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ORIGINAL ARTICLE

Remove Nickel (II) From Drinking Water Using Thiol-Functionalized Chitosan

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ABSTRACT
Some heavy metals are the causes of various diseases among humans. Thus, removing heavy metals is necessary in order to control environmental pollutants. The main purpose of this research is to enhance the separation of Nickel from water using thiol-functionalized chitosan. The functionalized chitosan was prepared by adsorption. For this purpose, a specific amount of chitosan beads were mixed with 3-mercaptopropyl and hydrochloric acid in ethanol. Then, the mixture was placed in a paraffin bath for the reaction to occur. The effective parameters in the adsorption process including the time of equilibrium, pH, and concentration were investigated. Next, surface morphology and FT-IR were studied. In this research, chitosan beads with porosities of 0.78 and diameters of 2.5 ± 0.05 were provided from 0.85% de-acetylated chitosan. The optimized equilibrium time was 220 minutes and the optimized PH was estimated to be 7. Increasing the amount of adsorbent led to an increase in the removal percentage. Furthermore, increasing the initial concentration of nickel in the water lowered the removal percentage of nickel from 72% to 50%. Our findings indicated that the maximum adsorption capacity of nickel was higher with the use of thiol-functionalized chitosan in comparison with the use of chitosan. Thus, this technique can substitute the common methods.
Keywords: *chitosan, thiol-functionalizing, nickel, adsorption technique*

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INTRODUCTION

Heavy metals are considered as serious environmental pollutants due to high toxicity, accumulation in the food chain, and persistence in nature. Nickel is a harmful heavy metal which may cause gastrointestinal irritation, lung cancer, etc. Nickel-iron alloy is often used to manufacture iron and steel cutlery [1]. In developed countries, heavy metals are removed from industrial waters and waste waters by using advanced technologies. Some of the techniques of removing heavy metals include ion exchange, chemical precipitation, filtration and electrochemical precipitation. However, these techniques are facing some problems due to relatively high costs and the lack of proper technologies in developing countries. Therefore, an inexpensive and effective method is proposed in order to solve this problem, which is the use of adsorbents. Adsorbents are able to absorb the metal in the form of ions using their ligands and functional groups [2]. Some of the effective, efficient and inexpensive adsorbents for the removal of metals include chitosan [3], silicate minerals [4], corn leaves [5], rice husk ash [6], papaya wood [7], potato peels [8], grape stalks waste (9), sago waste (10), etc. According to figure 1, chitosan bio-sorbent is a linear polysaccharide composed randomly of β- (1→4) D-glucosamine (de-acetylation unit) and β-(1→4)N-acetyl-D-glucosamine (acetylated unit).Chitosan is produced by thermochemical de-acetylation in sodium hydroxide [11, 12]. Chitosan is used in various fields as biopolymer, including biotechnology, food and nutrition, antioxidants and food supplements, drug delivery systems and gene therapy [11]. Recently, chitosan is being used as adsorbent to remove heavy metals from polluted waters (water engineering) [13]. Metal positive ions (cations) are absorbed through the composition process of metals in the amino groups of chitosan in near-neutral solutions [14].

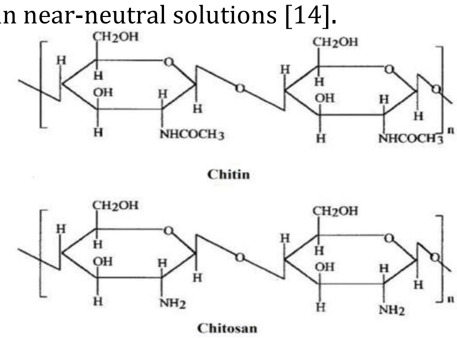

Figure 1: The structures of chitin and chitosan

The use of adsorption is a relatively new method. Adsorption was originally used to produce drinking water from salt water. In recent years, many efforts have been made in order to remove heavy metals from drinking water. Our purpose in this research is to investigate functionalized chitosan in adsorption techniques, which is a grand idea for lowering costs, preserving natural resources and improving the efficiency of the removal of metals from drinking water.

MATERIALS AND METHODS

Materials

Chitosan powder (85% de-acetylated from crab skin with a molecular mass of 12000 g/mol) and mercaptopropyl are provided from Sigma-Aldrich Corporation. Sodium hydroxide, nickel nitrate, hydrochloric acid, and acetic acid are provided from Merck Co. in Germany.

