



Wastewater Treatment by Modified Chitosan Nanoparticles

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Abstract: Chitosan nanoparticles are bio-adsorbent that have been studied for adsorption of metals. To enhance their adsorption capacity, chitosan nanoparticles were modified with citric acid to supplement the functional groups with high affinity for Co(II) ions. In the present study, chitosan-citric (Cs-Cit) nanoparticles were prepared to form a new amide linkage, by grafting the amino groups of chitosan in the presence of carboxylic groups of citric acid that acts as a cross-linking agent. The as-prepared Cs-Cit nanoparticles samples were characterized using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) techniques. The results showed that the cross-linking agent preserved during the chemical modifications. The adsorption capacity of the prepared nanoparticles for the removal of Co(II) ions in aqueous solution was studied in batch experiments and the maximum removal reached 79 mg g⁻¹ at optimum conditions.

keywords: Chitosan-citric; Nanoparticles; Removal; Adsorption; Wastewater.

1. Introduction

Presently, water contamination by heavy metals is looked as a very critical environmental issue, because they gather in the environment and contaminates the food chain, intensifying cancer risk [1]. The most commonly metal ions present in wastewater are lead, copper, zinc, cadmium, chromium, nickel and cobalt [2, 3]. Numerous methods were applied for heavy metals elimination from waste effluents, among these, filtration, reverse osmosis, chemical oxidation or reduction, coagulation, ion exchange, electro-dialysis, electrode position, and adsorption can be mentioned [4]. Cobalt is a common pollutant found in the wastewater of nuclear power plants. It can cause significant harm to the ecosystem. Among various methods studied to remove cobalt ions from wastewater, adsorption is generally used [5, 6,7,8]. Owing to their great biocompatibility, nontoxicity, and availability abundance, natural polymers received much concern in the past few years [9-12]. However, special peculiarities of adsorption suchlike high adsorptivity, adsorbents resistance in a varied pH range, easy working circumstances and maintenance, lack

of toxicity, availability and low cost, with the capability of sorbent recovery and reuse, is an efficient economic new technique that has been broadly used as the tolerable method [13].

Chitosan is a renewable biopolymer with proved, fascinating characteristics in surface adsorption. It also has excellent properties as high biodegradability, high biocompatibility, non-toxicity, bio adhesion, and excellent ability to form metal ion chelation with different compounds [17]. Most researches have been concerned about the use of chitosan to remove cobalt ions from wastewater by adsorption. Adsorption means selective concentration of specific solute from solution onto the surface of some solids. Chitosan can adsorb significant amounts of metal ions from a variety of effluents [15]. The recent efforts have stressed on modification of chitosan using the reactive primary and secondary hydroxyl and amine groups to improve its adsorptivity and selectivity. Numerous physical or chemical modification processes have been applied to increase the adsorption kinetics [16]. Modification of chitosan molecule can be performed either with grafting or cross-linking

reactions. Grafting is inserting functional groups and cross-linking is uniting the macromolecular chains to each other [17, 18].

The goal of the present study is to explore the modification of chitosan with citric acid and its performance to remove cobalt ions from wastewater. X-ray diffractometer (XRD), scanning electron microscope (SEM), and infrared spectroscopy (FT-IR) were used for nanoparticles characterization. The impact of parameters such like contact time, pH, and adsorbent dose were explored.

1. Experimental

1.1. Materials

Chitosan with high M.Wt.(100, 000-300.000, Acros), potassium persulfate ($K_2S_2O_8$), acetic acid, citric acid, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were of pure analytical grade. Cobalt (II) nitrate (Fisher chemical Co.) used for adsorption experiments was prepared by diluting 500 mg. L^{-1} of a stock standard solution using de-ionized water. The pH of the solution was adjusted by adding NaOH (1 M) or HCl (1 M) using a pH meter (Hanna, Italy). Calculations of amounts of adsorption of cobalt ions onto Cs-Cit were based on removal efficiency (R) and adsorption capacity (q_e) as follows:

$$R = \frac{C_o - C_e}{C_o} \times 100$$

$$q_e = \frac{V(C_o - C_e)}{M}$$

Where q_e is the amount of cobalt adsorbed by Cs-Cit ($mg\ g^{-1}$), C_o and C_e are the initial and equilibrium concentrations of cobalt ions ($mg\ L^{-1}$), respectively, V is the solution volume (L), and M is the weight of CS-Cit used in the adsorption tests (g).

