USE OF CHEMICALLY MODIFIED CHITOSAN FOR THE ADSORPTIVE REMOVAL OF TOXIC METAL IONS IN AQUEOUS SOLUTIONS

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Abstract. Chemical modification of chitosan was successfully carried out using three derivatives namely: 3-hydroxybenzaldehyde, 2,3-dihydroxybenzaldehyde, and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde by a condensation reaction. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area, thermal gravimetric analysis (TGA), and X-ray diffraction (XRD) methods were performed for characterization of the chitosan-derived Schiff base adsorbent materials. The efficiency of the prepared adsorbents in removing cobalt and nickel ions from aqueous solution was explored, and experimental data were analyzed using isothermal and kinetic models. The BET surface area of chemically modified chitosan was greatly enhanced 125.83 $m^2 g^{-1}$ with mesoporous characteristics. The maximum uptake was recorded at pH 5-6, while the maximum removal capacity was 243.90 $mg\ g^{-1}$ for cobalt ions whereas 166.67 $mg\ g^{-1}$ was achieved for nickel ions. The kinetic data were better fitted using pseudo-second-order.

Keywords: toxic ions, chitosan, wastewater treatment, adsorption, Schiff-based adsorbent.

1. Introduction

Water is a crucial and universal facilitator for life sustainability; with a growing population and immense demand for energy consumption, the water supply passes to deteriorate its quality. The main factors that essentially contribute to water quality are the unbalanced supply-chain management, the rapid global replication of industrialization and urbanization, and non-uniform waste discharge regulation.[1] There are many types of pollutants: organic and inorganic, living and non-living species in contaminated water. Therefore, it is extremely crucial to control and monitor water quality regarding standards related to the chemical, physical, and biological characteristics of standard water quality.

Several pollutants are recognized as harmful and toxic to the human health and the ecosystem. Among them, heavy metals consider to be an eminent priority one. Heavy metals are considered as the main pollutant that affect human health through air, soil and water, which threatens the environment and reduces life quality, due to its ability to accumulate through food chain and the non-degradable feature which afford serious problem.[2-4] For example, nickel metal is commonly used in molding zinc base, battery, mining, electroplating, and it can be found in the waste of silver refineries. These multiple uses of nickel are due to its desirable qualities and corrosion resistance as a result of its robustness. As a matter of fact, the exposure to this metal can cause nickel allergy that has many hazardous diseases like chest pain, nausea, vomiting and cancer of lungs, nose, and bone.[5] Whereas cobalt plays an important role in physiological functions like regulation of gene, immune system, and antioxidant defense this is true only for appropriate amounts. It also can be used in paint, leather tanning and other materials. These huge uses of cobalt may cause many health problems especially when the remnants of these products reach water. Some of these problems are anemia, estrogen hyper excretion, and problems of central nervous system.[6] Therefore, it is important to manage the quantity of toxic metal ions in waste liquids before entering the environmental system.

Many conventional methods have been commonly used for wastewater treatment. Such methods are chemical precipitation, membrane separation,[7] coagulation, and ion exchange technique. Among all techniques, adsorption is a more effective approach and has obtained a wider range of applications owing to its immanent low cost, easiness of design and operation, versatility, robustness, selectivity, and efficiency for removing pollutants at low concentration;[8,9] also, it implies low energy consumption and wide operation range of temperature and pH.[4,10]

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Most sorption-contaminated water applications are applied using different materials of adsorbents such as activated carbon,[11] fly ash,[12] silica gel,[13] zeolite,[14] sawdust,[15] clays,[16] cyclodextrin-based adsorbents,[17] graphene,[18] and many more. However, the use of bio-based materials will help the environment by lowering the impacts on human health. These materials possess significant biocompatibility characteristics, availability from many resources, renewability, relatively low cost, antibacterial activity, and biodegradability. Therefore, that will lead to environmental saving and the ability of chemically, physically, and enzymatically modification for certain ends of uses.

There are many kinds of biopolymers, such as starch, cellulose, pectin, and polysaccharides. Chitosan (the derivative of chitin) is considered polysaccharide materials with natural linear macromolecules. Chitosan provides chelating groups that include the noble reactive amino group besides primary and secondary hydroxyl. This enrichment of active groups offers versatility to the material with many possibilities of chemical modifications such as chelation, acylation, graft copolymerization, and crosslinking.

Chitosan-based materials are widely used as bio-adsorbents for wastewater treatment to remove heavy metals, and dyes exist at low concentrations.[3,19-22] A recent review article by Saheed *et al.*,[23] concluded that the modification of chitosan via different physical and chemical methods is a promising approach for the efficient removal of organic and inorganic pollutants from aqueous matrixes. Zalloum *et al.*[24] have modified chitosan using Schiff base derivatives and used it to study the uptake of Cu (II) ions in a batch adsorption experiment. Recently in our lab, the adsorptive removal of lead, cobalt, cadmium, and nickel from aqueous solutions was successfully investigated exploiting the chemical modification of chitosan with vanillin derivatives under batch conditions.[25]

To the best of our knowledge and as a continuation of our work, the present study attempts to modify chitosan with three benzaldehyde derivatives to obtain new Schiff base bio-sorbent materials. The new Schiff-based adsorbents are characterized and exploited in wastewater treatment by studying the removal of nickel and cobalt metal ions. The removal performance of the chemically modified chitosan toward metal ions at different variables: initial concentration, pH, contact time, temperature, and adsorbent weight are investigated. Adsorption isotherm, kinetics, and thermodynamic parameters of metal ion removal are studied as well.

2. Experimental

2.1. Materials and Instruments

Unless otherwise stated, all chemicals were obtained from commercial sources and were used as obtained. Chitosan ≥ 85 % deacetylated (Chem Cruz), 3-hydroxybenzaldehyde (99 %) (Merck Schuchardt), 2,3-dihydroxy-benzaldehyde (95 %) (AK Scientific), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (99.55 %) (CHEM-IMPEX INT'L INC), acetic acid glacial (99.8 %), methanol (UNIVAR), acetone (≥ 99.5 %), ethanol absolute (99.5 %) (Panreac), sodium acetate anhydrous (99 %) (labochemie), sodium chloride GR (labochemie), hydrochloric acid (min. 35.5 %), sodium hydroxide (96 %) (Avonchem), cobalt (II) nitrate hexahydrate (labochemie), nickel (II) acetate tetrahydrate (98 %) (Aldrich).

Thermal gravimetric analysis (Shimadzu, DTG-60H), surface area analyzer (Quantachrome-nova 1200e), atomic absorption spectrophotometer (Shimadzu, AA-7000), X-ray diffractometer (Shimadzu-XRD-7000), orbital shaker (SteadyShake, 757), Fourier transform infrared spectrometer (IRAFFINTT-2), SEM (Inspect S50, Czech Republic), pH meter (METTLER TOLEDO).

