



# Development of a bio-based sorbent media for the removal of nickel ions from aqueous solutions



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## ABSTRACT

The objective of this study is to develop a low cost bio-based sorbent for the removal of nickel ions from aqueous solutions. Chitosan/Polyethylene oxide (Cs/PEO) nanofibers were prepared by electrospinning technique and characterized. Batch adsorption experiments were then carried out to investigate the effect of contact time and Cs/PEO mass ratio on adsorption efficiency of nickel ions. Results indicate that a maximum nickel adsorption ( $q_m$ ) of 227.27 mg/g was achieved at 75 °C. Pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic models were used to fit kinetic adsorption data. Batch adsorption equilibrium tests were also carried out at different temperatures. Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevich models were fitted to experimental data. It was found that the pseudo-second order and the Langmuir models provided a high degree of correlation ( $R^2 > 0.99$ ) with experimental data. Adsorption was then assumed to be a spontaneous endothermic chemical process.

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## 1. Introduction

A major interest has been increasing recently (since 1970s) for heavy metals impact on environment and human health [1]. Nickel ions for instance, are considered to be a harmful heavy metal, especially when released in aquatic environment. Many studies associated nickel compounds to respiratory cancer [2,3] and human kidney cells mutations [4]. So far, many regulations and legislations regarding the discharge of these contaminants in wastewaters have been established in many countries. For instance, different standards were set by the United States National Pollutant Discharge and Elimination System (NPDES) and State Indirect Discharge (SID) permits [1]. A limit of 2.38 mg/L/month of nickel in wastewater was fixed as the average effluent standard in the US [5]. In Israel, the monthly average effluent standard of nickel should not exceed 0.05 mg/L for discharging into river, and 0.2 mg/L for unrestricted irrigation [6]. As results of strict governmental legislations, many wastewater treatment plants tried to adopt conventional methods for heavy metals treatment. Unfortunately, these technologies were either not sufficient to meet new environmental regulations (membrane filtration, precipitation . . .), uneconomically (activated carbon, ion exchange, . . .), or technically complicated (precipitation, reverse

osmosis, . . .) [5,7]. Recently, several studies were carried out regarding the development of new and innovative technologies for heavy metals removal from wastewaters [8]. Adsorption onto low cost adsorbents is becoming one of the most attractive, and inexpensive method for wastewater treatments [8]. We have recently developed an alternative biosorbent based on electrospun chitosan nanofibers [9]. Chitosan is a natural polyaminosaccharide derived from *N*-deacetylation of chitin. This polycationic polymer is well known for its non-toxicity, biocompatibility, and biodegradability. Chitosan is also an excellent adsorbent due mostly to its amino ( $-NH_2$ ) groups serving as sites for metal binding [10]. Thanks to these unique properties, chitosan was undoubtedly one of the most attractive candidates for heavy metals adsorption from aqueous solutions, particularly nickel ions.

Commonly, chitosan was used for this application as a sorbent in membrane process or in adsorption columns. However, these methods were not efficient and were limited due to unfavorable hydrodynamic properties, and hence high capital and energy costs [11]. In this study, we were interested to use chitosan as nanofibrous membrane for the removal of metal ions due to its high surface area and its favorable hydrodynamic properties. In this paper, electrospun Chitosan (CS)/Polyethylene oxide (PEO) nanofiber mats were prepared to study their potential at removing nickel ions from aqueous solutions. Batch adsorption experiments were carried out under carefully controlled conditions to investigate the effects of contact time, temperature, initial nickel

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concentration, and Cs/PEO mass ratio on adsorption capacity. Langmuir, Freundlich, Redlich-Petersen (R-P) and Dubinin-Radushkevich (D-R) isotherm models were applied to describe adsorption equilibrium data of nickel ions. The nature of nickel adsorption process was evaluated with respect to kinetic, equilibrium and thermodynamic studies.

## 2. Experimental

### 2.1. Materials

A low molecular weight chitosan (75–85% deacetylated, Sigma-Aldrich) was investigated in this study. Acetic acid (80–90%, Sigma-Aldrich) was employed as a solvent to prepare chitosan solutions. Polyethylene oxide (PEO, average Mw~900 000) was supplied by Sigma-Aldrich and used in this study as a co-electrospinning polymer in order to improve chitosan electrospinnability. Nickel sulfate hexahydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) (A.C.S reagent, 99%, from Sigma-Aldrich) was used as the target contaminant. All nickel solutions were prepared with distilled water. Sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 99+% A.C.S, OMEGA chemical company, USA) was employed for nanofiber neutralization treatment. Ethylene diaminetetraacetic acid (EDTA) was purchased, as well, from OMEGA Chemical Company (USA) and used to determine residual nickel ions concentration. Murexide ACS reagent (Acros Organics) was used as an indicator for nickel concentration determination by a complexometric titration procedure. All materials were used as received, without further purification.