1.1 .Procedure

Cs-Cit nanoparticles were prepared with weight ratio (3:1% w/w) of Cs-Cit according to the methods of Heidari et al. [19]. Chitosan was dissolved in an aqueous solution of 1% acetic acid with stirring for 3 hours till the solution became clear then, 1 M HCl was added to adjust the pH value to 4 with stirring for 7 hours at $70^\circ C$. Citric acid solution was slowly added to the chitosan solution and a certain amount of potassium persulfate (KPS) was added. After heating at $70^\circ C$ for definite time in an inert atmosphere, the mixture was put in an ice bath for 1 hour. The Cs-Cit

nanoparticles were separated by centrifugation and dried using freeze-dryer. For adsorption experiments, 100 ml samples of Co^{2+} solution were transferred to adsorption tubes and the effect of contact time, pH, and adsorbent dose in a batch experiments on Cs-Cit nanoparticles were studied. Sample aliquots were removed after equilibrium achievement for determining Co(II) ions concentration using inductively coupled plasma - optical emission spectrometry (ICP-OES, Optima 2000 DV, Perkin Elmer Inc.).

2. Results and Discussion

The X-ray diffraction patterns of Cs-Cit nanoparticles reveals two peaks; one at $2\theta = 20.12^\circ$ and a second peak with high intensity at 27.48° indicating its crystallinity structure.

The FT-IR spectra of pure Cs-Cit nanoparticles shown in Fig. 2. suggested that the presence of carboxyl (COO^-), amide I ($NH\ COO^-$) and amine II (NH_2) functional groups in the spectra assures the Cs-Cit. nanoparticles formation [20]. It also indicates that chitosan and carboxyl group of citric acid were crosslinked via covalent bond. It can be noticed that the peak at $1599\ cm^{-1}$, related to the $-NH_2$ bending vibration in the raw CS ring, disappeared in the FT-IR spectra of Cs-Cit nanoparticles and a new one appeared at about $1720\ cm^{-1}$ due to cross linking [20].

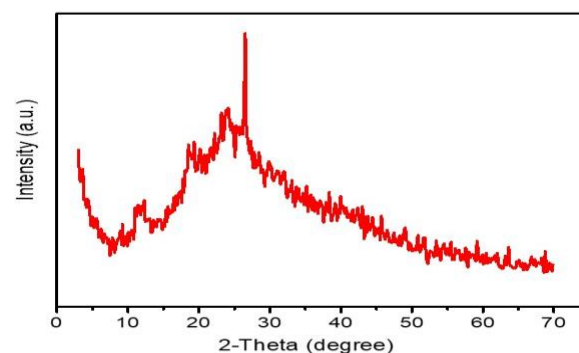


Fig. (1): XRD pattern of chitosan citric acid nanoparticles with ratio 3:1

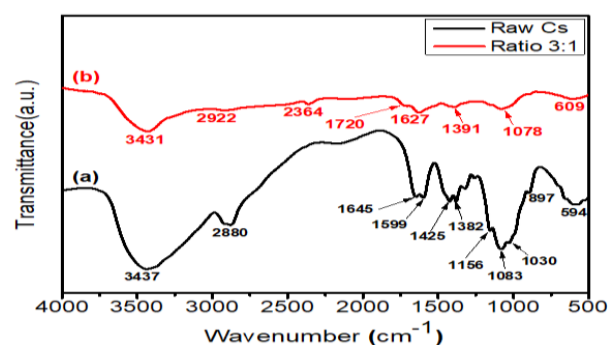


Fig. (2): FT-IR spectra of raw chitosan and chitosan citric acid nanoparticles with ratio 3:1