2.2. Synthesis and Characterization of Chitosan-Based Adsorbent Materials (Polymers I, II, III)

The bio-adsorbents were synthesized based on a method reported by Alakhras *et al.*[4] by refluxing 5.70 g of chitosan with 90 mmol of benzaldehyde derivatives for the three polymers (10.993 g of 3-hydroxybenzaldehyde for polymer I, 12.462 g of 2,3-di-hydroxybenzaldehyde for polymer II, 21.091 g of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde for polymer III) and mixed well with two solvents, 9 mL of glacial acetic acid and 90 mL of methanol for a period of 10 h. Thereafter, the acquired polymers were collected by filtration and washed with acetone and ethanol, respectively. Subsequently, Soxhlet extraction apparatus loaded with ethanol and acetone (1:1 ratio) for 24 hours was used to purify the materials from unreacted reactants. The resulted polymers were dried at 70 °C for 3 hours and sieved over the mesh to integrate the particle size.

The acquired adsorbents were then characterized and analyzed by TGA in the temperature range (from 10 to 600 °C under nitrogen atmosphere) to determine the dynamic weight loss; FTIR was used to emphasize the formation of imine group as the main character that distinctive Schiff base compounds, also BET was used to investigate the surface area before and after modification of chitosan, SEM was used to display the morphology before and after sorption. The XRD of chitosan and the modified polymers were recorded between ($2\theta = 5$ and 60), exhibiting the materials' crystallinity.

2.3. Preparation of Metal Ion Stock and Working Solutions

A stock solution of metal ion was made by dissolving an appropriate amount of its salt in deionized water

with the concentration of 1000 mg L^{-1}. The solution was freshly prepared for every time uses. Working solutions were obtained by dilution of the stock solution prepared earlier with various concentrations as needed.

2.4. Adsorptive Removal of Metal Ions onto Chitosan-Derived Schiff Bases

Removal experiments were executed by the batch contact method. A weighed amount (10.0 mg) of adsorbent material was equilibrated with 25 mL of adjusted buffer in a glass vial placed in thermostat shaker at fixed temperature (30 °C/ 150 rpm) till reach the equilibrium. Afterwards, 25 mL of known concentration of metal ion solution was mixed with the previous solution and then retained to the shaker for a period of 3 h. These are fixed conditions for the experiments and the study was taken one variable of each parameter to get the optimum conditions at the end of the experiments.

The effect of pH was studied by adjusted acetate buffer solution by adding an appropriate amount of acetic acid and sodium acetate anhydrous ranging from 4 to 7.

Similarly, to study adsorbent weight's influence, different weights of the dried polymers were taken (0.01, 0.02, 0.03, 0.05, and 0.1 g). Besides the adsorbate concentration-effect study, different initial concentrations were used (20, 30, 50, 70, 100, 150 mgL^{-1}). Same examinations were applied at different temperatures, including (30, 40, 50, 70 °C). Besides, for studying the impact of contact time, specific intervals were applied (10 to 360 min). Lastly, the samples were separated by filtration; the filtrate contains the un-removed metal ions were analyzed using AAS.

In the explanation of adsorption isotherm experiments, the quantity of adsorbed metal ion at equilibrium, q_e (mg g^{-1}), was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

where C_0 represents the initial ion concentration, C_e refers to the remaining concentration (mg L^{-1}) after equilibrium, V is the volume of solution (L), and W refers to the adsorbent material's weight (g).

Besides, to investigate the rate of the removal process, the value of the remaining ion concentration was investigated at several periods, which represented by the equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \qquad (2)$$

C_t (mg L^{-1}) represents the amount of remaining concentration in solution at a specific time t.

The removal efficiency (%) of metal ion by chitosan-derived Schiff base was calculated conferring to the following equation:

$$\%R = \frac{(C_0 - C_e)V}{C_0} \times 100 \qquad (3)$$

3. Results and Discussion

3.1. Synthesis and Characterization of the Adsorbent Materials (Polymers I, II, III)

Chitosan samples were modified using three kinds of benzaldehyde derivatives that include, 3-hydroxy-benzaldehyde (polymer I), 2,3-dihydroxybenzaldehyde (polymer II), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (polymer III). The association between chitosan and benzaldehyde derivative resulted in the Schiff base configuration for the corresponding polymers (Fig. 1) with the imine group's implementation. The reaction occurred *via* direct condensation between the primary amine group and the dynamic carbonyl group, where chitosan presented the principle amine and the carbonyl attained from the benzaldehyde derivative.

The IR data (Fig. 2) of chitosan and chitosan-derived adsorbent materials was in concurrence with the structures assigned to them. Subsequently, for unmodified chitosan, the broad band from the range of 2500-3800 cm^{-1} is allocated to the existence of hydroxyl groups and the incorporation of intermolecular hydrogen bonds.[4] Also, the N-H stretching vibration active group is overlapped at the same range of O-H. Nevertheless, at about 3000 cm^{-1}, the band related to C-H stretching of the chitosan groups appears. There is a strong peak in the range of 1000-1260 cm^{-1} assigned to the C-O group's stretching vibration.