### 2.2. Methodology

#### 2.2.1. Solutions preparation

4% chitosan and 4% PEO solutions were prepared separately in 50% acetic acid and distilled water, respectively, at room temperature for 18–24 h until obtaining a complete dissolution. Then, 4% Cs/PEO blend were prepared according to different mass ratios (50:50/70:30/90:10), at room temperature for 18–24 h, until homogeneous solutions were obtained. Solutions were degassed and left to rest before electrospinning.

#### 2.2.2. Electrospinning process

A schematic illustration of the electrospinning set up is shown in Fig. 1. A 5 mL plastic syringe, with a 20 gauge stainless steel blunt needle (Kimble chase, Gerresheimer) was filled with Cs/PEO solutions. The polymer solution was then pumped using a programmable micro-syringe pump (KD Scientific, model 100). The flow rate of solution was adjusted to 4 mL/h. A high voltage DC generator (Gamma High Voltage Research, USA) was used to apply a high voltage between the tip of the needle and the drum collector. The rotating drum collector (rotational speed of

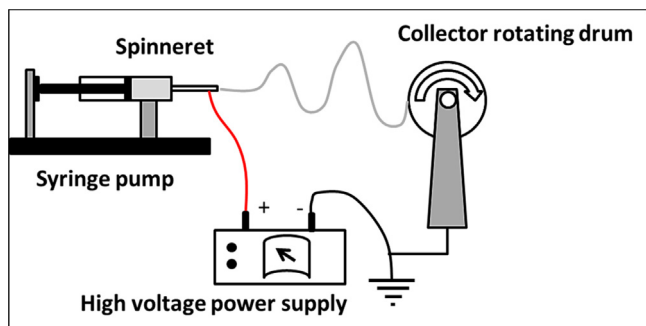


Fig. 1. Schematic illustration of the electrospinning setup.

1500 rpm) was covered with an aluminum foil and used to collect electrospun nanofibers. The optimum voltage applied was fixed to 25 kV and the distance between the needle and the collector was fixed to 10 cm. All electrospinning parameters were optimized based on literature and preliminary tests performed in our laboratory [12,13]. Electrospinning experiments were conducted at room temperature.

#### 2.2.3. Nanofibers neutralization treatment

At the end of electrospinning process, Cs/PEO nanofiber mats, collected on aluminum foil, were first dried in a vacuum oven at 70 °C for 24 h. At this stage, the nanofibers cannot be used further in aqueous solutions due to the presence of soluble protonated amino groups ( $\text{NH}_3^+$ ) on its structure. For that, the mats were immersed in a 0.1 M sodium carbonate solution (pH=11) for charge neutralization in order to improve their aqueous stability [14]. After 3 h of immersion, the nanofiber mats were washed with distilled water until reaching a neutral pH. Before characterization, nanofiber mats were dried at room temperature for 24 h, then, in the vacuum oven at 70 °C overnight.

#### 2.2.4. Nanofibers characterization

A JEOL-JSM 5500 scanning electron microscope (SEM), operating at 15 kV, was used to investigate the surface morphology of Cs/PEO nanofibers. Nanofiber mean diameter was determined with an image processing software, Image-J (using Diameter J plugin) [15]. The chemical analysis of adsorbent surface was examined by XPS (Axis ultra, Kratos), with a monochromatized  $\text{AlK}\alpha$  X-ray source (1486.7 eV) working in analytical chamber at 225W, 15 kV, 15 mA and base pressure of  $3 \times 10^{-9}$  Torr. For wide-scan spectra, an energy range of 0–1300 eV was used with pass energy of 160 eV. The high-resolution scans were conducted according to peak being examined with pass energy of 40 eV. XPS results were collected in binding energy forms and fit using the software of Vision (PR2.1.3) and CasaXPS (2.3.12Dev7). All spectra were calibrated with graphitic carbon as a reference at a binding energy of 285 eV, to compensate for the charging effect [16].

#### 2.2.5. Adsorption experiments

For kinetic experiments, the effect of adsorbent-adsorbate time contact on nickel adsorption efficiency was investigated. 25 mg of Cs/PEO nanofibers, with different mass ratios (50:50/70:30/90:10), were shaken in flasks containing 50 mL of 100 mg/L nickel solutions, using an orbital shaker (at a speed of 200 rpm) at room temperature (25 °C). Nickel solution samples were then collected at relevant time intervals. Residual nickel concentration was determined by titration using ethylene diaminetetraacetic acid (EDTA) with murexide as an indicator [17].

The amount of adsorbed nickel ( $q$  ( $\text{mg g}^{-1}$ )) is calculated using the following equation:

$$q = (C_0 - C_e) \frac{V}{m} \quad (1)$$

Nickel adsorption capacity was also determined by computing the percentage sorption using the following equation:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where:

$C_0$ : Initial concentration of nickel in solution (mg/L);

$C_e$ : Equilibrium concentration of nickel in solution (mg/L);

$V$ : Solution volume (L);

$m$ : Mass of nanofibers (mg).

For equilibrium experiments, the same method was adopted using different nickel initial concentrations (in the range of 25–400 mg/L) at different temperatures (25 °C, 50 °C, 75 °C).

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