of Heavy Metals Removal by Soil Washing with Chitosan Solution." *Applied Sciences* 13 (2022): 465-478.

50. A. A. Bazaine, A. C. Trujillo, M. O. Marquez, "Adsorption isotherms: Enlightenment of the phenomenon of adsorption." *Wastewater Treatment* 19 (2022): 1-5.

51. H. Alyasi, H. R. Mackey, G. McKay, "Removal of cadmium from waters by adsorption using nanochitosan." *Energy Environ.* 31 (2020): 517-534.

52. S. Azizian, S. Eris, "Adsorption isotherms and kinetics." Interface Sci. Elsevier, 33 (2021):445-509.

53. A. Babakhani, M. Sartaj, "Removal of Cadmium (II) from aqueous solution using tripolyphosphate cross-linked chitosan." *J. Environ. Chem. Eng.* 8 (2020): 103842-103853.

54. J. C. D. A. Neto, G. J. Pereira, A. d. A. M. Giannetti, "Chitosan and corn stover derivative bioadsorbent: characterization and application in hexavalent chromium adsorption processes." *Cellulose* 27 (2020): 6317-6331.

55. N. Akartasse, E. Mejdoubi, L. L. Elansari, B. Hammouti, "Chitosan-hydroxyapatite bio-based composite in film form: synthesis and application in wastewater." *Polym.* 14 (2022): 4265-4284.

56. Z. Lin, Y. Yang, Z. Liang, L. Zeng, A. Zhang, "Preparation of chitosan/calcium alginate/bentonite composite hydrogel and its heavy metal ions adsorption properties." *Polym.* 13 (2021): 1891-1909.

57. A. L. Taka, M. J. Klink, X. Y. Mbianda, E. B. Naidoo, "Chitosan nanocomposites for water treatment by fixed-bed continuous flow column adsorption: A review." *Carbohydr. Polym.* 255 (2021): 117398-117432.

58. G. D. V. Brião, J. R. D. Andrade, M. G. C. D. Silva, M. G. A. Vieira, "Removal of toxic metals from water using chitosan-based magnetic adsorbents. A review." *Environ. Chem. Lett.* 18 (2020): 1145-1168.

59. B. Tekin, U. Açıkel, "Adsorption isotherms for removal of heavy metal ions (copper and nickel) from aqueous solutions in single and binary adsorption processes." ***Gazi Univ. J. Sci.*** **36 (2022): 495-509.**

60. D. C. D. S. Alves, B. Healy, L. A. D. A. Pinto, T. R. S. A. Cadaval, C. B. Breslin, "Recent developments in chitosan-based adsorbents for the removal of pollutants from aqueous environments." ***Mol.*** **26 (2021): 594-638.**

61. Z. Li, X. Wang, X. Zhang, Y. Yang, J. Duan, "A high-efficiency and plane-enhanced chitosan film for cefotaxime adsorption compared with chitosan particles in water." ***J. Chem. Eng.*** **413 (2021): 127494-127503.**

62. R. Donat, "Removal of Cd^{2+} metal ions from aqueous solutions by Na-alginate-containingcomposite biosorbent." ***Turk. J. Chem.*** **46 (2022): 754-765.**

63. S. Samejo, J. A. Baig, T. G. Kazi, H. I. Afridi, H. E. Ali, S. Perveen, K. Akhtar, Sh. A. Solangi, F. Abbasi, S. Hussain, "Chitosan-integrated TiO_2 nanocomposite for adsorptive removal of Cd and Pb from drinking water." ***Chem. Pap.*** **78 (2024): 7827-7843.**

64. M. Abomosallam, M. Elalfy, Z. Zheng, K. Nagata, M. Suzuki, "Adsorption kinetics and thermodynamics of toxic metal ions onto chitosan nanoparticles extracted from shrimp shells." ***Nanotechnol. Environ. Eng.*** **7 (2022): 1-13.**

65. H. S. Mohamed, H. R. A. El-Mageed, H. S. Ali, T. R. Mahmoud, S. A. Ahmed, N. K. Soliman, "Adsorption of Mn^{+7} ions on chitosan/cellulose composite: Experimentally and theoretically approaches." ***J. Dispers. Sci. Technol.*** **43 (2022): 1525-1542.**

66. P. Rani, R. Johar, P. S. Jassal, "Adsorption of nickel (II) ions from wastewater using glutaraldehyde cross-linked magnetic chitosan beads: isotherm, kinetics and thermodynamics." ***Water Sci. Technol.*** **82 (2020): 2193-2202.**

67. Sh. Ashraf, R. Munir, M. Sayed, A. Muneer, M. Yaseen, M. Zahid, N. Mushtaq, S. Noreen, "Synthesis and applications of green waste-mediated nickel, manganese, cobalt, copper, and zinc green ferrites for wastewater remediation." ***Biomass Convers. Biorefin. 14*** **(2024): 1-34.**

68. A. Ghobadifar, Gh. B. Marandi, M. Kurdtabar, Gh. R. Bardajee, "Removal of Pb (II) and Cd (II) by $MnFe_2O_4$@ SiO_2@ VTMS nanocomposite hydrogel from aqueous

solutions." *J. Environ. Polym. Degrad.* 31 (2023): 2686-2704.

69. F. I. Abouzayed, N. T. A. El-Nassr, S. A. Abouel-Enein, "Synthesis, characterization of functionalized grafted cellulose and its environmental application in uptake of copper (II), manganese (II) and iron (III) ions." *J. Mol. Struct.* 1270 (2022): 133907-133920.

70. B. G. F. Mbanga, E. Prabakaran, K. Pillay, "Carbohydrate biopolymers, lignin based adsorbents for removal of heavy metals (Cd^{2+}, Pb^{2+}, Zn^{2+}) from wastewater, regeneration and reuse for spent adsorbents including latent fingerprint detection: A review." *Biotechnol. Rep.* 30 (2021): e00609-e00624.