Additionally, for chemically modified chitosan, we can distinguish the appearance peak of the aromatic stretching band =C-H that is allocated in the range of 2800-3000 cm^{-1}. We can also notice the peak's appearance related to C=N at the range of 1550-1700 cm^{-1} and emphasize Schiff base compounds' formation with no further doubt.[24] It is also noticed that there is an absence for the peak of the carbonyl group (C=O) of aldehyde that typically occurs on the fundamental matrix of benzaldehyde derivative before the integration. The peak typically appeared from the range of 1720-1740 cm^{-1}. In addition, after sorption with cobalt and nickel ions as shown in Fig. 2 we can differentiate the intensities before and after sorption occurs. The IR spectra showed the position of the peaks which were shifted to lower frequencies and some peaks appeared with less intensity, this can be in somehow assigned to the binding engagement between these active groups and the metal ions.
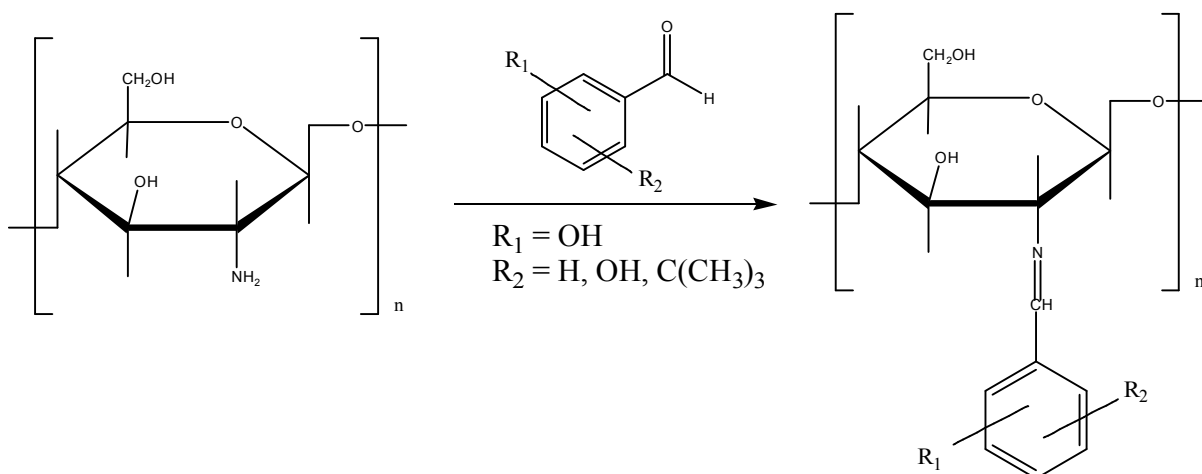
Fig. 1. Preparation of chitosan-benzaldehyde derivatives
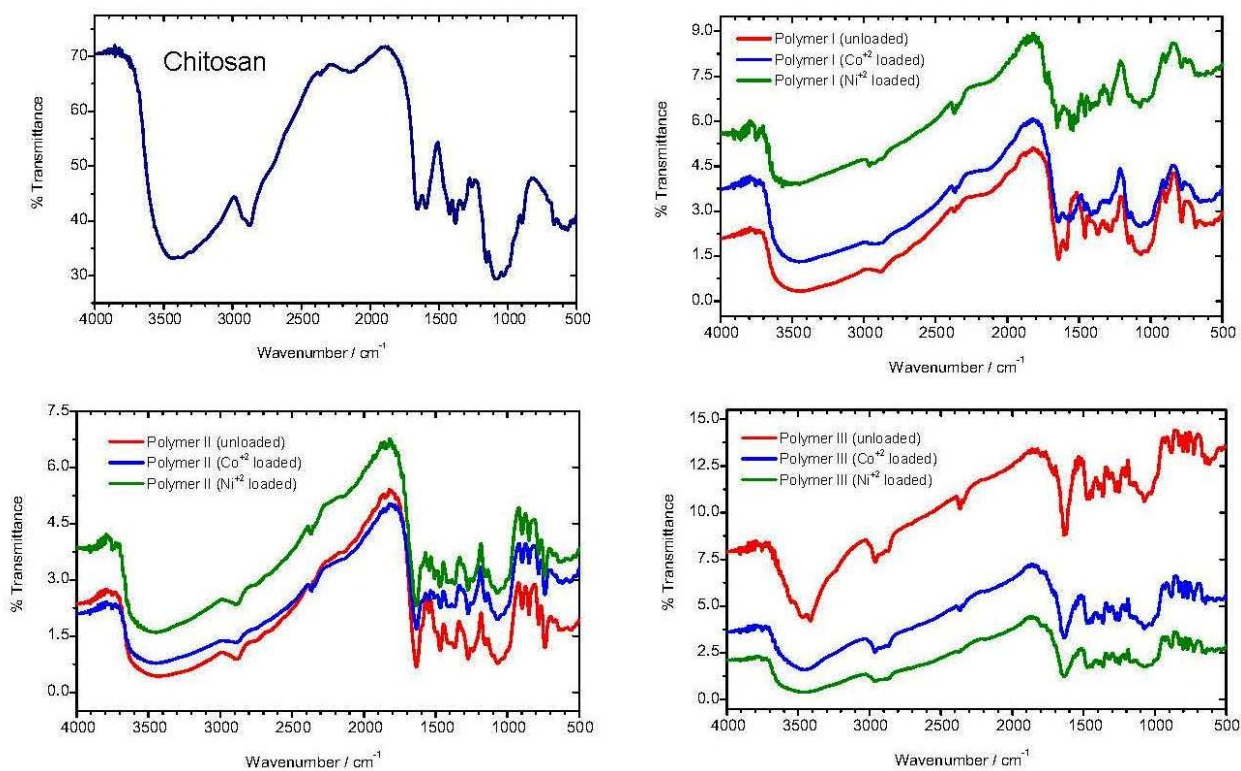
Fig. 2. FTIR spectra of chitosan and modified adsorbent materials

Table 1. BET analysis of chitosan-benzaldehyde Schiff base adsorbents

	BET surface area ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)	Average pore radius (nm)
Chitosan	6.905	5.909×10^{-3}	3.862
Polymer I	83.710	12.009×10^{-3}	12.948
Polymer II	125.833	18.052×10^{-3}	19.464
Polymer III	97.207	13.942×10^{-3}	15.036

Brunauer–Emmett–Teller (BET) analysis parameters listed in Table 1 present a variation of specific surface areas, total pore volume, and average pore radius of chitosan and the modified polymers. The modified adsorbent's surface area is increased significantly compared with raw chitosan specially for polymer II, whereas the average pore radius showing that chitosan and the modified polymers are mesoporous materials.

The thermal degradation implied the main stages of degradation resistance of the studied materials. For pure chitosan, as shown in Fig. 3, the first peak has shown the degradation process that interprets the endothermic peak observed at approximately 80°C; this peak denotes the evaporation of solvents that had been used in the proce-

dure of modification or purification. The second step is the exothermic peak shown at 304.5°C with 4.776 % of mass loss, which is characteristic of the bio-based sorbent's oxidative degradation.