Methodology

Providing Thiol-Functionalized Chitosan

First, 2 grams of chitosan powder are mixed with 100 milliliters of 2% acetic acid using a magnetic stirrer (160rpm, in a temperature of 50 degrees Celsius) for 80 minutes in a conical flask. Then, NaOH (0.5 M) is added to the obtained chitosan gel drop by drop to form the chitosan beads. After unifying the shape of the beads, they are dried using a filter paper and then washed three or four times with double-distilled water so that the pH is approximately neutral. Then, the chitosan beads are dried under a fume hood. For the purpose of functionalizing or cross-linking, the chitosan beads are mixed with 4 milliliters of 3-mercaptopropyl, 5 drops of chloric acid and 100 milliliters of ethanol in a flask. Then, the flask is moved into a paraffin container with a temperature of 75 degrees Celsius. The container is placed on a magnetic stirrer (140 rpm). One side of the flask is covered by a cork; and a balloon is placed on the other side. After aeration with a nitrogen capsule, the balloon is removed. These conditions are preserved for 48 hours before the SH group is added to the chitosan for the reaction to occur. After filtering, the mixture is washed with 96% alcohol and placed under a hood for 24 hours. Then, it's transferred to a vacuum oven for 48 hours in order to dry up completely.

Surface Morphology

For this purpose, a scanning electron microscope or SEM (Philips XL30S-FEG) is used before and after thiol-functionalizing the adsorbent to determine the surface and pores.

FT-IR Hybrid Analysis Spectrum

The hybrid analysis spectrum is provided by an infrared spectrometer after the production of thiol-functionalized chitosan.

Studying the Time of Equilibrium

In order to investigate the time parameter, 20 milligrams of functionalized chitosan and 25 Ccs of nickel nitrate (200 ppm) are mixed in 12 polyethylene containers with lids. These containers are placed on a shaker for different amounts of time: 10, 20, 30, 50, 70, 100, 130, 150, 180, 220, 240, and 250 minutes. Then, the mixture is poured through a filter and diluted. The collected fractions are measured by anatomic absorption spectrophotometer in different time intervals in order to obtain the optimal time.

Studying the pH Effect

For this purpose, a 200 ppm nickel nitrate solution is obtained from the 1000 ppm solution. Then, 20 milligrams of the functionalized chitosan and 25cc of the 200 ppm nickel nitrate solution are mixed in five containers. The samples are placed on the shaker for 220 minutes (the optimal time). After passing through the filter paper and dilution, the pH is investigated in the range of 3-9 (acid- alkaline). The collected fractions are measured by the atomic absorption spectrophotometer in order to obtain the optimal PH.

The Effect of the Thiol Amount

For this purpose, different amounts of thiol (1, 2, 3.5, 4.5, and 5.5 mg/mm) are investigated for cross-linking chitosan. The removal percentage of metal ions by the adsorbent (R) is calculated using equation 1.

(1) $\%R = \frac{C_0 - C_1}{C_0} \quad 100$

R: Removal percentage of metal ions by the adsorbent

C_0: Initial Concentration of metal ions in the solution (mg/l)

C_1: Concentration of metal ions in the solution in each moment (mg/l)

The Effect of the Concentration of Nickel (II) in the Bond Rate

The effect of the initial concentration of metal ions is investigated in concentration range of 10-100 ppm. Different amounts of adsorbent (10, 20, 30, 40, 50, and 60 mg/mm) with the optimal pH (pH 7) are used in a sufficient time. Then, the collected fractions are studied using the atomic absorption spectrophotometer and the amount of absorbed metal by the adsorbent (q(t)) is calculated using equation 2.

$q(t) = \frac{(C_0 - C_1)V}{m}$ (2)

q(t): Adsorption capacity of metal ions (mg/g)

V: Volume of the solution (ml)

m: Adsorbent mass (g)

Statistical Analysis

The research data are studied by the SPSS software version 11. A P-value of less than 0.05 was considered to be statistically significant

RESULTS

Identification of Chitosan Beads

Chitosan beads with porosities of 0.78, humidity of 90.3%, and an average diameter of 2.5 ± 0.05 are identified and presented.

Surface Morphology

Figures 2 and 3 indicate that the thiol-functionalized adsorbent (chitosan) has more pores on its surface in comparison with the adsorbent before functionalizing.