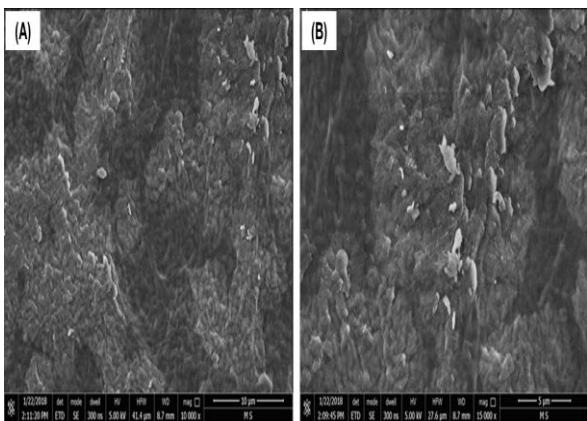


Fig. (3): SEM images of chitosan citric acid nanoparticles with ratio 3:1; (A) scale bar 10 µm; (B) scale bar 5µm.

The microstructure of Cs-Cit nanoparticles is displayed in **Fig. 3**, the particles were spherical but aggregated. The effect of contact time on cobalt adsorption process was estimated by applying adsorption experiments at different time periods. The concentration of metal ions was 200 mg L⁻¹; initial pH of solution; dose of adsorbent 0.025g and temperature 25 °C. Results are shown in Table 1. which depicts that the removal percent of cobalt was high at the beginning due to the large surface area of Cs-Cit adsorbent at start of the adsorption. Equilibrium time and maximum efficiency of Cs-Cit particles is 120 min and 38.54 %. It is clear from the results that the adsorption of cobalt was time dependent.

Table (1): % removal of Co²⁺ ions from aqueous solution at different time periods using 0.025g dose of Cs-Cit nanoparticles

Time (min)	C ₀ , mg L ⁻¹	C _F , mg L ⁻¹	% removal	Ads.capacity, mg g ⁻¹
15	205	140	31.71	65
30	205	140	31.71	65
45	205	138	32.68	67
60	205	134	34.63	71
90	205	132	35.61	73
120	205	126	38.54	79

Table 2 shows the effect of Co²⁺ adsorption onto Cs-Cit nanoparticles (3:1 wt. ratio) performed with various doses keeping other parameters constant during 60 min contact time, initial pH of solution 200 mg L⁻¹ concentration of Co²⁺, stirring at 250 rpm at 25 °C. When the dose of Cs-Cit adsorbent increases, the active sites on its surface increases resulting in increasing Co²⁺ ions removal percentage [21]. But after a 0.25 g

dose of adsorbent, the removal percentage begins to decrease from 56% to 55% owing to the collision between Cs-Cit nanoparticles [22].

In the case of cobalt metal ions adsorption by Cs-Cit nanoparticles, increasing pH leads to higher removal of metal ions, so that the most removal percentage is at pH 7 due to increase of OH⁻ ions that lead to reduction of adsorbent surface [23,24].

Table (2): % removal of Co²⁺ ions from aqueous solution at different doses of Cs-Cit nanoparticles for time period 1 hour and at initial pH=5.

Dose (g)	C ₀ , mg L ⁻¹	C _F , mg L ⁻¹	% Removal
0.025	205	134	34.634
0.05	205	130	36.585
0.075	205	134	34.634
0.10	205	129	37.073
0.125	205	124	39.512
0.172	205	114	44.390
0.25	205	90	56.098
0.325	205	92	55.122

Table (3): % removal of Co ions from aqueous solution at different pH values of Cs-Cit nanoparticles for time period 1 hour and dose of 0.05g.

pH	C ₀ , mg L ⁻¹	C _F , mg L ⁻¹	% Removal	Ads. capacity, mg g ⁻¹
2	205	130	36.59	37.5
3	205	125	39.02	40.0
4	205	122	40.49	41.5
5	205	115	43.90	45.0
6	205	114	44.39	45.5
7	205	113	44.88	46.0

1 .Conclusion

The adsorption manner of Cs-Cit nanoparticles to remove Co²⁺ ions from wastewater was studied. The Cs-Cit nanoparticles were produced via crosslinking citric acid with chitosan biopolymer. The pH, contact time, and adsorbent dose were noted to considerably control the adsorption process. The maximum adsorptivity found was 79 mg g⁻¹ after 120 min. of contact time.

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4. References

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