Furthermore, the degradation temperature of the three modified polymers was higher than pure chitosan, recorded between 336.36°C and 385.12°C with average 4.428 % of mass loss. Accordingly, from the degradation patterns, it can be concluded that the increase of degradation temperature is assigned for the stability of modified adsorbent against heat rising, in which the imine group has been involved. The imine group is thermally stable and needs a higher temperature to start decomposition.
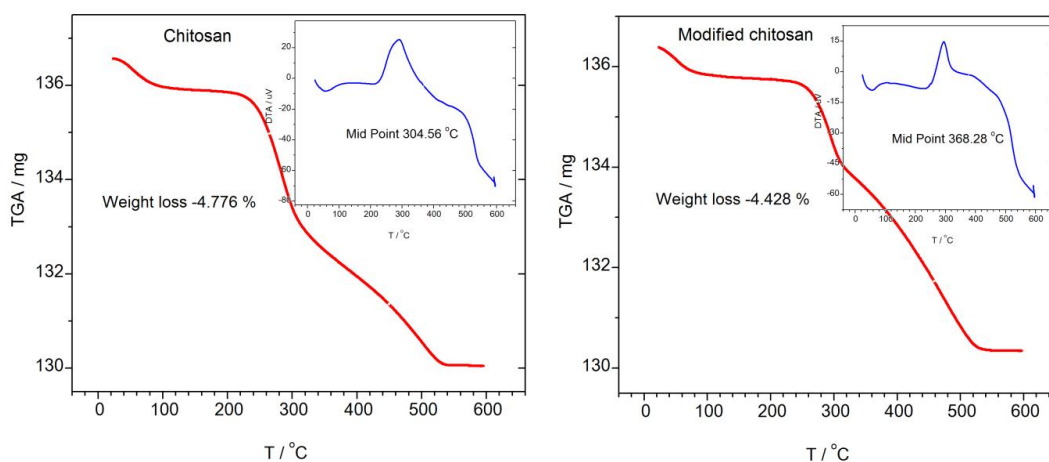
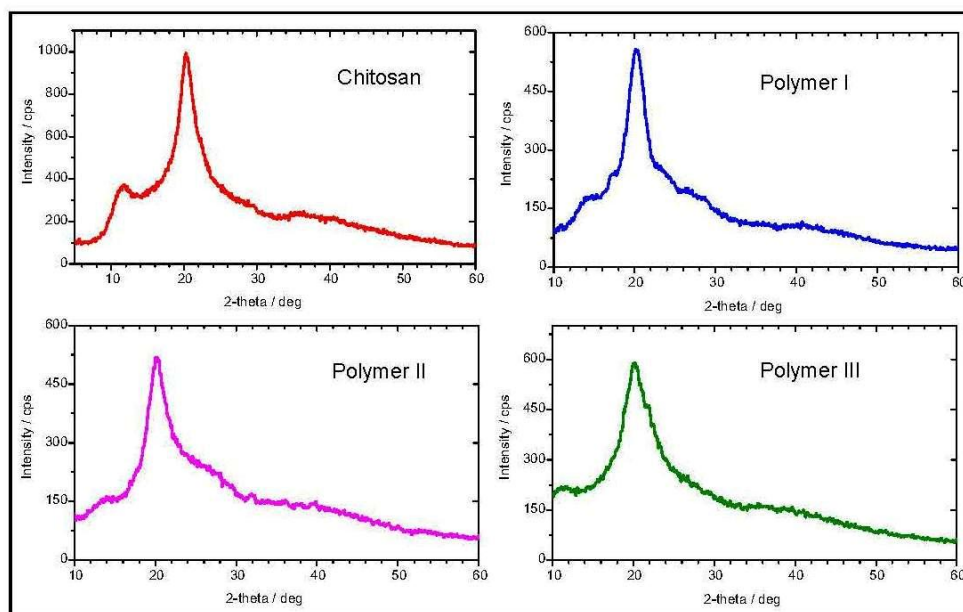**Fig. 3.** TGA curves of chitosan and chitosan-based material (polymer II)

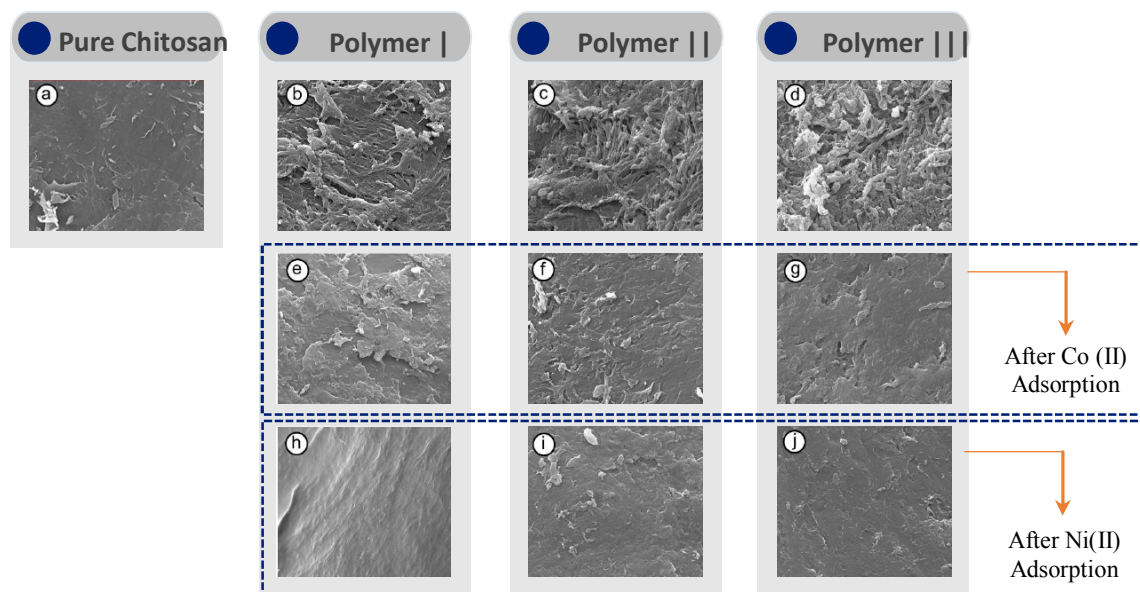**Fig. 4.** XRD patterns of Chitosan and modified adsorbent materials

Fig. 5. SEM micrographs of pure chitosan and chitosan-Schiff based before and after removal

The XRD spectra of chitosan and the modified adsorbents have been shown in Fig. 4, exhibiting a slight crystalline state of chitosan powder. Two prominent peaks are observed at ($2\theta = 11°$ and $20.25°$), and these typical crystalline peaks also exist for modified chitosan-benzaldehyde Schiff base adsorbent but with lower intensities. This lowering is probably attributed to the Schiff base conformation between the amino group of chitosan and the carbonyl group of benzaldehyde, which might break hydrogen bonds between $-NH_2$ and $-OH$ present naturally in raw chitosan, result in a low crystallinity structure. A similar discussion of crystal structure had been presented in another reference.[26,27]

SEM is widely used to study the surface morphology and microstructure of biomaterials. Fig. 5 shows the SEM micrographs of the pure and the modified bio-adsorbent materials before metal ion removal. From the electronic images, it is evident that the pure chitosan's surface morphology and microstructure are different from the modified one. The surface of pure chitosan is somehow smooth and solid, whereby only fewer channels are visible.

The modified adsorbent's unlikelihood shows the distinct surface features with a rough surface, numerous wide-ranged pores, suggesting the development of large exposure areas and channels for loading pollutants. The appearance of developed channels is more evident for chitosan-Schiff-based as compared with unmodified chitosan. The appearance of developed meso-channels is more obvious for polymers I and II (see panel b and c) compared to polymer III. Upon adsorbing of Co and Ni ions as shown in Fig. 5 (e–j), it can be seen that the micro-structure of the bio-sorbent polymers has been altered from rough to nearly smooth surfaces; hardly any pores are visible as shown in the panels. The alteration of surface features and diminishing of channels are attributed to the adsorption of heavy metals on the surface levels as well on the channels inside via strong interactions between energetic sites of polymeric membranes and metallic ions.[28]

The surface of polymer I (as shown in Fig. 5h) was the smoothest among the polymers, suggesting the high degree of combining with Ni ion confirming smooth coating of monolayer combining through this polymeric membrane. From this, it can be concluded that polymer I has high affinity and more selectivity toward Ni ion.