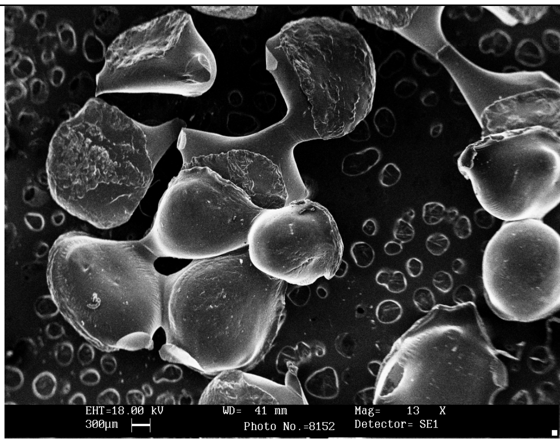

Figure 2: Chitosan before functionalizing

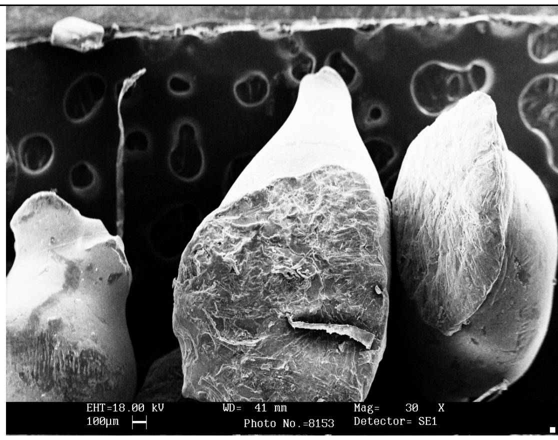

Figure 3: Chitosan after functionalizing

FT-IR Hybrid Analysis Spectrum

According to the hybrid analysis spectrum (illustrated in figure 4), the SH functional group is added to the structure of the adsorbent. The peaks of thiols usually occur in the ranges of 1000 to 1200 and 2000 to 2500. These peaks are clearly evident in the figure.

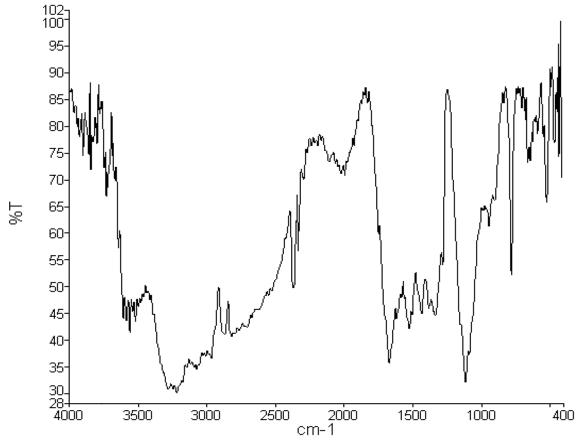

Figure 4: FT-IR taken from the functionalized chitosan

The Effect of the Time of Equilibrium

By studying within different time intervals, it can be concluded that by increasing the time of shaking up to 220 minutes, the removal percentage increases by 61.5%. For times longer than 220 minutes, the removal percentage decreases gradually; because the pores of the adsorbent are filled with metals.

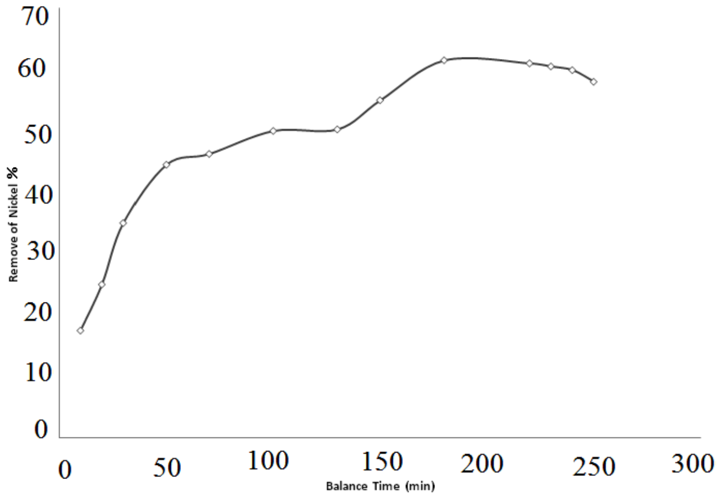

Figure 5: Studying the time of equilibrium

The PH Effect

Figure 6 indicates that chitosan beads dissolve in pH ≤ 3; and the metal ions precipitate as metal hydroxides in pH ≥ 7. The optimal amount for pH in this research is 7. A noteworthy point is the increase in the removal percentage of metal ions by increasing the PH.

Figure 6 : Studying the effects of the measured pH values in the absorption of nickel ions

The Effect of the Thiol Amount

According to figure 7 which indicates the effect of the cross-linking factor amount in the adsorption capacity and instability with respect to time, the optimal value obtained is equivalent to 4.5 mg/ml.