3.2. Effect of pH on Metal Ion Removal

The influence of pH is considered one of the most critical environmental factors for removing toxic metal ions. In our study, the investigated sorption onto modified adsorbents was carried out between pH values from 4 to 7 under continuous shaking with a fixed contact time of 3 h at 30°C with an initial concentration of 20 mg L^{-1}. From the experimental data, it is obvious from Fig. 6 that the removal attitude of the two kinds of metal onto chitosan-derived Schiff bases took place upon increasing of pH. The highest percentage of removal was achieved in slightly acidic and near neutral media.

For the uptake of cobalt ion, it is optimized that the best pH for the removal process according to the highest value of removal percentage by the three polymers occurred at pH 6. The results showed that the three polymers had approximate values of sorption capacities which were

higher than 50 % of adsorbate molecules. At this pH value, the hydrolysis of metal ions may take place for easily movement from the bulk of solution to the walls of bio-sorbents. We could demonstrate about the possible mechanisms that participated for the uptake, which may include one of chelation (complexation), or electrostatic attractions. As the media is almost neutral, so through the productive lone pair of electrons that is mainly significant for control the sorption process.[29] The lone pair of electrons can conduct for binding with the metal ions resulting chelation for polymer I and III by sharing the lone pair of electrons from N and OH groups, while for polymer II complexation might occur due to the presence of two neighboring hydroxyl groups. Consequently, on this mechanism the exterior side of the polymer might have additional uptake for the metallic ions under these conditions. The modified biosorbents also have a point of zero-charge (pH_{Pzc}) at value more than pH 6.3 measured according to the drift method.[28] With increasing pH value, the adsorbent's charge becomes more negative by losing a proton from hydroxyl group and this second mechanism allows for electrostatic attractions.
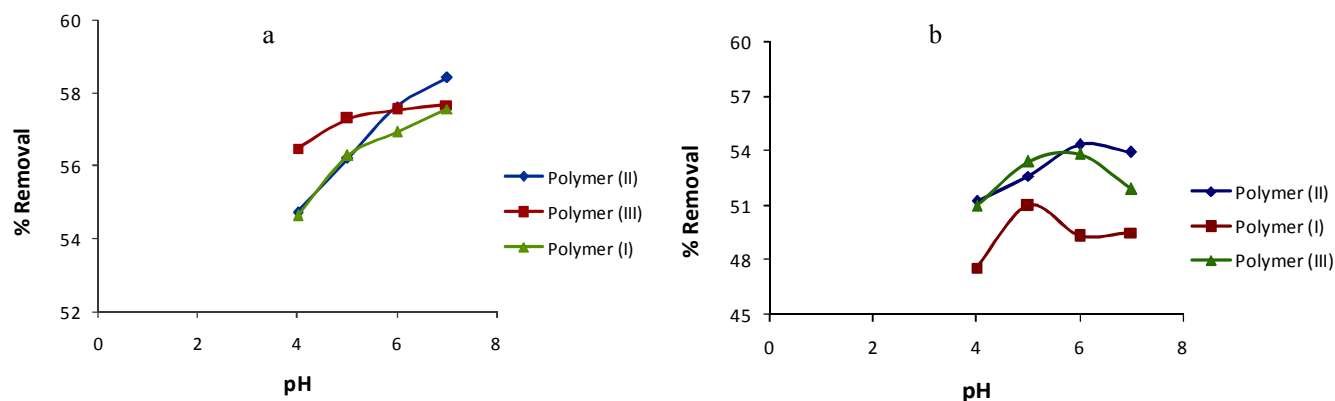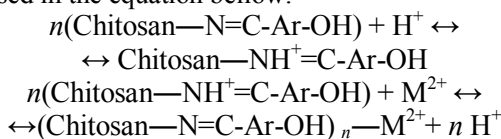

Fig. 6. Effect of pH on % removal (a) cobalt, (b) nickel

For the uptake of nickel, generally the same trend was observed for the three polymers. Polymers II and III had the best sorption media at pH 6, although polymer I had favorable uptake at pH 5. At pH 6 the same approach of mechanisms might occur for polymers II and III as described previously with cobalt. Nevertheless, polymer I at pH 5 could have slightly different mechanism and that regarding to the media that has less value than the value of pH_{zpc} 6.6 which may indicate for partial protonation and thus providing positive charge at the surface of the polymer. This might result an ion exchange mechanism, by release H^+ ions from the backbone of chitosan-based polymer into solution and substituted with the cation, as proposed in the equation bellow:

$$n(\text{Chitosan—N=C-Ar-OH}) + H^+ \leftrightarrow$$
$$\leftrightarrow \text{Chitosan—NH}^+\text{=C-Ar-OH}$$
$$n(\text{Chitosan—NH}^+\text{=C-Ar-OH}) + M^{2+} \leftrightarrow$$
$$\leftrightarrow (\text{Chitosan—N=C-Ar-OH})_n\text{—M}^{2+} + n\,H^+$$

Additionally, at lower pH values the uptake capacity decreased, which might be due to the conformation of H^+ ions in solution that could take place on the uptake process rather than the metal ions, so subsequently that will attribute the capacity uptake for each polymer.

3.3. Effect of Adsorbent Dosage

For cobalt ion uptake, some hesitance values on the removal percentage are noticed, but overall there was slight increasing on the removal when the polymer dosage got increased due to the increasing of accessible polymer sites. The highest removal value for polymer I was achieved around 0.05 g, polymer II at 0.1 g, and polymer III at 0.05 g which has the greatest removal percentage of 61.954 % and that might be due to the hydrophobic interactions of the tertiary butyl groups that stand against aggregation. In general, increase in the mass of bio-sorbents result in diminishing of the equilibrium concentration of metal ions. However, we realized vacillation values by the three polymers on the overall cobalt removal. This vacillation behavior might occur due to the amphiphilic character of chitosan that has two kinds of interactions which include hydrophilic and hydrophobic characters, owing to an increase or decrease on the uptake according to the binding way between intra and enter-molecules.[30] The decreasing can be illustrated as the formation of aggregates, owing to the presence of hydrogen bonds that configurated by the polar groups of the macromolecules which contribute to minimize the distance between these molecules. So, when aggregates occur there could be decreasing for particle diffusion, thus decreasing the accessibility to available sites on the polymer surface.

This can help for illustrating the behavior of polymer II that has its effectiveness at more dosage amount, by the means of presence of more polar groups (OH). Hence, the formation of hydrogen bonds may take place

and make the process of particle diffusion more complicated, for that higher amount of polymer is needed to achieve the best removal.

For nickel uptake process, different behavior is noticed for the metal toward cell walls of the bio-sorbents that with mass increasing an equilibrium mode was detected by polymers II and III which got almost constant values while mass increased after 0.03 g. Polymer I reached its highest removal at 0.01 g, when compared to other polymers that got the lowest removal value, which might be caused by the creation of smooth layer of nickel ion on the top of the polymer surface that will limit the sorption with no further uptake, as discussed in the SEM analysis.
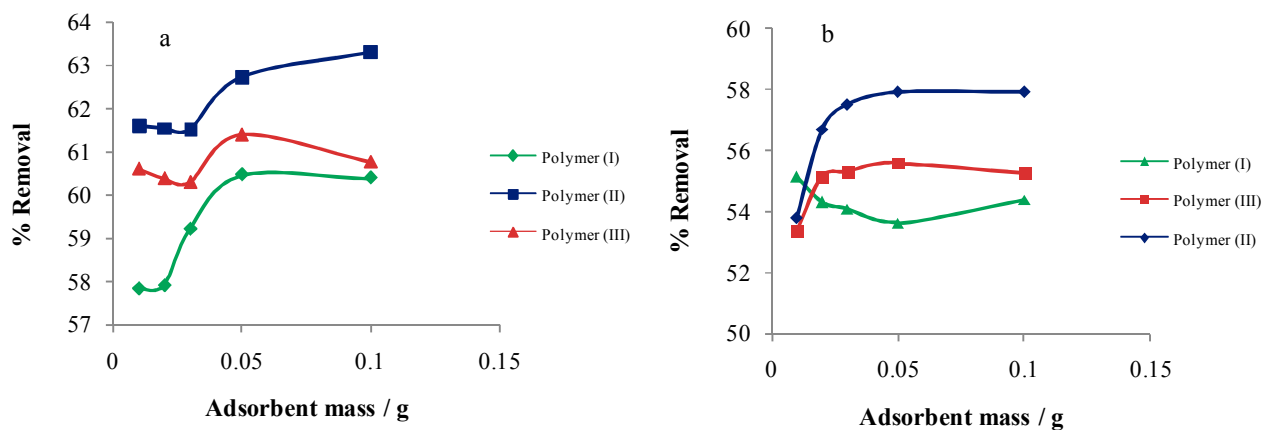
3.4. Effect of Temperature and Thermodynamic Analysis

As presented in Fig. 8, the two metals had the same tendency toward the three polymers. While temperature increased, the removal efficiency increased too. The enhancement of temperature rising could be explained as a result of increasing the pore size which proceeds to stir up the diffusion rate and more collision of metal particles moving to the external layer and then inside the pores. This could happen as a result of reducing the viscosity of the mixture, increase in the movement of ions between the solid/liquid interfaces. Under these circumstances, the equilibrium capacity of bio-sorbents will increase correspondingly as a result of swilling within internal sites.

Fig. 7. Effect of adsorbent dosage on % removal (a) cobalt, (b) nickel
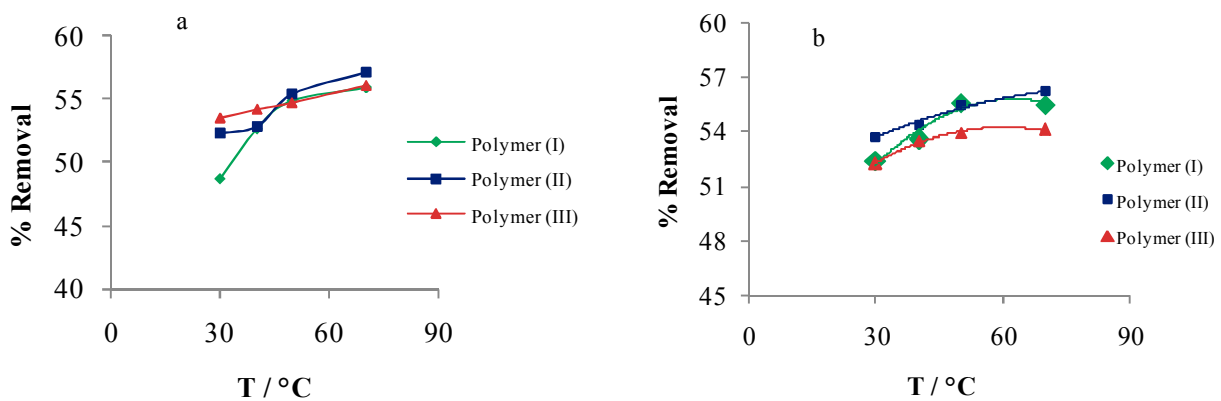

Fig. 8. Effect of temperature on % removal (a) cobalt, (b) nickel

Polymer II achieved the best elimination of removal percentage with 57.12 %; this could be due to the inducing of temperature to facilitate the diffusion of adsorbate particles toward the two (OH) groups that are mainly responsible for the complexation, to present tightly metal complex (as discussed previously in the effect of pH). We can also notice that there was no significant impact on temperature rising since there was no big difference between temperature 30 and 70°C, which will result in lower energy needed to discharge trace metal ions. The

thermodynamic parameters are assessed with four different temperatures for evaluating the values of ΔG, ΔH and ΔS, which were accomplished using Van't Hoff Eq. (4).[5]

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (4)$$

It is presented that temperature rising from 30 to 70 °C proceeds in capacity increasing and that agrees with the endothermic nature for sorption of cobalt and nickel ions onto the three polymers. As shown in Table 2 below, the enthalpy values were positive and that confirmed the endothermic reaction process.

Observing the values reported in Table 1, all the values of ΔG° at all temperatures were lower than zero, meaning the adsorption process was spontaneous. Also, the magnitude of ΔH° is <10 kJ mol⁻¹, which is well-matched with the physical adsorption of metal ions with the modified chitosan. The positive value of ΔS° is compatible with an increase in the randomness with the ions biding onto the adsorbent surface.

It can be noticed that with expanding temperature ΔG° values got nearly constant and that gave conception that the sorption is more expected to happen and not altered with higher temperatures, which means low energy needed for ions removal.

3.5. Effect of Time and Kinetic Analysis

In designing the batch adsorption experiments, it is important to consider the influence of contact time required to ambit equilibrium. The experiment's interval time was set from 5 to 1440 minutes at fixed conditions and optimum pH. Fig. 9 interpreted the removal percentage of cobalt and nickel ions as a function of time and clearly revealed that the removal process was fast even at 5 min of exposure with almost 55 % removal was achieved. The increasing of percentage removal was shown until equilibrium conditions had accomplished after around 3 hrs of study. At equilibrium, the distribution of adsorbate molecules in the bulk of the mixture is in balanced energetic with that on the surface of bio-sorbents.