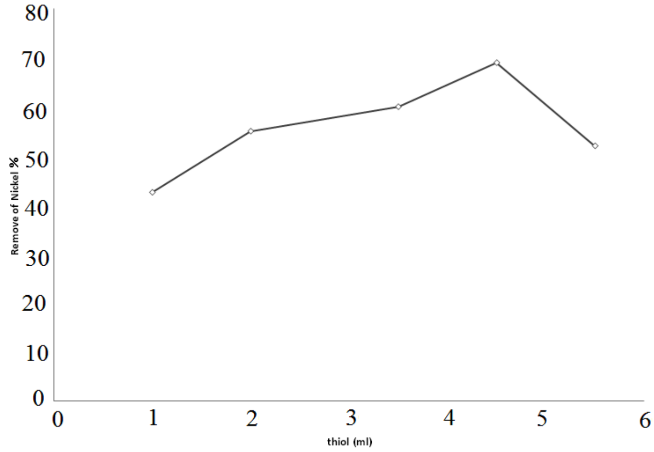

Figure 7: Diagram indicating the effect of the thiol amount

The Effect of the Concentration of Nickel (II) in the Bond Rate

According to figure 8, the removal percentage lowers by increasing the initial concentration of metal ions. The maximum removal percentage of nickel is approximately 15 mg/ml which is obtained by thiol-functionalized chitosan with a concentration of 10 mg/l, 5 milligrams of adsorbent and pH = 7. It is completely evident that the adsorption rate is not high in the first 10 minutes, but starts to increase after that. 45% of nickel is removed by raw chitosan in the same conditions. Synthesized chitosan is a better adsorbent than chitosan. The reason is porosity in the same order of magnitude as the diameter of nickel which enhances selectivity, and also the specific surface area of the synthesized chitosan and the cross-linking factor.

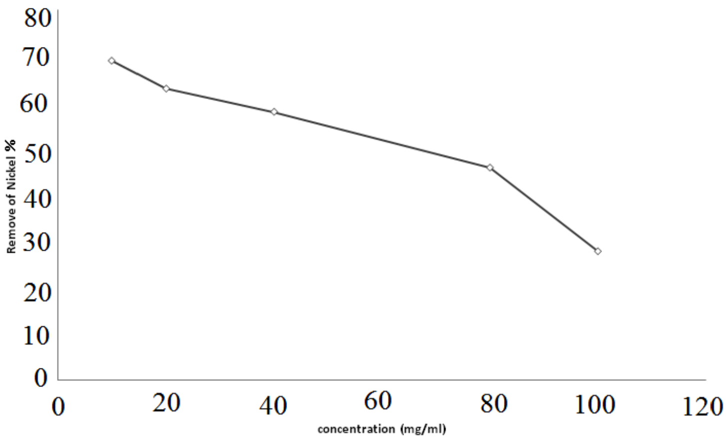

Figure 8: The effect of the initial concentration of nickel in the solution

DISCUSSION

Drinking waters are always subject to pollution by heavy metals such as nickel (II), etc. Environmental regulations require the reduction of concentration to a satisfactory amount. This research aimed to evaluate and optimize the efficiency of thiol-functionalized chitosan in removing nickel (II) from drinking water. The research results indicated that the adsorption capacity of nickel (II) with the functionalized chitosan was higher than the adsorption capacity with chitosan. In general, methods of synthesizing functionalized chitosan are proven to be useful in the removal of heavy metals [13]. However, it is very important to evaluate the effective parameters in adsorption when using chitosan to remove metals [13]. The role of chitosan as adsorbent in the removal of different metals is studied in various researches. For instance: in a case study in 2004 [14], Guibal E et al. studied chitosan as an adsorbent for metals and revealed their evaluations of the ability of chitosan to form strong compounds with heavy metal ions, specifically with Hg, Cu, Cd, Zn, Pb, Ni, Cr, etc. The present research clearly showed that functionalized chitosan is an effective adsorbent for the removal of nickel from drinking water [15]. The adsorption process is influenced by the effective parameters such as time, the pH of the solution and the amount of adsorbent. The optimized time was determined to be 220 minutes for nickel. The pH parameter showed great significance in adsorption rates. The removal percentage of nickel (II) was approximately 62% with pH 7. The removal percentage of nickel (II) improved by increasing the amount of adsorbent. However, it decreased by increasing the concentration of the dissolved nickel (II) in water. While optimizing the stirrer speed, it became clear that the removing ability of the adsorbent improved by increasing the stirrer speed. The analysis data from the scanning electron microscope (SEM) indicated that the thiol-functionalized chitosan has more pores on its surface compared to chitosan before functionalizing, which leads to the increase of adsorption rates.

CONCLUSION

The research at hand shows that using adsorption is extremely useful in removing heavy metals such as nickel from drinking water. This method is accepted and recommended by international standards. In the end, it is recommended to use chitosan that is functionalized by adsorption as a proper substitution for other heavy metals in drinking water in the near future.

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