Table 2. Evaluation of thermodynamic parameters for adsorption of Co and Ni onto three polymers at four different temperatures

	ΔH° (kJ mol⁻¹)	ΔS° (J mol⁻¹ K⁻¹)	Co (II)			
			ΔG° (kJ mol⁻¹)			
			T=30 °C	T=40 °C	T=50 °C	T=70 °C
Polymer I	5.994	33.133	-4.049	-4.380	-4.712	-5.374
Polymer II	4.424	28.693	-4.274	-4.561	-4.848	-5.421
Polymer III	2.227	21.9	-4.411	-4.630	-4.849	-5.287
	ΔH° (kJ mol⁻¹)	ΔS° (J K.mol⁻¹)	Ni (II)			
			ΔG° (kJ mol⁻¹)			
			T=30 °C	T=40 °C	T=50 °C	T=70 °C
Polymer I	2.821	23.613	-4.337	-4.573	-4.809	-5.281
Polymer II	2.277	22.141	-4.4348	-4.656	-4.8777	-5.320
Polymer III	1.4983	19.206	-4.324	-4.516	-4.708	-5.092
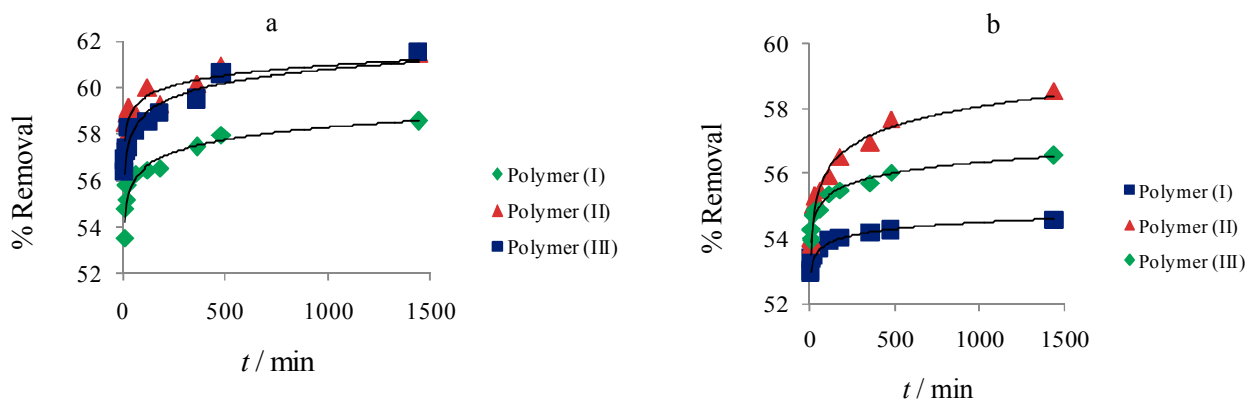
Fig. 9. Effect of contact time on % removal (a) cobalt, (b) nickel

The first stage of rapid sorption can refer to the high extent of initial vacant of dynamic sites on the surface of bio-sorbents. The relatively slow process caused by diffusion of particles to the interior surface at equilibrium consider to be as a matter of the number of remaining unoccupied sites, (which might be difficult to be occupied), due to the forces that are mainly presented in solution between adsorbate molecules bound on the material, and the bulk phase.[31]

This current work tested the linear pseudo-first-order and pseudo-second-order kinetic models.[32] The effectiveness of the models was assured by the durability of the straight lines of R^2 values and the conformity of the uptake values between the theoretical and experimental ones. The data for the sorption of cobalt and nickel ions was mentioned in Table 3. The theoretical $q_{e(Cal)}$ values premeditated from pseudo-first order offered meaningfully different values compared with the experimental ones, with slightly lower values of correlation coefficients. On the other hand, pseudo-second order showed very estimable fit with correlation coefficients which were close to the unity, and the theoretical values of $q_{e(Cal)}$ is compatible with the investigational values of $q_{e(Exp)}$ representing pseudo-second order as the suitable model for explaining the kinetic of the two systems.

Valence forces through sharing of electrons or ion exchange mechanism can be considered as the rate deter-mining step over the entire sorption system of Co (II) and Ni (II) ions on chitosan-derived Schiff base biopolymers.

3.6. Effect of Initial Ion Concentration and Isothermal Analysis

From the outcome of the two systems, the trend of the three biopolymers took the same pathway with cobalt and nickel ions. It is shown in Fig. 10 that when the initial concentration of metallic ions increased, the removal percentage decreased. This can be illustrated as when there is a raise in the concentration of the particles, there will be a rapid occupation of metal ions till they reach the limited available sites. Besides, at excessively higher concentration the sites will be eventually saturated at specific concentration compared to the moles number of the remaining particles. Hence, the removal percentage is reliant upon the initial metal ions concentrations. The magnitude value of removal percentage shows that cobalt ions were more favorable to get removed by the three polymers than nickel ions. Polymer II achieved the greater removal value with 62.38 %. The capacity of polymer II and III at each concentration were greater than the capacity of polymer I. According to the BET results, the average pore radius of polymer II and III where higher than polymer I, indicating the more ability to gain more numbers of metallic ions.

Table 3. Kinetic parameters of adsorption of Co and Ni ions onto three polymers

	$q_{e\,(Exp)}$ (mg g^{-1})	Co (II)					
		Pseudo-first order			Pseudo-second order		
		$q_{e\,(cal)}$ (mg g^{-1})	K_1 (min^{-1})	R_1^2	$q_{e\,(cal)}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R_2^2
Polymer I	58.548	3.436	0.002303	0.898	58.824	0.012	0.999
Polymer II	61.507	4.395	0.002303	0.917	62.513	0.009	0.999
Polymer III	61.468	3.177	0.006909	0.849	61.502	0.012	0.999
		Ni (II)					
Polymer I	54.549	1.225	0.002303	0.891	55.56	0.046	0.999
Polymer II	58.541	4.102	0.002303	0.936	58.82	0.011	0.999
Polymer III	56.557	2.118	0.002303	0.897	55.556	0.025	0.999
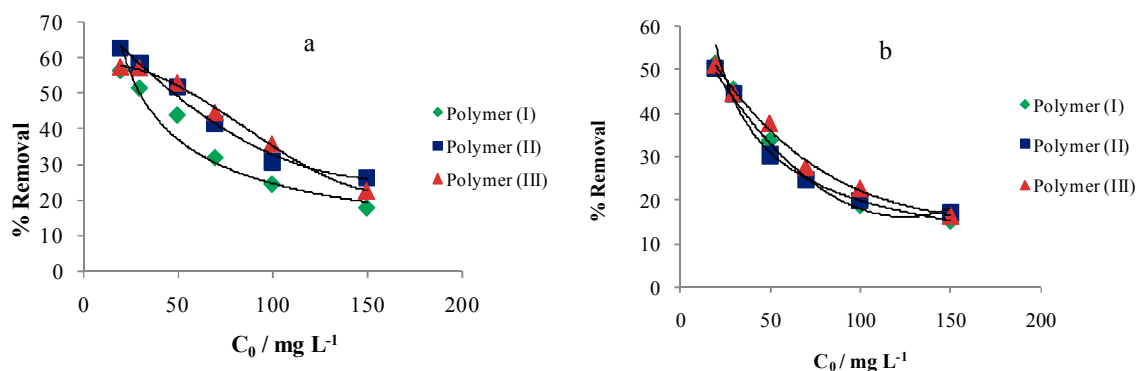
Fig. 10. Effect of metal ion concentration on % removal (a) cobalt, (b) nickel

Table 4. Isotherm parameters for adsorption of Co and Ni ions onto chemically modified chitosan

	Polymer I	Polymer II	Polymer III
Co (II)			
Langmuir			
q_{max} (mg g^{-1})	166.667	243.902	196.078
K_L (L mg^{-1})	0.067	0.044	0.069
R_L	0.429	0.534	0.421
R^2	0.984	0.997	0.981
Freundlich			
K_F (mg g^{-1} (mg L^{-1})$^{-1/n_F}$)	32.434	30.8319	28.5102
n_F	3.215	2.494	2.371
R^2	0.896	0.856	0.841
Ni (II)			
Langmuir			
q_{max} (mg g^{-1})	125.152	166.667	142.857
K_L (L mg^{-1})	0.060	0.032	0.055
R_L	0.454	0.607	0.478
R^2	0.985	0.953	0.996
Freundlich			
K_F (mg g^{-1} (mg L^{-1})$^{-1/n_F}$)	28.840	23.227	25.351
n_F	3.521	2.916	2.941
R^2	0.823	0.869	0.842

Adsorption isotherm of the two metal ions onto chemically modified chitosan was modeled using Langmuir[33] and Freundlich[34] isotherms. The calculated constants for the investigated isotherm models are presented in Table 4.

It is showed that the isotherm modeling analysis displayed Langmuir model perfectly with high coefficient values for the two metallic ions, more closely than Freundlich isotherm, demonstrating that monolayer adsorption might take place onto a homogenous surface structure. The values of q_{max} show the following uptake order: Co^{2+}>Ni^{2+} representing cobalt ion is more favorable and desired for the uptake than that of nickel ion.

There is a clear variety in the ionic radius of the metal ions; cobalt (200 picometer) has higher cationic radius value than nickel (163 picometer), and according to a study[35] it was shown that as long as the ionic radius is smaller there will be less opportunity to incorporate into the structure of the materials. Therefore, it was previously established when comparing the removal values in all experimental factors, that the affinity toward Co^{2+} was significantly more than Ni^{2+}. Overall, the q_{max} of the polymers got the same order in the uptake as follows: polymer II > polymer III > polymer I.

An essential characteristic can be illustrated by dimensionless constant (R_L) referred to separation factor realized by Weber & Chakravorti[36] according to the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

Table 5. Comparison of maximum monolayer removal capacities of different adsorbent materials for cobalt and nickel

Type of adsorbent	Co (II) q_{max} (mg g^{-1})	Ni (II) q_{max} (mg g^{-1})	Reference
Chitosan	-	86.51	[37]
Crosslinked chitosan–clay beads	-	32.36	[38]
Chitosan/magnetite	-	23.30	[39]
Chitosan/PVC	-	120.5	[40]
Chitosan-*O*-Vanillin	7.651	-	[5]
Chitosan-montmorillonite	150.1	-	[41]
Activated carbon	153.6	-	[42]
Bentonite clay	38.6	-	[43]
Polymer I	166.667	125.0	present study
Polymer II	243.902	166.667	present study
Polymer III	196.078	142.857	present study

Since all values of R_L were in the range of 0–1, it is proposed that the three chemically modified polymers were favorable to the medium of cobalt and nickel. Moreover, since the R_L values of Co^{2+} is to some extent smaller than the values of Ni^{2+}, it may conclude a highly favorable sorption process toward cobalt ion by the three modified chitosan biosorbents.

The maximum sorption capacity of chitosan-derived Schiff bases toward the two metal ions is compared with reported adsorbent materials (Table 5). It is evident that q_{max} mainly demonstrates better performance, making this material a potential candidate for adsorptive removal from aqueous solutions.

4. Conclusions

In this paper, new Schiff base composite materials are synthesized and characterized using eco-friendly chitosan and three benzaldehyde derivatives. The synthesized bio-based adsorbent materials are effective for the removal of cobalt and nickel ions from aqueous solutions. The increase of pH from 3 to 10 and adsorbent dosage from 0.2 to 2 g L^{-1} had a positive effect on the adsorption. Isothermal studies revealed a maximum sorption capacity of 243.90 mg g^{-1} for cobalt ion onto the adsorbent at pH 6 and 166.67 mg g^{-1} for nickel ion. Hence, chemically modified chitosan adsorbents are proved to be excellent candidates for ions removal from wastewater solutions. The kinetic investigations are better fitted using linear pseudo-second-order model. Moreover, it is concluded that the process is spontaneous and endothermic in nature and favorable – the magnitude of ΔH° supports the physical adsorptive removal process of two ions onto the modified chitosan.

Acknowledgments

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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ВИКОРИСТАННЯ ХІМІЧНО МОДИФІКОВАНОГО ХІТОЗАНУ ДЛЯ АДСОРБЦІЙНОГО ВИЛУЧЕННЯ ІОНІВ ТОКСИЧНИХ МЕТАЛІВ У ВОДНИХ РОЗЧИНАХ

Анотація. *Реакцією конденсації було успішно здійснено хімічну модифікацію хітозану з використанням трьох похідних, а саме: 3-гідроксибензальдегіду, 2,3-дигідроксибензальдегіду та 3,5-ди-трет-бутил-2-гідроксибензальдегіду. Методи інфрачервоної спектроскопії з перетворенням Фур'є (FTIR), сканувальної електронної мікроскопії (СЕМ), площі поверхні Брунауера–Еммета–Теллера (БЕТ), термогравіметричного аналізу (ТГА) та рентгенівської дифракції (XRD) були виконані для характеризації адсорбентів-основ Шиффа – похідних хітозану. Досліджено ефективність синтезованих адсорбентів щодо вилучення іонів кобальту і нікелю з водного розчину та проаналізовано експериментальні дані за допомогою ізотермічної та кінетичної моделей. Площа поверхні за БЕТ хімічно модифікованого хітозану була значно збільшена до 125,83 м² · г⁻¹ з мезопористими характеристиками. Максимальне поглинання зафіксовано за pH 5-6, а максимальна здатність вилучення становила 243,90 мг · г⁻¹ для іонів кобальту та 166,67 мг · г⁻¹ для іонів нікелю. Кінетичні дані краще описуються за допомогою псевдодругого порядку.*

Ключові слова: *токсичні іони, хітозан, очищення стічних вод, адсорбція, адсорбент-основа Шиффа.*